4

Entropy

Entropy is a virus that has escaped from the laboratory and infected many people who are not scientists, especially people with a literary bent. R. Z. Sheppard reviewing in *Time* (1 May 1995) *The Information* by Martin Amis asserts that "By now the literary uses of entropy are threadbare even for Amis." And in an article by Ivan Hannaford, The Idiocy of Race (*Wilson Quarterly*, Spring 1994), we find "All that remained . . . was the shell of an orthodox race-relations policy that only exacerbates the state of civic entropy." These examples were not searched for carefully; they were stumbled upon in the course of everyday reading. Countless other examples can be found. You can amuse yourself by noting the ways in which entropy is used outside thermodynamics and puzzle over the connection, if any, between scientific and literary entropy.

In some ways, increased use of the term *entropy* by people who haven't the foggiest idea what it means is a good thing. As a term becomes part of everyday speech and writing, it loses its mystery, and people think they understand it. Familiarity breeds contentment. We usually don't agonize over the meaning of words we encounter every day. Energy, for example, is not the fearsome creature that entropy is merely because energy is more familiar. Energy is used in so many different ways by so many different people, often in ways unrelated to or even incompatible with its use in physics, that students rarely find energy so formidable as entropy. Yet entropy in its scientific sense is no more mysterious than energy. The defining characteristic of energy is that it is a measurable physical quantity that remains constant (for an isolated system), whereas the defining characteristic of entropy is that it is a measurable physical quantity that can only increase (for an isolated system). Why is it inherently more puzzling that one quantity can only increase whereas another quantity must remain constant?

Entropy used by nonscientists who want to appear up-to-date in a scientific world vaguely conveys undesirability, often associated with disorder or dysfunction. Civic entropy, in the example cited in the first paragraph, presumably is meant to convey the breakdown of law and order and social cohesiveness. We critically examine the association of entropy with disorder, but first we determine the mathematical form of the entropy of an ideal gas and examine how it changes in various processes. We

believe that this is a more satisfactory approach than defining entropy as an abstract quantity. Having understood a concrete example of entropy, we are better prepared to grasp it in the abstract.

4.1 Entropy of an Ideal Gas

The first law of thermodynamics applied to a closed system for which the working rate is $-p\ dV/dt$ is

$$Q = \frac{dU}{dt} + p\,\frac{dV}{dt} \tag{4.1}$$

Except for a constant-volume process, the heating rate Q cannot be expressed as a time derivative of a thermodynamic variable or combination of variables. But we can obtain from Q such a quantity, called *entropy*. We do so for an ideal gas, although the concept of entropy has a much wider applicability.

The rate of change of internal energy of an ideal gas can be written

$$\frac{dU}{dt} = C_V \frac{dT}{dt} \tag{4.2}$$

If we divide Eq. (4.1) by T and use Eq. (4.2) and the ideal gas law $pV = NkT$, we obtain

$$\frac{Q}{T} = \frac{C_V}{T} \frac{dT}{dt} + \frac{Nk}{V} \frac{dV}{dt} \tag{4.3}$$

Recall that $C_p - C_V = Nk$, which, with a bit of algebra, allows us to write Eq. (4.3) as

$$\frac{Q}{T} = C_V \left(\frac{1}{T} \frac{dT}{dt} + \frac{\gamma - 1}{V} \frac{dV}{dt} \right) \tag{4.4}$$

If C_V is independent of temperature, the equation

$$\frac{dS}{dt} = \frac{Q}{T} \tag{4.5}$$

has the solution

$$S = S_o + C_V \ln\left(\frac{TV^{\gamma-1}}{T_o V_o^{\gamma-1}} \right) \tag{4.6}$$

where the subscript 0 indicates a reference state and S_o is the value of S for this state. S is a thermodynamic variable, called *entropy*, with the property that its time derivative is Q/T. This thermodynamic variable owes its name to Rudolf Clausius (b. Köslin, Prussia, 1822; d. Bonn, Germany, 1888), a German physicist who in 1850 wrote that "I propose to name the magnitude S the *entropy* of the body from the Greek word ἡτροπή, a transformation. I have intentionally formed the word *entropy* so as to be as similar as possible to the word *energy*, since both these quantities . . . are so nearly related to each other in their physical significance that a certain similarity in their names seemed to me advantageous."

Sometimes we are slightly careless and write the entropy of an ideal gas with heat capacity independent of temperature as

$$S = C_V \ln(TV^{\gamma-1}) \tag{4.7}$$

This equation is dimensionally incorrect. According to Eq. (4.6), the dimensions of entropy are the same as those of heat capacity, energy divided by temperature. Although we sometimes use Eq. (4.7) to save effort, we should use Eq. (4.6) to compute entropies (strictly, entropy differences).

Sometimes it is more convenient to express the entropy of an ideal gas as a function of the intensive variables p and T

$$S - S_o = C_p \ln\left(\frac{T}{T_o}\right) - Nk \ln\left(\frac{p}{p_o}\right) \tag{4.8}$$

which follows from Eq. (4.6) and the ideal gas law.

Having derived the entropy of an ideal gas by way of a particular idealized process (one for which $W = -p \, dV/dt$), we may forget about how we obtained entropy and consider it to be yet another thermodynamic variable. That is, the entropy of an ideal gas is *defined* by Eq. (4.6) or (4.8), which also happen to give the entropy change of an ideal gas in a particular process. The best way to understand entropy is to examine how it behaves. As we shall see, entropy behaves differently from energy.

Entropy Change in a Free Expansion

Consider an ideal gas in a closed, insulated container divided into two chambers by an impermeable partition (Fig. 4.1). The volume of one chamber is V_1 and that of the
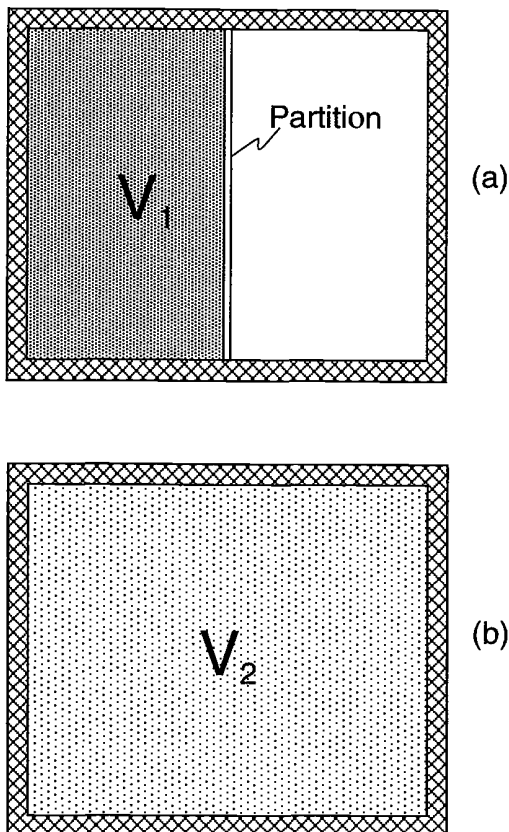

Figure 4.1 Free expansion of an isolated ideal gas. When the partition separating the gas in volume V_1 (a) from adjacent empty space is removed, the gas expands to fill the entire volume V_2 (b).

two chambers taken together is V_2. The temperature of the gas is T and initially is confined to V_1, and hence its entropy is

$$S_i = C_V \ln(TV_1^{\gamma-1}) \tag{4.9}$$

where the subscript i denotes the initial state. We punch a hole in the partition and allow the gas freely to occupy both chambers. Because the gas is ideal, its temperature does not change when its volume increases. The final entropy is

$$S_f = C_V \ln(TV_2^{\gamma-1}) \tag{4.10}$$

and the entropy change (of the universe) is

$$\Delta S = S_f - S_i = C_V (\gamma - 1) \ln\left(\frac{V_2}{V_1}\right) = Nk \ln\left(\frac{V_2}{V_1}\right) \tag{4.11}$$

Because $V_2 > V_1$, $\Delta S > 0$. In this process, the entropy of the universe increased even though there was no heating and no working, and hence no change in internal energy. This is our first hint that entropy behaves differently from energy.

We could not have obtained the entropy change in this free expansion by integrating

$$\frac{dS}{dt} = \frac{Q}{T} \tag{4.12}$$

which would give $\Delta S = 0$. This is because underlying the correct use of Eq. (4.12) is the requirement that the working rate be $-p \, dV/dt$, whereas in an adiabatic free expansion $W = 0$. Although volume increases in this process, and hence $-p \, dV/dt$ does not vanish, the integral of this quantity is not the work done, which is zero.

Left to itself, the system will not return spontaneously to its state before the free expansion, when all the molecules were crowded into V_1. This is equivalent to scrambling eggs. Once they have been scrambled, they cannot be unscrambled without effort. And so it is with the free expansion of a gas. To restore it to its initial state requires doing work

$$W_{tot} = -\int_{V_2}^{V_1} p \, \frac{dV}{dt} \, dt \tag{4.13}$$

If this compression is carried out at constant temperature T, the ideal gas law in Eq. (4.13) yields

$$W_{tot} = NkT \ln\left(\frac{V_2}{V_1}\right) = T \, \Delta S \tag{4.14}$$

where the entropy change ΔS is that in the original free expansion (Eq. 4.11). Thus in this process the entropy increase of the universe requires doing work on the system to restore it to its original state.

Entropy Changes Upon Heating and Cooling

As our next example of an entropy change, consider the heating or cooling of an ideal gas. For simplicity, we take a fixed volume of gas in contact with a much larger
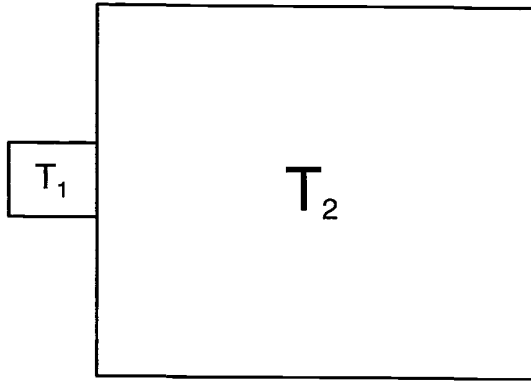
Figure 4.2 Two rigid containers filled with an ideal gas at different initial temperatures T_1 and T_2 are placed in contact and isolated from their surroundings.

volume of the same gas. We call the larger volume a *reservoir*. You can imagine the gases to be enclosed in rigid metal tanks (Fig. 4.2). The two volumes are insulated from their surroundings. Initially, the temperature of the small volume is T_1, and that of the large volume is T_2, where $T_2 > T_1$. With the passage of time, both volumes come to the same temperature T. In this process, total internal energy is conserved:

$$C_{V1} T_1 + C_{V2} T_2 = C_{V1} T + C_{V2} T \tag{4.15}$$

This equation can be solved for the final temperature:

$$T = \frac{C_{V1}}{C_{V1} + C_{V2}} T_1 + \frac{C_{V2}}{C_{V1} + C_{V2}} T_2 \tag{4.16}$$

Volume does not change in this process, and hence the entropy changes from Eq. (4.7) are

$$\Delta S_1 = C_{V1} \ln\left(\frac{T}{T_1}\right), \qquad \Delta S_2 = C_{V2} \ln\left(\frac{T}{T_2}\right) \tag{4.17}$$

By using Eq. (4.16), the total entropy change can be written

$$\Delta S = \Delta S_1 + \Delta S_2 = C_{V1} \left[\ln\left(\frac{\mu + x}{1 + \mu}\right) + \frac{1}{\mu} \ln\left(\frac{1 + \mu/x}{1 + \mu}\right) \right] \tag{4.18}$$

where

$$\mu = \frac{C_{V1}}{C_{V2}}, \qquad x = \frac{T_2}{T_1} \tag{4.19}$$

Our task is simpler if we take the limiting case of an infinite reservoir, which requires us to determine ΔS in the limit as μ goes to zero. The first term in brackets in Eq. (4.18) poses no problems:

$$\lim_{\mu \to 0} \ln\left(\frac{\mu + x}{1 + \mu}\right) = \ln x \tag{4.20}$$

The second term requires more effort because $1/\mu$ is infinite in the limit of zero μ, whereas the limit of the logarithmic term is zero. To evaluate the second limit, we use the expansion

$$\ln(1 + z) \approx z, \qquad |z| \ll 1 \tag{4.21}$$

Thus for sufficiently small values of μ we have

$$\ln\left(\frac{1+\mu/x}{1+\mu}\right)=\ln(1+\mu/x)-\ln(1+\mu)\approx\frac{\mu}{x}-\mu \qquad (4.22)$$

which yields the limit

$$\lim_{\mu\to0}\frac{1}{\mu}\ln\left(\frac{1+\mu/x}{1+\mu}\right)=\frac{1}{x}-1 \qquad (4.23)$$

With this result, the entropy change of the universe is

$$\Delta S=C_{V1}\left(\ln x+\frac{1}{x}-1\right) \qquad (4.24)$$

By supposition the reservoir is hotter than the volume V_1 of gas. If the reservoir is infinite, it follows from Eq. (4.16) that $T=T_2$. Thus we can describe this process as a heating process: The temperature of the smaller volume of gas increases, whereas that of the (infinite) reservoir does not change. What happens to the total entropy in this process? To answer this question requires examining the sign of the function

$$f(x)=\ln x+\frac{1}{x}-1 \qquad (4.25)$$

in Eq. (4.24) for $x>1$. Note that $f(1)=0$ and that

$$\frac{df}{dx}=\frac{1}{x}-\frac{1}{x^2} \qquad (4.26)$$

is positive for $x>1$. Thus in this heating process, the entropy of the universe increases.

We now might be tempted to surmise that if entropy increases in a heating process, entropy decreases in a cooling process. This is a reasonable expectation, but it is not true, which attests to the peculiarity of entropy. From Eq. (4.26) it follows that df/dx is zero only at $x=1$, and hence f has an extremum at this value. This extremum is a minimum because the second derivative of f is positive at $x=1$. Because the minimum value of f is zero at $x=1$, $f>0$ for $x>1$ (heating) and for $x<1$ (cooling). Thus for both heating and cooling, the entropy of the universe increases.

Unlike for the free expansion, we could have obtained the entropy change for heating and cooling by integrating Eq. (4.12). This is because $W=0$ and is equal to $-p\ dV/dt$ (by supposition, V is constant). Let Q be the rate of heating (cooling) of the smaller volume of gas. The rate of cooling (heating) of the reservoir is thus $-Q$. By supposition, the reservoir is infinite, and hence its temperature does not change during the process. The entropy change of the reservoir is therefore

$$\Delta S_2=\int -\frac{Q}{T_2}\ dt=-\frac{1}{T_2}\int Q\ dt=-\frac{1}{T_2}C_{V1}(T_2-T_1) \qquad (4.27)$$

The entropy change of the smaller volume is

$$\Delta S_1 = \int \frac{Q}{T} \, dt = \int \frac{1}{T} \frac{dU}{dt} \, dt = C_{V1} \int \frac{1}{T} \frac{dT}{dt} \, dt = C_{V1} \ln\left(\frac{T_2}{T_1}\right) \qquad (4.28)$$

Thus we obtain the same total entropy change as in Eq. (4.24).

Before we try to make sense out of this result, let us consider a process in which entropy does not increase. Such a process is adiabatic ($Q = 0$) with working rate $-p \, dV/dt$. We already showed that in this process

$$TV^{\gamma-1} = \text{const} \qquad (4.29)$$

This result in Eq. (4.6) yields no entropy change, another example in which we get the same result using Eq. (4.12). Note that the best we have been able to do is find a process in which entropy is constant. In the other processes considered, entropy increased. A process in which entropy is constant is said to be *isentropic*. For the first adiabatic process we considered (free expansion), entropy increased, whereas for the second adiabatic process, entropy was constant. Although some adiabatic processes are isentropic, not all are.

We obtained what, on reflection, is a disturbing result: The entropy of a fixed-volume (ideal gas) reservoir changed, yet its temperature remained constant. Suppose that before the smaller volume was put into contact with the reservoir we measured its temperature. When our backs were turned, someone put the smaller volume in contact with the reservoir, then removed this volume when its temperature was that of the reservoir. We turned around, oblivious to what happened when we weren't looking, and measured the temperature of the reservoir. We recorded no change. Thus we would have had to conclude that nothing happened. But the entropy of the reservoir changed even though we could not make any macroscopic measurement that indicated a change in its state. It seems that the only way out of this embarrassing fix is to assert that infinite reservoirs do not exist; they are idealizations not found in nature. In any energy transfer process between a reservoir and a system, the temperature of the reservoir must change even though that change be exceedingly small. Another way of looking at this problem is to note that according to Eq. (4.16), $T = T_2$ in the limit of an infinite reservoir (C_{V2} becomes infinite). But if we set C_{V2} to infinity and $T = T_2$ in Eq. (4.17), we obtain an indeterminate result for the entropy change of the reservoir. So we sneak up on the infinite reservoir by taking the limit of the entropy change as C_{V2} approaches (but never reaches) infinity. This *limit* exists:

$$\lim_{C_{V_2} \to \infty} \Delta S_2 = C_{V1} \left(\frac{1}{x} - 1 \right) \qquad (4.30)$$

even though the infinite reservoir does not.

Now we tackle some of the confusing and sometimes contradictory terminology of thermodynamics. A *quasistatic* process is a continuous succession of equilibrium states (see Section 1.6 for the conditions under which a real process is approximately quasistatic). It is sometimes said that a quasistatic process is also a *reversible* process, which is not true (as we shall show). Reversibility and its antonym irreversibility are difficult concepts to grasp. No two authors seem to agree precisely on what they mean. A working rate $-p \, dV/dt$ is quasistatic and reversible. By reversible is meant the following. We can imagine a compression (or expansion) described by $-pdV/dt$

as being realized by successively adding tiny weights to a piston enclosing a gas within a cylinder. These weights can be imagined to be taken from slots within the walls of the cylinder, so that as each weight is added to the piston another slot is uncovered, which enables us to slide a weight from a slot onto the piston without doing any work. Friction doesn't exist in this idealized process. At any stage of the process, we can reverse it by pushing weights back into the slots, following which the piston will rise.

We have already seen that if a quasistatic compression or expansion is carried out adiabatically, the entropy of the universe does not change. What happens if the same process is carried out isothermally? To achieve this, we would have to put the cylinder in contact with a large (strictly, infinite) constant-temperature reservoir. The change in entropy of the gas in an isothermal expansion from volume V_1 to V_2 is exactly the same as that in the free expansion (Eq. 4.11). But now because the gas interacts with its surroundings, the reservoir, we have to compute its entropy change to obtain the total entropy change of the universe. We showed that the entropy change of a reservoir can be obtained by integrating Q_{res}/T:

$$\Delta S_{res} = \int_1^2 \frac{Q_{res}}{T} \, dt = \frac{1}{T} \int_1^2 Q_{res} \, dt \tag{4.31}$$

Here, Q_{res} is the negative of that appropriate to the gas (cooling of the gas means heating of the reservoir and vice versa), which from the first law for an ideal gas is $p \, dV/dt$ in an isothermal process. Thus the entropy change of the reservoir is

$$\Delta S_{res} = \frac{1}{T} \int_1^2 -p \, \frac{dV}{dt} \, dt \tag{4.32}$$

which is (using the ideal gas law)

$$\Delta S_{res} = -Nk \int_1^2 \frac{1}{V} \frac{dV}{dt} \, dt = -Nk \ln\left(\frac{V_2}{V_1}\right) \tag{4.33}$$

When this entropy change of the reservoir is added to that of the gas in the cylinder (Eq. 4.11), the result is zero net entropy change. On the basis of what we have done to this point, we conclude that a reversible process is one in which the entropy of the universe does not change. A process that is not reversible is irreversible.

The entropy of the universe did change in heating or cooling of a volume of a gas in contact with an (infinite) reservoir (see Eq. 4.24). But in the limit as x approaches unity (the small gas volume and reservoir approach the same initial temperature), the entropy of the universe does not change. Could we carry out the heating or cooling of the small gas volume in such a way that the entropy of the universe does not change?

To answer this question, consider the following arguments. The small volume, which henceforth we call our system, is brought into successive contact with N infinite reservoirs having temperatures $T_1 < T_2 < T_3 < \cdots < T_N$ separated in temperature by $\Delta T/(N-1)$, where $\Delta T = T_N - T_1$ (Fig. 4.3). Initially, the system is in equilibrium with reservoir 1, then comes into equilibrium with each reservoir in turn. The succession of N equilibrium states of the system is an approximation to a quasistatic process; in the limit as N approaches infinity this discontinuous process approaches a
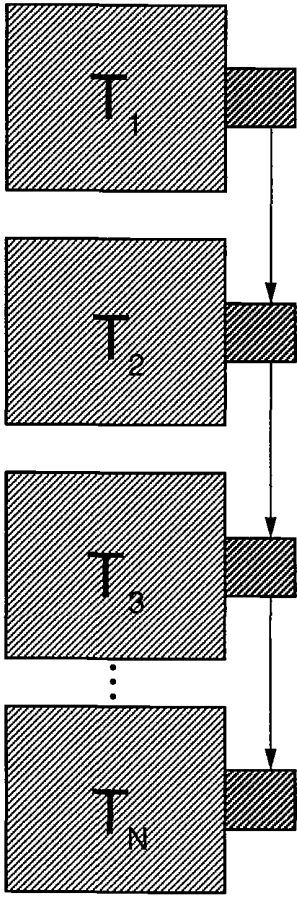
Figure 4.3 A set of N ideal gas reservoirs with temperatures T_1, T_2, . . . T_N, where the temperature difference between successive reservoirs is arbitrarily small. A rigid container filled with an ideal gas is successively placed in contact with each reservoir and allowed to come into temperature equilibrium with it. By this process the temperature of the gas in the container evolves in small steps from T_1 to T_N.

continuous process (i.e., a quasistatic process). The jth entropy change of the universe is

$$\Delta S_j = C_V \left[\ln\left(\frac{T_{j+1}}{T_j}\right) + \frac{T_j}{T_{j+1}} - 1 \right] \tag{4.34}$$

where C_V is the heat capacity of the system. After a bit of algebra, the total entropy change can be written

$$\Delta S = \Sigma_j \Delta S_j = C_V \left(\ln \frac{1}{y} - \frac{1}{N} \Sigma_{j=2}^N \frac{1}{\frac{y}{1-y}+\frac{j-1}{N-1}} \right) \tag{4.35}$$

where $y = T_N/T_1$. What is the limit of the sum in this equation as N approaches infinity? To answer this question first change the index in the sum in Eq. (4.35) from j to $k+1$ and let $N = M+1$. With these transformations of indices the sum becomes

$$\frac{1}{M+1} \Sigma_{k=1}^M \frac{1}{\mu+z_k} \tag{4.36}$$

where $z_k = k/M$ and μ is $y/(1-y)$. Because $M \gg 1$, Eq. (4.36) is to good approximation replaced by

$$\Sigma_{k=1}^M \frac{\Delta z}{\mu+z_k}, \qquad 0 \le z_k \le 1 \tag{4.37}$$

where $\Delta z = z_{k+1} - z_k = 1/M$. In the limit as M becomes infinite, this sum becomes an integral:

$$\lim_{M\to\infty} \Sigma_{k=1}^M \frac{\Delta z}{\mu + z_k} = \int_o^1 \frac{dz}{\mu + z} = -\ln y \qquad (4.38)$$

which when substituted into Eq. (4.35) yields $\Delta S = 0$. To check this result we chose y at random, then computed the total entropy change (relative to the heat capacity) from Eq. (4.35) for various values of N. For $N = 50,000$, the entropy change (relative to the heat capacity) was 0.0000221. This process can be said to be reversible. We have a huge set of reservoirs, each differing in temperature from its nearest neighbors by a small amount. We can successively put the system in contact with these reservoirs, one after the other arranged in order of increasing temperature, then reverse the process to restore the system to its initial temperature. And all without any permanent change in the universe. But note that to conjure up this reversible heating and cooling process we had to invoke a considerable degree of unreality: an infinite number of infinite reservoirs.

Now what about the free expansion? We can imagine this process to be carried out quasistatically: The space into which the gas expands is divided by partitions into a set of thin chambers (Fig. 4.4). We puncture each partition in turn, allowing the expanded gas to come into equilibrium between punctures. The result is a set of equilibrium states, and in the limit of an infinite number of partitions this set of states is continuous. Yet even in this quasistatic process, the entropy of the universe increases according to Eq. (4.11). Moreover, this process would not be described as reversible: If we were to repair each hole in the partition in succession, the gas would not reoccupy its initial volume V_1. Thus we conclude that for a process to be reversible it is necessary for it to be quasistatic but not sufficient. Now we can define a reversible process as one in which the entropy of the universe does not change. No real process is reversible. Reversibility is an idealization. In all real (irreversible) processes the entropy of the universe increases.

We can define the entropy change of any system between two states as

$$S_2 - S_1 = \int_1^2 \frac{Q}{T} dt \qquad (4.39)$$

where the only restriction on the process connecting states 1 and 2 is that it be reversible (provided such a process exists). This definition is consistent with the en-

Figure 4.4 The volume on the left encloses an ideal gas. The volume on the right initially encloses empty space, subdivided into compartments by a set of very many exceedingly thin partitions. Each partition is punctured in turn and the gas is allowed to reach equilibrium before the next partition is punctured. The limit of an infinite number of partitions corresponds to a continuous sequence of equilibrium states (i.e., a quasistatic process).
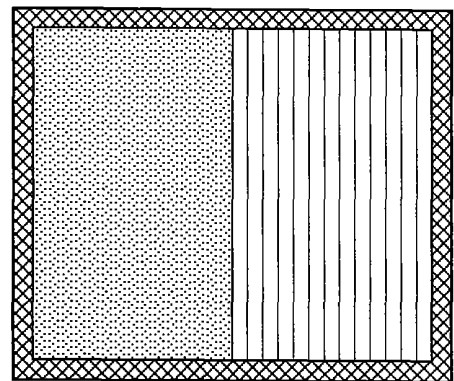
tropy change derivations for an ideal gas undergoing reversible processes. Note that Eq. (4.39) is not in conflict with our assertion that a reversible process is one in which the entropy change of the *universe* is zero. In such a process the entropy of a system changes according to Eq. (4.39), and the change in entropy of its surroundings is equal and opposite in sign so that the total entropy change of the universe, the system together with its surroundings, is zero.

Alert readers may have noticed an apparent contradiction. Equation (4.39) applied to a fixed volume of ideal gas heated or cooled by contact with a single reservoir yields the correct value for the entropy change of this volume even though the heating or cooling process is not reversible (the entropy of the universe increases). This is because the volume could have evolved by a reversible process between the same initial and final equilibrium states as in the irreversible process. For example, instead of the volume interacting with a single reservoir, it could have evolved from a given initial to a given final temperature by interacting with an infinite sequence of reservoirs, and this process, as we showed previously, is reversible. Entropy is a state variable, it depends only on the state of the system, not on its history. Thus the entropy change of the volume of gas when it is irreversibly heated or cooled (entropy of the universe increases) is the same as when it is reversibly heated or cooled (entropy of the universe is constant).

For a process to be reversible it is necessary that the working be reversible ($W = -p \, dV/dt$) but not sufficient. Again, consider the example of a fixed volume of ideal gas interacting with a single reservoir at a temperature different from the initial temperature of the volume. Here the working rate is quasistatic (indeed, it is static because the volume is fixed) and reversible, and yet the entropy of the universe increases.

All the specific examples we have given for an ideal gas are special instances of the second law of thermodynamics:

$$\Delta S_{universe} \geq 0 \qquad (4.40)$$

It is with some trepidation that we present this law in the form of Eq. (4.40), for we are well aware of Clifford Truesdell's assertion that "Every physicist knows exactly what the first and second laws [of thermodynamics] mean, but it is my experience that no two physicists agree about them." To forestall critics we merely note that Eq. (4.40) is only one of the many forms of the second law of thermodynamics.

Another statement of the second law is that the entropy of an *isolated* system can never decrease. Such a system, by definition, does not interact with its surroundings, and hence is a universe unto itself to which the second law in the form Eq. (4.40) is applicable.

The Second Law and Stability

The second law of thermodynamics gives us a criterion for the stability of an isolated system. One meaning of stability is resistance to change. A stable system will not change its state spontaneously or when slightly perturbed. Thus an isolated system in a state of maximum entropy is stable. According to the second law, a change in the state of the system would entail an increase in its entropy (or, at best, no change). But if the entropy of the system is a maximum, there are no states of higher entropy

accessible to it. When you are on the summit of a mountain you cannot climb higher. By a maximum here is meant a *local* maximum, not an absolute maximum. At the summit you can go higher, but to do so you have to undergo a transformation from the mortal to the immortal state. Similarly, a state of maximum entropy is one for which the entropy is larger than that of all states accessible to the system.

As an example, let us apply this stability criterion to the free expansion considered previously. When the partition separating the gas from a region of very low pressure is removed or punctured, the gas evolves to a state of maximum entropy by filling the entire volume accessible to it. Once the gas has done so, it does not retreat into a smaller volume. To do so would entail a decrease in entropy, which is not allowed by the second law. Departures from the second law are not prohibited absolutely; they are merely exceedingly unlikely. Thermodynamics applies to macroscopic systems, and thermodynamic variables are averages for such systems. Pressure and temperature, and hence entropy, are averages and have meaning only for systems composed of many molecules. Wherever there are averages there are deviations from these averages (fluctuations) lurking in the background. On average, the entropy of a confined gas cannot increase, but there always will be fluctuations giving rise to transitory (and small) violations of the second law. A fluctuation so large that all the gas molecules in a room spontaneously migrate into one corner is not impossible, merely exceedingly unlikely, for which we should be thankful.

Entropy of Mixtures; Entropy of Mixing and Gibbs's Paradox

Given that the atmosphere is a mixture of gases, we can hardly proceed without first determining the entropy of a mixture of noninteracting gases. Although we could make a judicious guess at the entropy of a mixture as a function of the entropies of its components, the safest approach is to begin anew. We showed in Section 3.7 that internal energies of ideal gases in a mixture are additive, and hence the total rate of change of internal energy of a mixture is

$$\frac{dU}{dt} = \Sigma C_{Vj} \frac{dT}{dt}$$ (4.41)

where C_{Vj} is the heat capacity (at constant volume) of the jth component. From Dalton's law of partial pressures

$$p = \Sigma p_j$$ (4.42)

where p_j is the partial pressure of the jth component. Equations (4.41) and (4.42) together with the first law Eq. (4.1), yield

$$Q = \Sigma C_{Vj} \frac{dT}{dt} + \Sigma p_j \frac{dV}{dt}$$ (4.43)

Each component of the mixture satisfies the ideal gas law

$$p_j = \frac{N_j kT}{V}$$ (4.44)

where V and T are their common volume and temperature. If we combine the preceding equations, we obtain

$$\frac{Q}{T} = \Sigma C_{pj} \frac{1}{T} \frac{dT}{dt} - \Sigma \frac{N_j k}{p_j} \frac{dp_j}{dt} = \frac{dS}{dt} = \frac{d}{dt} \Sigma S_j \qquad (4.45)$$

where the entropy of the jth component is

$$S_j = C_{pj} \ln T - N_j k \ln p_j \qquad (4.46)$$

For simplicity we omitted the constants of integration. From inspection of Eq. (4.8) it is evident that the entropy of the mixture is the sum of the partial entropies of each of its components acting independently, which comes as no surprise.

Given that entropies of noninteracting gases are additive, we can determine entropy changes upon mixing of different ideal gases at constant pressure and temperature. Suppose that the gases are initially in chambers with volumes V_j separated by impermeable partitions. Each chamber contains an ideal gas at the same pressure p and temperature T. The initial entropy S_i of this system is the sum of entropies

$$S_i = \Sigma C_{pj} \ln T - \Sigma k N_j \ln p \qquad (4.47)$$

When the partitions are removed, the gases mix freely until they occupy the same volume $V = \Sigma V_j$. The final entropy S_f is

$$S_f = \Sigma C_{pj} \ln T - \Sigma k N_j \ln p_j \qquad (4.48)$$

where

$$p_j = \frac{N_j kT}{V} \qquad (4.49)$$

We also have from the ideal gas law

$$p_j = \frac{N_j}{N} p \qquad (4.50)$$

where N is the total number of molecules of all kinds. From Eqs. (4.49) and (4.50)

$$S_f = \Sigma C_{pj} \ln T - \Sigma k N_j \ln p - \Sigma k N_j \ln \left(\frac{N_j}{N}\right) \qquad (4.51)$$

From Eq. (4.47) it follows that

$$S_f = S_i - \Sigma k N_j \ln \left(\frac{N_j}{N}\right) \qquad (4.52)$$

The quantity

$$-\Sigma k N_j \ln \left(\frac{N_j}{N}\right) \qquad (4.53)$$

is called the *entropy of mixing* and is necessarily positive because $N_j/N \le 1$. The origins of this entropy are not a deep mystery. After mixing, each component occupies a greater volume than it did initially. Yet Eq. (4.53) does lead to a paradox. Nothing in this expression for the entropy of mixing depends on any specific property (e.g., molecular weight, specific heat capacity, etc.) of the molecules in the mixture. Thus if we had taken all the molecules in the separate chambers to be identical, we would have obtained the same entropy of mixing even though no macroscopic mixing

had taken place. This paradox, called Gibbs's paradox, can perhaps be made clearer by considering a simpler example. A fixed volume $2V$ is divided into two volumes V separated by an impermeable partition. Each subvolume contains N molecules of the same kind of ideal gas at the temperature T. The partition is removed. What is the entropy change? There are two possible answers to this question. The first answer, the obvious, common sense one, is that there is no entropy change because, in effect, nothing has happened. The second answer comes about from applying (perhaps we should say misapplying) Eq. (4.53). According to this equation, the entropy change is

$$\Delta S = 2Nk \ln 2 \qquad (4.54)$$

Both entropy changes cannot be correct. We arrive at this conundrum because we applied Eq. (4.53) in the limit as the different kinds of mixing molecules become the same. Yet this equation was derived under the implicit assumption that the molecules are different. Once we decide they are different, they are forever different, and if we decide they are not, no matter how small the difference, we cannot use Eq. (4.53).

Entropy Changes Upon Mixing of Two Gases with Different Temperatures and Pressures

Now let us consider the entropy change when two gases, initially with different temperatures and pressures, mix to form a gas with uniform temperature and pressure. This problem is tackled most easily if we take the two gases to be in adjacent volumes separated by a partition. Subscripts 1 and 2 are appended to the thermodynamic variables of these gases before mixing. When the partition is removed, the gases mix to occupy the same volume $V = V_1 + V_2$ and come to the same temperature T. Because this process occurs adiabatically and without any work being done, total internal energy is conserved. It follows from Eq. (4.6) and additivity of entropy that the total entropy change is the sum of two entropy changes, one resulting from a temperature change, the other from a volume change:

$$\Delta S = \Delta S_{temp} + \Delta S_{vol} \qquad (4.55)$$

where

$$\Delta S_{temp} = C_{V1} \ln\left(\frac{T}{T_1}\right) + C_{V2} \ln\left(\frac{T}{T_2}\right) \qquad (4.56)$$

$$\Delta S_{vol} = N_1 k \ln\left(\frac{V_1 + V_2}{V_1}\right) + N_2 k \ln\left(\frac{V_1 + V_2}{V_2}\right) \qquad (4.57)$$

Because $V_1 + V_2$ is greater than both V_1 and V_2, the entropy change Eq. (4.57) associated with the volume change is necessarily positive. The entropy change Eq. (4.56) associated with the temperature change is identical to what we obtained previously (Eq. 4.18):

$$\Delta S_{temp} = C_{V1}\left[\ln\left(\frac{\mu + x}{1 + \mu}\right) + \frac{1}{\mu} \ln\left(\frac{1 + \mu/x}{1 + \mu}\right)\right] \qquad (4.58)$$

where μ and x are defined in Eq. (4.19). The quantity μ, the ratio of heat capacities of the two gases, is arbitrary. To determine the sign of the entropy change ΔS_{temp}, we examine the extrema of the function $f(x) = \Delta S_{temp}/C_{V1}$. The first derivative of this function

$$\frac{df}{dx} = \frac{1}{\mu + x} - \frac{1}{x(\mu + x)} \tag{4.59}$$

vanishes only at $x = 1$, and $f(1) = 0$. The second derivative of f

$$\frac{d^2 f}{dx^2} = \frac{1}{(x + \mu)^2}\left(\frac{2x + \mu}{x^2} - 1\right) \tag{4.60}$$

is positive at $x = 1$. Thus the minimum value of f is zero only when the initial temperatures of the two gases are the same, but otherwise f is positive. In this mixing process, therefore, the entropy of the universe always increases, and hence the process is irreversible.

An Entropic Derivation of Joule's Law

For a reversible process

$$\frac{dS}{dt} = \frac{1}{T}\frac{dU}{dt} + \frac{p}{T}\frac{dV}{dt} = \frac{\partial S}{\partial T}\frac{dT}{dt} + \frac{\partial S}{\partial V}\frac{dV}{dt} \tag{4.61}$$

from which follow

$$\frac{\partial S}{\partial T} = \frac{1}{T}\frac{\partial U}{\partial T} \tag{4.62}$$

$$\frac{\partial S}{\partial V} = \frac{1}{T}\left(\frac{\partial U}{\partial V} + p\right) \tag{4.63}$$

because V and T are independent variables. If we differentiate Eq. (4.62) with respect to V and Eq. (4.63) with respect to T, we obtain

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} \tag{4.64}$$

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{1}{T}\left(\frac{\partial^2 U}{\partial T \partial V} + \frac{\partial p}{\partial T}\right) - \frac{1}{T^2}\left(\frac{\partial U}{\partial V} + p\right) \tag{4.65}$$

The cross partial derivatives of a function $f(x, y)$ are equal

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \tag{4.66}$$

if f is a continuous function of x and y. Thus with the assumption that S is a continuous function of T and V, Eqs. (4.64) and (4.65) can be set equal to each other. And if U is a continuous function of T and V

$$\frac{\partial U}{\partial V} = T\frac{\partial p}{\partial T} - p \tag{4.67}$$

This is a general result, which we can apply to liquids as well as gases (see the following paragraph). For an ideal gas

$$\frac{\partial p}{\partial T} = \frac{p}{T} \tag{4.68}$$

from which follows

$$\frac{\partial U}{\partial V} = 0 \tag{4.69}$$

This is the defining equation for an ideal gas. What we have shown by way of entropy is that Eq. (4.69) is consistent with the ideal gas law, which is comforting even if expected.

We now have enough tools to go beyond our discussion of specific heats in Section 3.2, in which we obtained the general result

$$C_p = C_V + \left(\frac{\partial U}{\partial V} + p \right) \frac{\partial V}{\partial T} \tag{4.70}$$

By using Eq. (4.67), Eq. (4.70) can be written

$$C_p = C_V + T \frac{\partial p}{\partial T} \frac{\partial V}{\partial T} \tag{4.71}$$

From Eq. (3.60) it follows that

$$C_p = C_V + \frac{TV\alpha^2}{\kappa_T} \tag{4.72}$$

where the isothermal compressibility κ_T is the relative change in volume with change in pressure

$$\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial p} \tag{4.73}$$

and the isobaric coefficient of thermal expansion α is the relative change in volume with change in temperature

$$\alpha = \frac{1}{V} \frac{\partial V}{\partial T} \tag{4.74}$$

The compressibility is positive for materials that shrink when subjected to increased pressure (we don't know of any exceptions). For such materials, the second term on the right side of Eq. (4.72) is inherently positive, and hence $C_p \geq C_V$. It also follows from Eq. (4.72) that C_p for liquid water is identically equal to C_V at the temperature ($\approx 4°C$) where the density of water is a maximum, and hence $\alpha = 0$ (see Fig. 3.8).

Entropy and Disorder: A Persistent Swindle

Generations of desperate teachers, faced with the cries of anguished students for an immediate, concise, and readily digestible explanation of what this mysterious quantity entropy really is, have seized upon a pacifier: Don't fret, entropy is just a measure

of disorder; in fact, entropy *is* disorder. The greater the entropy, the greater the disorder. Indeed, entropy used by people who are ignorant of science, as in the examples with which we began this chapter, is merely a fancy scientific synonym for disorder, and entropy increases are taken to be indications of increased disorder in all its forms, ranging from a messy room to civil disturbances.

Good explanations often are characterized by the reduction of the unfamiliar to the familiar. Thus those who propose to explain entropy (unfamiliar) by saying it is merely disorder (familiar) are assuming that the consumers of this putative explanation have an intuitive and unambiguous sense of what is meant by disorder. If only this were true!

We began our discussion of entropy by showing that in an adiabatic free expansion the entropy of an ideal gas increases. When the volume of such a gas increases, does this unambiguously signal an increase in its disorder? Perhaps it does—to some people. Yet it is not likely to be obvious to everyone that increased volume, and hence increased entropy, means increased disorder unless we *define* this to be so. But if we do, we have defeated our purpose of supposedly explaining entropy as disorder. That is, we have defined disorder by means of entropy, not the other way around.

The entropy of an ideal gas increases with temperature. Does this correspond to increased disorder? Again, it depends on what we mean by disorder. As the temperature of the gas increases, so does the mean kinetic energy of its molecules. If we agree that when gas molecules move faster they are more disordered, we have another correlation between increased entropy and increased disorder. But again, we achieved this correlation by defining disorder in a particular way.

As we shall see in Section 5.3, the entropy per unit mass of a solid, such as ice, is less than the entropy of its liquid at the same temperature, which in turn is less than the entropy of the vapor phase. Here is an example in which greater entropy is associated with an increase in what most people would probably intuitively accept as increased disorder: A (crystalline) solid is more ordered than its liquid, which is more ordered than its vapor.

Let us consider some examples that cast serious doubts on the notion that entropy equals disorder. Suppose we have a subcooled liquid isolated from its surroundings. A subcooled (or supercooled) liquid exists as a liquid at a temperature below the nominal freezing point (we have more to say about subcooling in Chapter 5). Suppose that some of this liquid freezes because of the introduction of a freezing nucleus. According to the second law, the entropy of this isolated system cannot decrease. Yet we end up with a system that is more ordered, at least as far as outward appearances are concerned. It is indeed true that in the process of partial freezing of the subcooled water, the temperature of the system increases, which corresponds to an entropy increase. But now we have to argue that the entropy increase because of the temperature increase just happens to be greater than the entropy decrease because of the phase transition from liquid water to ice, which is by no means obvious. For this example, we could retain the entropy equals disorder equation, but only by stretching.

Now let us turn to an example that really knocks the correlation between entropy and disorder into a cocked hat. Consider an isolated supersaturated solution, a liquid in which a solid has been dissolved to a concentration greater than it would be for equilibrium. Such a supersaturated solution is unstable (or, as is sometimes said, metastable), but can exist that way more or less indefinitely. A crystal suddenly and

spontaneously forms in the solution. Again, the entropy of the system cannot decrease. Yet the appearance of the crystal certainly would be regarded as an increase in order. But in this example the temperature of the system could *decrease.* How on earth can we retain the disorder interpretation of entropy when the system has undergone a partial transition from liquid to solid and its temperature also has decreased? Only by heroic efforts might it be possible to do so.

Our heretical criticisms of the disorder interpretation of entropy are neither new nor original. As long ago as 1944, K. K. Darrow, in a superb expository article on the concept of entropy noted that "We cannot . . . always say that *entropy is a measure of disorder* without at times so broadening the definition of 'disorder' as to make the statement true by definition only."

Many years later P. G. Wright published a critical essay on the association of entropy with disorder. He demonstrated by examples that "no exact correlation should be expected between precise quantitative concepts and imprecise qualitative concepts." Entropy is a precisely defined thermodynamic variable that in principle is measurable. Disorder is not such a variable. Wright draws one of his examples (crystallization in a supersaturated solution) from an earlier paper by M. L. McGlashan, whose criticism of thermodynamics taught as "muddled metaphysics" and "bogus history" makes for great reading. Thus there have been a few lone voices crying out against the dubious notion that entropy is disorder. Entropy is entropy, just as energy is energy, unpalatable though this may be. To understand entropy, use it in as many ways as possible, until entropy in your mind is an independent entity, complete and whole in itself, not a mere synonym for the vague concept of disorder. (For another example undermining the notion that entropy is synonymous with disorder, see Problem 31 in Chapter 5.)

Because our heretical remarks about equating entropy with disorder are likely to stir up violent emotions, especially in the countless pedagogues who have resorted to this shaky crutch, we briefly play devil's advocate and criticize the critics. The examples adduced by some of them entailed matter in metastable equilibrium (e.g., subcooled liquid, supersaturated solution), about which we have more to say in Section 5.4. It could be argued that entropy is not defined for matter in metastable states, that entropy is strictly the property of matter in stable equilibrium, and hence that throwing cold water on the equivalence of entropy to disorder by invoking metastable states is fallacious. Yet entropy is just one among several thermodynamic variables. If we argue that entropy is not defined for metastable states, we cannot stop there. We also would have to argue that temperature, pressure, internal energy, and even volume are not defined. But we would be highly reluctant to abandon the view that the temperature and pressure of, say, subcooled water, are well defined—we measure these variables.

*Integrating Factor and Entropy

At the beginning of this section we derived an expression for entropy by way of the first law for an ideal gas. Yet the concept of entropy is not restricted to ideal gases. For an ideal gas, the quantity 1/T transformed Q into the time derivative of a function of thermodynamic state variables, which we called entropy. Yet such a transformation is possible for any simple system.

As our point of departure, we take the first law of thermodynamics in the form

$$Q = \frac{dU}{dt} - W \tag{4.75}$$

For a simple system, the internal energy U depends only on V and T:

$$\frac{dU}{dt} = \frac{\partial U}{\partial V}\frac{dV}{dt} + \frac{\partial U}{\partial T}\frac{dT}{dt} \tag{4.76}$$

We assume that the rate of working W is

$$W = -p\frac{dV}{dt} \tag{4.77}$$

The previous three equations can be combined to obtain

$$Q = \left(\frac{\partial U}{\partial V} + p\right)\frac{dV}{dt} + \frac{\partial U}{\partial T}\frac{dT}{dt} \tag{4.78}$$

Equation (4.78) has the form

$$Q = M(V,T)\frac{dV}{dt} + N(V,T)\frac{dT}{dt} \tag{4.79}$$

Although Q is not, in general, the time derivative of some function of state variables T and V, it is possible to fiddle with Q for a simple system to obtain such a function. Consider the differential equation

$$M(V,T)\frac{dV}{dt} + N(V,T)\frac{dT}{dt} = 0 \tag{4.80}$$

Assume that this equation has only one solution

$$\phi(V,T) = \text{const} \tag{4.81}$$

From this equation we have

$$\frac{d\phi}{dt} = \frac{\partial\phi}{\partial V}\frac{dV}{dt} + \frac{\partial\phi}{\partial T}\frac{dT}{dt} = 0 \tag{4.82}$$

It follows from Eq. (4.82) that

$$-\frac{\partial\phi}{\partial V}\bigg/\frac{\partial\phi}{\partial T} = \frac{dT}{dt}\bigg/\frac{dV}{dt} \tag{4.83}$$

If we combine Eqs. (4.80) and (4.82) we obtain

$$\frac{M}{N} = \frac{\partial\phi}{\partial V}\bigg/\frac{\partial\phi}{\partial T} \tag{4.84}$$

Equation (4.84) is satisfied if

$$\frac{\partial\phi}{\partial T} = \mu(V,T)N(V,T) \tag{4.85}$$

$$\frac{\partial \phi}{\partial V} = \mu(V,T)M(V,T) \tag{4.86}$$

where $\mu(V,T)$ is a unique function (because of our assumption of the uniqueness of ϕ). Now multiply Eq. (4.79) by μ

$$\mu Q = \mu M \frac{dV}{dt} + \mu N \frac{dT}{dt} \tag{4.87}$$

By using Eqs. (4.85) and (4.86), Eq. (4.87) can be written

$$\mu Q = \frac{\partial \phi}{\partial V} \frac{dV}{dt} + \frac{\partial \phi}{\partial T} \frac{dT}{dt} = \frac{d\phi}{dt} \tag{4.88}$$

Thus although Q, in general, cannot be expressed as the time derivative of some thermodynamic function, the quantity μQ can so be expressed. The function μ is called an *integrating factor*. Once we have found one such factor, we can find an infinite number of them. Multiply Eq. (4.88) by some arbitrary continuous function F of ϕ:

$$F(\phi)\mu Q = F(\phi) \frac{d\phi}{dt} \tag{4.89}$$

Define the function G by an integral:

$$G(\phi(t)) = \int_a^{\phi(t)} F(x) \, dx \tag{4.90}$$

where a is a constant. If we differentiate Eq. (4.90), we obtain

$$\frac{dG}{dt} = F(\phi) \frac{d\phi}{dt} \tag{4.91}$$

Thus it follows that

$$F\mu Q = \frac{dG}{dt} \tag{4.92}$$

Hence if μ is an integrating factor for Q, so is $F\mu$, and there are an infinite number of such integrating factors.

When we derived an expression for entropy by way of the ideal gas law, we introduced an integrating factor (not called such). This integrating factor was $1/T$. When Q was multiplied by this integrating factor, we obtained an expression for the time rate of change of entropy

$$\frac{Q}{T} = \frac{dS}{dt} \tag{4.93}$$

But this was only for an ideal gas. The preceding analysis indicates that for any simple system in which the rate of working is given by $-p \, dV/dt$, we have a hope of finding an integrating factor.

4.2 Entropy Changes of Liquids and Solids

We were able to obtain a simple analytical expression for the entropy of an ideal gas as a function of temperature and pressure (or volume) because of the ideal gas equation relating pressure, temperature, and volume. We cannot follow the same path for liquids and solids because there is no simple, universal equation relating their state variables. Nevertheless, we can obtain simple expressions for entropy changes of solids and liquids in the kinds of processes of interest to us.

The rate of change of entropy of a homogeneous substance undergoing a constant-volume process is

$$\frac{dS}{dt} = \frac{Q}{T} = \frac{1}{T}\frac{dU}{dt} = \frac{C_V}{T}\frac{dT}{dt} \tag{4.94}$$

Similarly, for a constant-pressure process

$$\frac{dS}{dt} = \frac{1}{T}\frac{dH}{dt} = \frac{C_p}{T}\frac{dT}{dt} \tag{4.95}$$

With a bit of algebra we can rewrite Eq. (4.72) as

$$\frac{C_V}{C_p} = 1 - \frac{T\alpha^2}{\rho c_p \kappa_T} \tag{4.96}$$

We showed in the previous section that $C_p = C_V$ at the temperature of maximum density of water ($\approx 4°C$), so let's pick a somewhat higher temperature, say 20°C. At this temperature the compressibility of water is about 5×10^{-10} Pa^{-1}, its coefficient of thermal expansion is 2.1×10^{-4} K^{-1}, its density is 1000 kg/m^3, and its specific heat capacity at constant pressure is 4200 J/kg K. With these values in Eq. (4.96) we obtain 0.994 for the ratio of heat capacities. Thus the two heat capacities of liquid water are the same within less than one percent. What about ice? The density of ice is slightly less than and its specific heat capacity about half that of water. The coefficient of thermal expansion of ice is about 1.7×10^{-4} K^{-1} and its compressibility is about 1.2×10^{-10} Pa^{-1}. With these values in Eq. (4.96) we obtain 0.966 for the ratio of heat capacities of ice (at 0°C). Thus the two heat capacities of ice are the same within a few percent.

Because $C_p \approx C_V$ for liquids and solids, Eqs. (4.94) and (4.95) suggest that for *any* process undergone by a liquid or solid, the rate of change of entropy is given by

$$\frac{dS}{dt} = \frac{C}{T}\frac{dT}{dt} \tag{4.97}$$

where we need not worry about whether C is the heat capacity at constant pressure or constant volume. If C is approximately independent of temperature over the range of interest, we can integrate Eq. (4.97):

$$S - S_o = C \ln\left(\frac{T}{T_o}\right) \tag{4.98}$$

where S is the entropy at temperature T and S_o is the entropy at some reference temperature T_o.

The previous arguments suggesting that Eq. (4.97) can be used to determine entropy changes of liquids and solids for any process were of the quick and dirty kind. If you are satisfied with these arguments, skip what follows, but if you would like more convincing arguments, read on.

The change in entropy of a homogeneous system for any process in which temperature and pressure change is approximately

$$\Delta S \approx \frac{\partial S}{\partial T} \Delta T + \frac{\partial S}{\partial p} \Delta p \qquad (4.99)$$

This equation is essentially the first two terms in a Taylor series expansion of entropy. We rewrite Eq. (4.99) in a form more suitable for our purposes:

$$\Delta S = T \frac{\partial S}{\partial T} \frac{\Delta T}{T} + p \frac{\partial S}{\partial p} \frac{\Delta p}{p} \qquad (4.100)$$

The magnitude of the ratio

$$p \frac{\partial S}{\partial p} \bigg/ T \frac{\partial S}{\partial T} \qquad (4.101)$$

tells us the relative contributions to the entropy change in the process for the same fractional changes in temperature $\Delta T/T$ and in pressure $\Delta p/p$.

From the first law of thermodynamics for a reversible process and the definition of entropy, we have

$$\frac{dS}{dt} = \frac{1}{T} \frac{dH}{dt} - \frac{V}{T} \frac{dp}{dt} \qquad (4.102)$$

By using the chain rule to expand dS/dt in Eq. (4.102) in terms of dT/dt and dp/dt and equating the coefficients of these two derivatives on both sides of Eq. (4.102), we obtain

$$\frac{\partial S}{\partial T} = \frac{1}{T} \frac{\partial H}{\partial T} = \frac{C_p}{T} \qquad (4.103)$$

$$\frac{\partial S}{\partial p} = \frac{1}{T} \frac{\partial H}{\partial p} - \frac{V}{T} \qquad (4.104)$$

Applying the same arguments to Eqs. (4.103) and (4.104) as those leading from Eqs. (4.62) and (4.63) to Eq. (4.67) yields

$$\frac{\partial H}{\partial p} = V - T \frac{\partial V}{\partial T} \qquad (4.105)$$

This equation, the enthalpic counterpart to Eq. (4.67), combined with Eq. (4.104) gives

$$\frac{\partial S}{\partial p} = -\frac{\partial V}{\partial T} \qquad (4.106)$$

Now we have all the ingredients to determine the ratio Eq. (4.101), which with a bit of algebra becomes

$$p\,\frac{\partial S}{\partial p}\bigg/T\,\frac{\partial S}{\partial T}=-\frac{p\alpha}{\rho c_p} \qquad (4.107)$$

Does the term on the right side of this equation look familiar? We obtained it in Eq. (3.119) as the ratio of working to heating in a constant-pressure process. We also showed that the magnitude of this ratio for water at one atmosphere is around 10^{-5}. This implies that for any atmospheric process undergone by a liquid or solid (but not a gas) in which both temperature and pressure change, the entropy change is overwhelmingly dominated by the temperature change. This provides the justification for using Eq. (4.97) for determining entropy changes of liquids and solids in atmospheric processes.

4.3 Potential Temperature: Meteorologist's Entropy

Consider a height in the atmosphere at which the pressure and temperature are p and T. The *potential temperature* Θ of the air at this height is defined as the temperature a parcel would have if it were brought adiabatically and reversibly to a reference height where the pressure is p_o (usually taken to be 1000 mb). From Poisson's relation Eq. (3.82) it follows that

$$\Theta = \left(\frac{p_o}{p}\right)^{(\gamma-1)/\gamma} T \qquad (4.108)$$

With this definition of potential temperature we can write Eq. (4.8) in the form

$$S - S_o = C_V\,\gamma\,\ln\left[\left(\frac{T}{T_o}\right)\left(\frac{p_o}{p}\right)^{(\gamma-1)/\gamma}\right] = C_p\,\ln\left(\frac{\Theta}{T_o}\right) \qquad (4.109)$$

where T_o is some reference temperature. Given that our intended applications are to the atmosphere, we write Eq. (4.109) in terms of intensive variables (i.e., specific entropy and specific heat capacity at constant pressure):

$$s - s_o = c_p\,\ln\left(\frac{\Theta}{T_o}\right) \qquad (4.110)$$

Except for a scale factor, potential temperature (strictly, its logarithm) is the same as entropy. Thus an isentropic process is also a constant-potential-temperature process. The lapse rate of entropy is obtained by differentiating Eq. (4.110) with respect to z:

$$\frac{ds}{dz} = \frac{c_p}{\Theta}\,\frac{d\Theta}{dz} \qquad (4.111)$$

The lapse rate of Θ follows from differentiating Eq. (4.108):

$$\frac{d\Theta}{dz} = \frac{\Theta}{T}\left(\frac{dT}{dz} - \frac{\gamma-1}{\gamma}\frac{T}{p}\frac{dp}{dz}\right) \qquad (4.112)$$

By using the equation of hydrostatic balance, Eq. (4.112) can be written

$$\frac{d\Theta}{dz} = \frac{\Theta}{T}\left(\frac{dT}{dz} + \Gamma_d\right) \qquad (4.113)$$

where Γ_d is the dry adiabatic lapse rate. Thus if the temperature profile follows the dry adiabatic lapse rate, potential temperature is constant. Because of Eq. (4.112) we can express our previous criteria for static stability (see Section 3.5) in terms of the gradient of potential temperature:

$$\frac{d\Theta}{dz} > 0, \qquad \text{stable} \tag{4.114}$$

$$\frac{d\Theta}{dz} = 0, \qquad \text{neutral} \tag{4.115}$$

$$\frac{d\Theta}{dz} < 0, \qquad \text{unstable} \tag{4.116}$$

A knee-jerk response to questions about stability is that the atmosphere is stable if temperature increases with height because less dense air overlies more dense air. Conversely, the atmosphere is unstable if temperature decreases with height. This response is based on the notion that density is inversely proportional to temperature, which is not true unless pressure is constant (which it is not in the atmosphere). But if by temperature we mean *potential* temperature, which incorporates both pressure and temperature, we obtain the correct stability criteria Eqs. (4.114)–(4.116). These criteria are easier to remember than when cast in terms of temperature gradients.

As with entropy, once we have defined potential temperature, we need not dwell on its origins and may treat it as another thermodynamic variable. Because entropy is conserved in a reversible adiabatic process, and because the entropy of an ideal gas is proportional to the logarithm of potential temperature, it follows that potential temperature is also conserved in such a process. Indeed, it follows from the definition of potential temperature and the first law of thermodynamics applied to an ideal gas undergoing a process in which $W = -p \, dV/dt$ that

$$C_p \frac{d\Theta}{dt} = \frac{\Theta}{T} Q \tag{4.117}$$

You will not find potential temperature mentioned in physics textbooks. Meteorologists can claim this quantity as their own. Its roots can be traced to an 1888 paper by Herman von Helmholtz, one of the greatest scientists of his time and, indeed, of all times. He used the symbol Θ to designate a quantity he called *Wärmegehalt,* the total heat contained in a mass of air. To measure this "heat" he considered the absolute temperature a mass of air would have if it were brought adiabatically to "normal" pressure. W. von Bezold suggested that *Wärmegehalt* be replaced by the more descriptive term potential temperature, which met with Helmholtz's approval. In 1908, L. A. Bauer succinctly demonstrated the relationship between potential temperature and entropy and suggested that entropic temperature might be a more appropriate term. But he decided against pushing for this because by then potential temperature had come into common use.
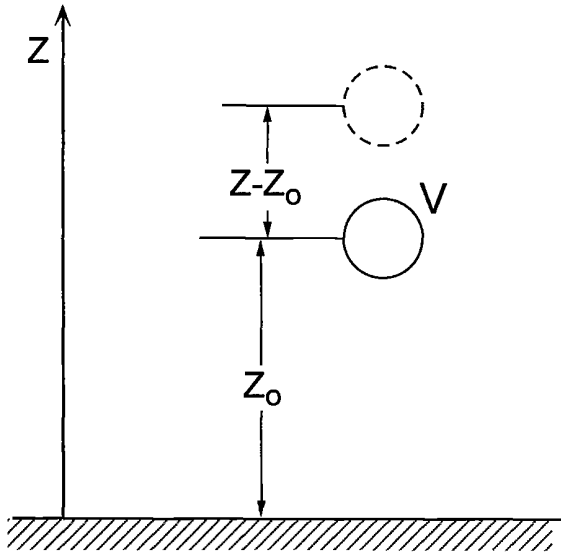
Figure 4.5 A parcel of air with volume V is in stable equilibrium at height z_0. When the parcel is perturbed slightly, its displacement from equilibrium $z - z_0$ will oscillate in time with a characteristic frequency determined by the gradient of potential temperature.

Parcel Oscillations

Whenever a mechanical system has a position of stable equilibrium, small-amplitude oscillations are possible. Consider a parcel of sufficiently small volume V that its properties are uniform. The equation of vertical motion of the center of mass of this parcel (see Fig. 4.5) is

$$F = -g(\rho_p - \rho_s)V = M\frac{d^2z}{dt^2} = \rho_p V\frac{d^2z}{dt^2} \tag{4.118}$$

where the subscripts p and s denote parcel and surroundings, respectively. Let z_o be the equilibrium position from which the parcel is displaced slightly upward or downward. The previous equation of motion can be written

$$\frac{d^2}{dt^2}(z - z_o) = g\left(\frac{\rho_s - \rho_p}{\rho_p}\right) \tag{4.119}$$

By supposition, the pressure p of a displaced parcel is always that of its surroundings:

$$p = \rho_s T_s R = \rho_p T_p R \tag{4.120}$$

Equations (4.118) and (4.120) combined give

$$\frac{d^2}{dt^2}(z - z_o) = g\left(\frac{T_p - T_s}{T_s}\right) \tag{4.121}$$

Because the parcel and its surroundings are always at the same pressure, the ratio of their temperatures is that of their potential temperatures:

$$\frac{d^2}{dt^2}(z - z_o) = g\left(\frac{\Theta_p - \Theta_s}{\Theta_s}\right) \tag{4.122}$$

According to Eq. (4.117), the potential temperature of a system undergoing an adiabatic, reversible process is conserved, and hence the potential temperature of the parcel is constant. At $z = z_o$ the potential temperatures of parcel and surroundings are

equal, so only the potential temperature of the surroundings changes. We can expand the inverse of this potential temperature in a Taylor series

$$\frac{1}{\Theta_s} = \frac{1}{\Theta_p} - \left(\frac{1}{\Theta_s^2} \frac{\partial \Theta_s}{\partial z}\right)_o (z - z_o) + \cdots \tag{4.123}$$

and retain only the first two terms (small-amplitude approximation), which yields an approximate equation of motion

$$\frac{d^2}{dt^2}(z - z_o) = -g\left(\frac{1}{\Theta_s} \frac{\partial \Theta_s}{\partial z}\right)_o (z - z_o) \tag{4.124}$$

We previously showed that the condition for static stability is a positive gradient of potential temperature. Equation (4.124) is the equation of motion of a simple harmonic oscillator with frequency ω_g given by

$$\omega_g^2 = g\left(\frac{1}{\Theta} \frac{\partial \Theta}{\partial z}\right)_o \tag{4.125}$$

where we omit the subscript s. This frequency is the *Brunt–Väisälä* frequency, a fundamental frequency of the atmosphere determined by the product of g and the vertical gradient of potential temperature. The greater this gradient, the more stable the atmosphere, the stronger the restoring force acting on a parcel, and the higher its oscillation frequency. For a typical tropospheric potential temperature gradient of 3°C/km, the period $(2\pi/\omega_g)$ of a buoyancy oscillation is about 10 minutes; for an inversion layer in which the potential temperature gradient is 10°C/km, this period decreases to about 3 minutes. Brunt in a 1927 paper derived the buoyancy oscillation frequency (Eq. 4.125) and noted that the frequencies he obtained for typical tropospheric potential temperature gradients were consistent with frequencies of pressure oscillations sometimes observed in microbarograph traces. He also noted that after submitting his original manuscript he learned that Väisälä had published an article in a Finnish journal 2 years previously, giving a similar derivation for the frequency of buoyancy oscillations. Hence the designation Brunt–Väisälä frequency, or, to be historically accurate, Väisälä–Brunt frequency.

The Brunt–Väisälä frequency is related to the frequency of internal gravity (or buoyancy) waves. As with simple one-dimensional buoyancy oscillations, the restoring force associated with these waves is buoyancy, although parcel motions are not confined to only vertical oscillations. These transverse waves can propagate both vertically and horizontally in the atmosphere. Internal gravity waves should not be confused with external gravity waves (such as those on the ocean), which propagate along the interface between two dissimilar fluids. In recent years there has been a move to call internal gravity waves buoyancy waves because buoyancy is the restoring force (buoyancy requires both gravity and density differences). Furthermore, the term *buoyancy waves* avoids confusion with the gravitational waves of general relativity.

Buoyancy waves are associated with mountain lee waves and can cause the clear-air turbulence sometimes experienced by aircraft. Air deflected by mountain barriers and convective elements impinging upon a stable layer are two mechanisms for generating buoyancy waves in the atmosphere. Lines of clouds parallel to mountain

ridges often mark the upward-moving air associated with lee waves. The distance between these lines is the wavelength, and the corresponding frequency is proportional to the Brunt–Väisälä frequency.

4.4 Atmospheric Applications of the Second Law

The first law of thermodynamics, energy is conserved for an isolated system, usually is emphasized more than the second law, entropy cannot decrease for an isolated system. Yet the first law by itself is a rudderless ship, adrift in a boundless sea. To show this, and to set the stage for an entropy maximization problem of relevance to the atmosphere, we consider the simple example of what happens when two bodies, denoted 1 and 2, with initially different temperatures, are allowed to interact with each other but not with their surroundings (Fig. 4.6). We take this process to occur isobarically. When the composite system comes to equilibrium, what are the temperatures T_{1f} and T_{2f} of its two components for given initial temperatures T_{1i} and T_{2i}, where subscripts i and f denote initial and final? Until we invoke some kind of physical law, we cannot answer this question. All we can say is that the point (T_{1f}, T_{2f}) lies somewhere in the first quadrant in Fig. 4.7. The first law narrows this range of possibilities, but not as much as you might think.

The actual process of isobaric interaction between the two bodies is irreversible. But each body proceeds from a definite equilibrium state to another such state. We may not know how the bodies traverse thermodynamic space, but we do know their points of departure and eventual destinations. Enthalpy is a state function that de-

(a)
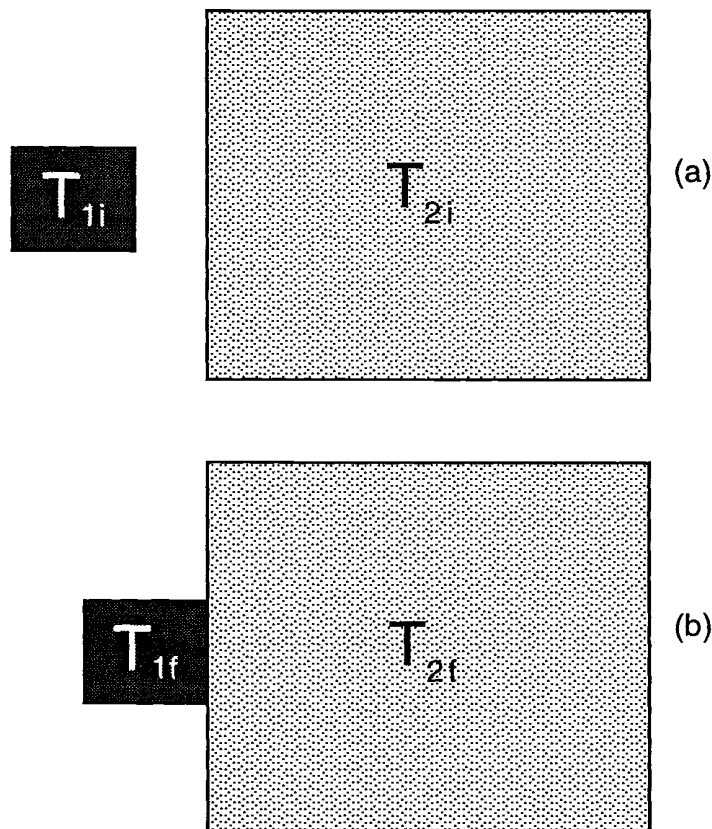
(b) Figure 4.6 Two bodies with different initial temperatures T_{1i} and T_{2i} (a) are brought into contact (b). What are the final temperatures T_{1f} and T_{2f} of these bodies if the interaction between them is isobaric?
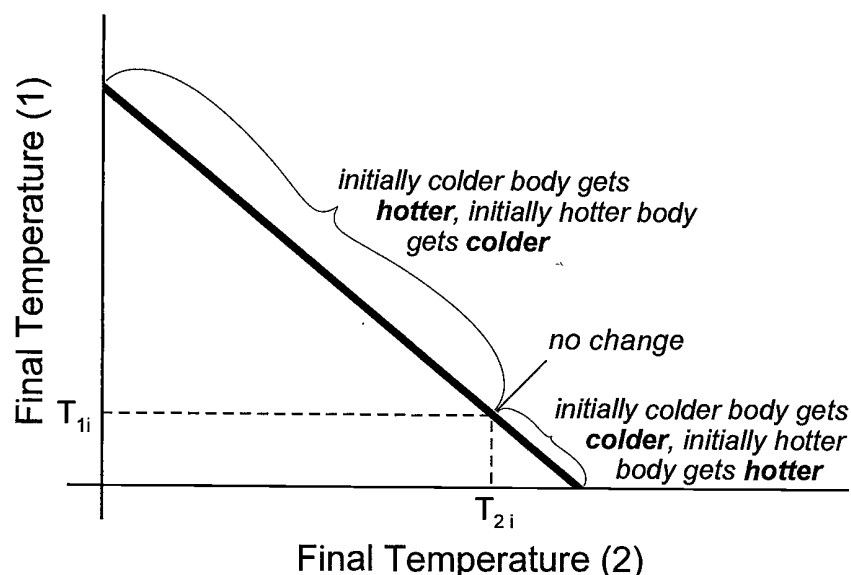
Figure 4.7 The possible outcomes allowed by the first law of thermodynamics of the thought experiment depicted in Fig. 4.6.

pends only on thermodynamic variables (temperature and pressure). The one body evolves by inscrutable processes from a state specified by (p,T_{1i}) to a state specified by (p,T_{1f}), and the other body evolves from a state specified by (p,T_{2i}) to a state specified by (p,T_{2f}). Let us set aside the actual process and assume that body 1 can undergo a reversible, isobaric process from the initial equilibrium state (p,T_{1i}) to the final equilibrium state (p,T_{1f}), and similarly for body 2. This could be achieved, for example, by placing body 1 (or 2) in contact with a series of many reservoirs having arbitrarily small temperature differences beginning with a reservoir at temperature T_{1i} (T_{2i}) and ending with a reservoir at temperature T_{1f} (T_{2f}). As far as body 1 is concerned, it could just as well have undergone this idealized process instead of the real irreversible process: The end result is the same. From the first law, it follows that for the idealized isobaric process, total enthalpy is conserved because the process undergone by the composite system is adiabatic:

$$\Delta H = 0 \qquad (4.126)$$

Let us assume that the heat capacities (at constant pressure) for the two bodies, C_{p1} and C_{p2}, are independent of temperature. With this assumption, Eq. (4.126) yields

$$C_{p1}(T_{1f} - T_{1i}) + C_{p2}(T_{2f} - T_{2i}) = 0 \qquad (4.127)$$

which can be solved for T_{2f}:

$$T_{2f} = \left(\frac{C_{p1}}{C_{p2}} T_{1i} + T_{2i}\right) - \frac{C_{p1}}{C_{p2}} T_{1f} \qquad (4.128)$$

Although we obtained this result for the idealized reversible process, it is also true for the real irreversible process because enthalpy is a state variable: It depends only on the state of the system (as determined by its temperature), not on how it evolved to that state.

The first law shrinks the range of possible outcomes from any point in a rectangu-

lar domain to any point on the straight line Eq. (4.128). But we still are very much at sea. The first law allows for the possibility that the initially colder body will get hotter and the initially hotter body will get colder, or no change in temperature of either body, or the initially colder body will get colder and the initially hotter body will get hotter. All these qualitatively different outcomes are equally likely if our only guide is the first law. Not very satisfying, is it? To find our way along a line of possibilities to a single point requires invoking the second law.

Again, the real process undergone by the two bodies in contact is irreversible. So to determine the total entropy change we have to resort to reversible processes that take each body from its initial equilibrium state to its final equilibrium state. In a reversible, isobaric process, the heating rate is given by

$$Q = \frac{dH}{dt} = C_p \frac{dT}{dt} \tag{4.129}$$

The corresponding entropy change is

$$\Delta S = \int_i^f \frac{C_p}{T} \frac{dT}{dt} \, dt \tag{4.130}$$

which can be integrated under the assumption that C_p is independent of temperature over the range of interest:

$$\Delta S = C_p \ln\left(\frac{T_f}{T_i}\right) \tag{4.131}$$

The total entropy change in the idealized reversible process undergone by the composite system of two bodies is

$$\Delta S = C_{p1} \ln\left(\frac{T_{1f}}{T_{1i}}\right) + C_{p2} \ln\left(\frac{T_{2f}}{T_{2i}}\right) \tag{4.132}$$

But again, because entropy is a state variable, the entropy change Eq. (4.132) for the reversible process is the same as for the irreversible process connecting the same initial and final states.

To find the final state for which the entropy is an extremum, differentiate Eq. (4.132) with respect to T_{1f}, making use of Eq. (4.122) specifying T_{2f} as a function of T_{1f}, and set the result to zero:

$$\frac{d}{dT_{1f}} \Delta S = \frac{C_{p1}}{T_{1f}} - \frac{C_{p2}}{T_{2f}} \frac{C_{p1}}{C_{p2}} = 0 \tag{4.133}$$

which has the solution

$$T_{1f} = T_{2f} \tag{4.134}$$

To determine if this extremum is a minimum or a maximum, take the second derivative

$$\frac{d^2}{dT_{1f}^2} \Delta S = -C_{p1}\left(\frac{1}{T_{1f}^2} + \frac{C_{p1}}{C_{p2}} \frac{1}{T_{2f}^2}\right) \le 0 \tag{4.135}$$

from which it follows that the extremum is a maximum.

We conclude from this analysis that when the two bodies reach the same temperature, no further entropy increase is possible. And if we believe the second law, namely, that the entropy of an isolated system cannot decrease, we conclude that equality of temperature characterizes the final equilibrium state of the two bodies in contact. No further evolution (on average) of the composite system is possible because a change would entail a decrease in entropy, which is not allowed by the second law.

We have not explained anything. Our thermodynamic analysis tells us what happens, not why or how fast. Thermodynamics tells us nothing about the detailed mechanisms by which the initially hotter body cools and the initially colder body warms until they both reach the same temperature. Moreover, this equalization of temperature could occur in the blink of an eye or over the age of the universe. Thermodynamics by itself is powerless to predict the rate at which temperature equalization occurs.

At this point you may be saying to yourselves, All that we have done with the first and second laws and a bit of mathematics is show what everyone knows (and what we previously assumed): Bodies in contact eventually come to the same temperature. This is indeed true, and it is also not surprising given that thermodynamics is firmly rooted in observations of macroscopic systems. We should not be surprised when thermodynamics tells us what everyone knows because this is what went into the making of thermodynamics.

To show that learning about entropy maximization is worth our effort, let us apply this principle to an atmospheric problem for which not everyone knows the answer.

Entropy Maximization in the Atmosphere

The total mass (per unit area) of atmosphere (on a flat earth) between two altitudes z_1 and z_2 is

$$\int_{z_1}^{z_2} \rho \, dz \tag{4.136}$$

Under the assumption of hydrostatic equilibrium, Eq. (4.136) becomes

$$-\int_{z_1}^{z_2} \frac{1}{g} \frac{dp}{dz} \, dz = \frac{1}{g}(p_2 - p_1) \tag{4.137}$$

Thus if we consider a layer of the atmosphere between two constant-pressure surfaces (planes), the total mass of this layer is constant. Suppose that the layer is isolated from its surroundings, neither heated nor cooled by radiation nor by interaction with adjacent air (or ground). What is the equilibrium temperature profile in this layer? To answer this question we need only two tools: the first and second laws of thermodynamics.

The total enthalpy (per unit area) of the layer is

$$\int_{z_1}^{z_2} \rho c_p T \, dz \tag{4.138}$$

where c_p is the specific heat capacity of air. If the layer were not in a gravitational field, total enthalpy would be conserved. But because of Earth's gravitational field, the atmosphere also possesses potential energy (per unit area):

$$\int_{z_1}^{z_2} \rho g z \, dz \tag{4.139}$$

Equations (4.137) and (4.139) account for all the forms of energy the layer can have, and because it is isolated, the sum of these energies must be constant:

$$\int_{z_1}^{z_2} \rho(c_p T + gz) \, dz = \text{const} \tag{4.140}$$

Note that the quantity $c_p T + gz$ is the dry, static energy discussed in Section 3.4.

The total entropy of the layer is the integral of the specific entropy (entropy per unit mass) Eq. (4.110):

$$S = \int_{z_1}^{z_2} \rho s \, dz = \int_{z_1}^{z_2} \rho c_p \ln \Theta \, dz \tag{4.141}$$

where additive constants are omitted and we are being sloppy by taking the logarithm of a quantity with dimensions.

Now we can formulate our entropy maximization problem as follows: What temperature and pressure profile maximizes the total entropy Eq. (4.141) subject to the constraint Eq. (4.140)? To answer this question requires casting the problem in a more felicitous form.

First, we transform from height to pressure by way of the hydrostatic equation. With this transformation Eqs. (4.140) and (4.141) become

$$\int_{p_2}^{p_1} (c_p T + gz) \, dp = \text{const} \tag{4.142}$$

$$S = \frac{c_p}{g} \int_{p_2}^{p_1} \ln \Theta \, dp \tag{4.143}$$

If we combine Eqs. (4.111) and (4.112) and use the ideal gas law together with the relation

$$\frac{\gamma - 1}{\gamma} = \frac{R}{c_p} \tag{4.144}$$

we obtain

$$T \frac{ds}{dz} = \frac{d}{dz} (c_p T + gz) \tag{4.145}$$

or, in pressure coordinates,

$$T \frac{ds}{dp} = \frac{d}{dp} (c_p T + gz) \tag{4.146}$$

Equation (4.111) in pressure coordinates is

$$\frac{ds}{dp} = \frac{c_p}{\Theta} \frac{d\Theta}{dp} \tag{4.147}$$

which, when combined with Eq. (4.146), yields

$$\frac{T}{\Theta} c_p \frac{d\Theta}{dp} = \frac{d}{dp}(c_p T + gz) \tag{4.148}$$

From the defining equation for potential temperature

$$\frac{T}{\Theta} = \left(\frac{p}{p_o}\right)^{(\gamma-1)/\gamma} = \left(\frac{p}{p_o}\right)^{0.28} \tag{4.149}$$

According to this equation T/Θ decreases uniformly from 1 to about 0.64 over the range of pressures from 1000 to 200 mb (about 80% of the atmosphere). Thus if we restrict our attention to layers several hundred mb thick, we make no serious errors if we set the factor T/Θ in Eq. (4.148) equal to 1:

$$c_p \frac{d\Theta}{dp} \approx \frac{d}{dp}(c_p T + gz) \tag{4.150}$$

which can be integrated to yield

$$c_p \Theta \approx c_p T + gz + \text{const} \tag{4.151}$$

Because of Eq. (4.151), Eq. (4.142) is equivalent to

$$\int_{p_2}^{p_1} \Theta \, dp = \text{const} \tag{4.152}$$

One more step makes our problem mathematically simpler: Transform the variable of integration from p to x, where

$$p = x + \frac{p_1 + p_2}{2} \tag{4.153}$$

With this transformation of variables, the mathematical statement of our problem is as follows: Find the function Θ for which the entropy (divided by the constant c_p/g)

$$S = \int_{-\alpha}^{\alpha} \ln \Theta \, dx \tag{4.154}$$

is a maximum subject to the constraint

$$\int_{-\alpha}^{\alpha} \Theta \, dx = \text{const} \tag{4.155}$$

where

$$\alpha = \frac{p_1 - p_2}{2} \tag{4.156}$$

To make this maximization problem mathematically simple, we confine ourselves to the restricted set of linear potential temperature profiles:

$$\Theta = a + bx \tag{4.157}$$

where a and b are arbitrary. Equation (4.157) in Eq. (4.155) yields

$$\int_{-\alpha}^{\alpha} (a + bx) \, dx = 2\alpha a = \text{const} \tag{4.158}$$

and hence a is constant and S depends on b only. The condition for S to be an extremum is that its derivative vanish:

$$\frac{dS}{db} = \frac{d}{db} \int_{-\alpha}^{\alpha} \ln(a+bx) \, dx = \int_{-\alpha}^{\alpha} \frac{x}{a+bx} \, dx = 0 \qquad (4.159)$$

which yields

$$2\alpha b = \ln\left(\frac{a+b\alpha}{a-b\alpha}\right) \qquad (4.160)$$

The solution to Eq. (4.160) is $b = 0$. To determine the nature of this extremum, we differentiate dS/db:

$$\frac{d^2S}{db^2} = -\int_{-\alpha}^{\alpha} \frac{x^2}{(a+bx)^2} \, dx < 0 \qquad (4.161)$$

Thus the extremum is a maximum.

Of all linear potential temperature profiles, a constant potential temperature maximizes the entropy of an isolated layer of the atmosphere in hydrostatic equilibrium. Could we have guessed this without appealing to entropy maximization? Stability considerations alone would not lead to this result. We probably would not guess that an unstable layer corresponds to maximum entropy, yet a constant potential temperature is merely the dividing line between stability and instability.

Entropy maximization requires the equilibrium temperature of an isolated atmospheric layer subjected to mixing with no condensation or evaporation of water to decrease with height at the dry adiabatic rate. This result might appear to be at odds with our everyday experiences. Why isn't the equilibrium profile isothermal? If a solid is isolated from its environment and initially has a nonuniform temperature, conduction eliminates all temperature gradients. But in the atmosphere, energy transfer in an isolated layer is dominated by convection rather than conduction. Lord Kelvin recognized this in an 1862 paper on the convective equilibrium of temperature in the atmosphere: "The particles composing any fluid mass are subject to various changing influences, in particular of pressure, whenever they are moved from one situation to another. In this way they experience changes of temperature altogether independent of the effects produced by the radiation and conduction of heat. When all parts of the fluid are freely interchanged and not sensibly influenced by radiation and conduction, the temperature of the fluid is said to be in a state of convective equilibrium."

Energy transfer in the atmosphere and other fluids differs fundamentally from energy transfer in solids, in which mass motion is absent. Because pressure decreases with height in the atmosphere (a consequence of gravity) and air is fluid and compressible, ascending parcels expand (cool) and descending parcels compress (warm). Thus the example of conduction in solids can impede our understanding of atmospheric convection.

To show how dry convection produces a dry adiabatic lapse rate in the atmosphere consider an isolated layer that is stable, and hence has a lapse rate less than dry adiabatic. Suppose that a parcel moves from one level to another within this layer and then mixes with its surroundings. The temperature of parcels is not conserved as

they move up or down. If a parcel moves to a higher level and then mixes with the air at that level, the layer is destabilized (i.e., the lapse rate increases) because a rising parcel cools at the dry adiabatic rate, and hence will be cooler than its surroundings. Similarly, if a parcel moves to a lower level and then mixes with the air at that level, the layer is also destabilized because a descending parcel warms at the dry adiabatic rate, and hence will be warmer than its surroundings. Mixing therefore increases the entropy of the layer even though it is stable. Only in the absence of gravity would the dry adiabatic lapse rate be zero and the equilibrium temperature profile isothermal.

A few points must be added to this brief description of mixing in the atmosphere. The potential for mixing to occur in a layer depends on its stability and wind shear (variation of wind velocity with height). Mixing is much slower in a stable than in an unstable layer. In the free atmosphere we routinely observe stable layers but rarely observe unstable layers. Why? An unstable layer (if unsaturated) would quickly mix to the dry adiabatic rate. For a stable layer with little wind shear, however, mixing is suppressed, which allows other processes (e.g., radiation, advection) to play a larger role in the vertical temperature profile. In our idealized treatment of entropy maximization of an isolated layer we can ignore motions within the layer and the rate at which the equilibrium state is reached. We have all the time in the world. But we cannot ignore processes other than mixing if we attempt to explain observed temperature profiles. Globally averaged tropospheric and stratospheric temperature profiles, for example, can be explained as a consequence of radiative–convective equilibrium with the additional complication of condensation and evaporation of water. Furthermore, horizontal and vertical advection and energy transfer from the surface can substantially affect local vertical temperature profiles. But regardless of how other processes alter air temperature, local mixing can only increase entropy and, for dry processes, force the temperature profile closer to the dry adiabatic lapse rate.

Although our discussion has focused on the maximum entropy state of an isolated layer, well-mixed layers are most often observed near Earth's surface, where there may be substantial energy transport to and from the layer. Over land, for example, heating of the surface by solar radiation during the day can result in the formation of a shallow, very unstable layer near the surface. Convection generated in this layer can penetrate and stir the air above to form a well-mixed (constant-Θ) layer. This convection also can transport energy into the layer from the surface and cause the mixed layer to warm and deepen as the temperature of the surface increases. This example illustrates the danger of invoking conduction or processes that depend on gradients to explain the vertical transfer of energy in the atmosphere because energy transports are large even though Θ (or equivalently, dry static energy) is constant with height in the mixed layer. Parcels close to the surface can be heated and thus be warmer than air near the bottom of the mixed layer. As these positively buoyant parcels rise, they cool at the dry adiabatic rate. But because temperature in the mixed layer also decreases at this rate, the rising parcels remain warmer than the mixed layer. Thus as they mix with surrounding air, they increase the temperature of the mixed layer even though there is no gradient of Θ. This process is different from conduction in a solid. Although the example given here is associated with warming of the surface by solar radiation, mixed layers also can form and be maintained as cold air moves over a warmer surface. An example of a mixed layer maintained in
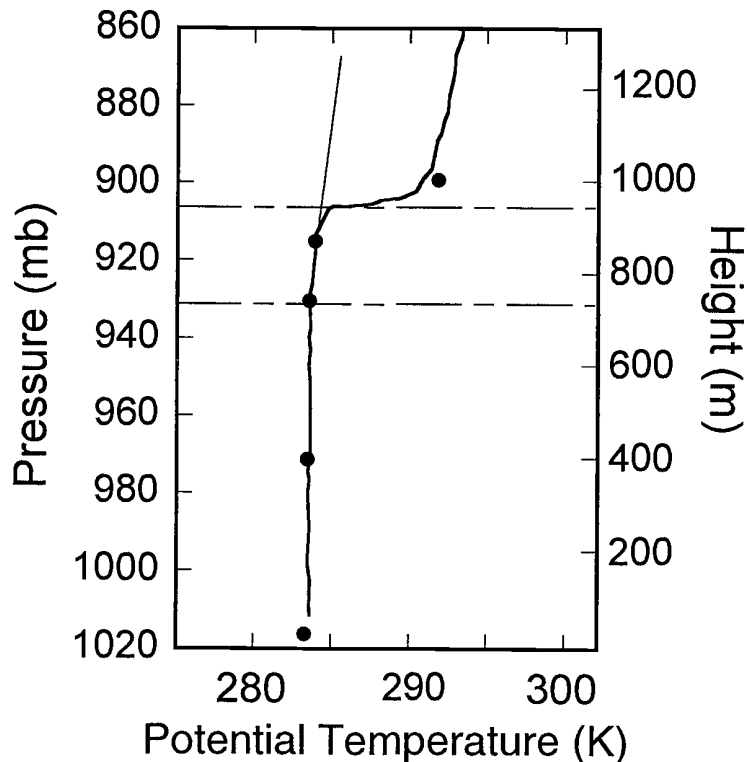
Figure 4.8 Potential temperature profile calculated from temperature and pressure measurements obtained from an instrumented aircraft flown about 500 km off the coast of California. The solid circles are from 10-min averages flown at constant-pressure levels in the same air mass but at different times. The sounding (solid line), from data taken during a slow descent of the aircraft over about 5 min, was obtained before the constant-level measurements were made. A shallow stratus cloud (indicated by dashed lines) was present in the top 200 meters of the mixed layer. Consequently, potential temperature in this part of the layer increases slightly because the lapse rate is less than the dry adiabatic lapse rate due to condensation of water vapor. The sea surface temperature is only about 14°C (Θ = 285.5 K), but colder air advected into the study area resulted in a positive energy flux at the surface, which helped maintain a well-mixed boundary layer. Radiative cooling at the top of the thin cloud also may have enhanced mixing.

this way is illustrated in Fig 4.8, a potential temperature profile obtained from an instrumented aircraft flown off the coast of California where strong winds advected colder air over relatively warmer water. In oceanic regions like this the boundary layer is often fairly moist, resulting in the formation of clouds at the top of the mixed layer. Strong radiative cooling near the tops of these clouds can further promote convection, which helps maintain a mixed layer even if surface heating becomes small.

*Entropy Maximization in the Atmosphere: General Case

In the previous section we showed that among all linear potential temperature profiles, a constant potential temperature maximizes the entropy of an isolated layer of the atmosphere. In this section, we give a more general proof without the restriction

of a linear profile. Let Θ_m be the function for which the entropy Eq. (4.154) is an extremum and let η be a function that specifies the deviation of Θ from Θ_m:

$$\Theta(x) = \Theta_m(x) + \epsilon\eta(x) \qquad (4.162)$$

where ϵ is a parameter. The function $\eta(x)$ is arbitrary subject to the restriction that it must yield a constant integrated potential temperature:

$$J(\epsilon) = \int_{-\alpha}^{\alpha} [\Theta_m(x) + \epsilon\eta(x)]\ dx \qquad (4.163)$$

which requires that

$$\frac{dJ}{d\epsilon} = \int_{-\alpha}^{\alpha} \eta(x)\ dx = 0 \qquad (4.164)$$

Equation (4.162) substituted into Eq. (4.154) yields

$$S(\epsilon) = \int_{-\alpha}^{\alpha} \ln[\Theta_m(x) + \epsilon\eta(x)]\ dx \qquad (4.165)$$

The condition for an extremum is therefore

$$\frac{dS}{d\epsilon} = 0, \qquad \epsilon = 0 \qquad (4.166)$$

which yields

$$\int_{-\alpha}^{\alpha} \frac{\eta(x)}{\Theta_m(x)}\ dx = 0 \qquad (4.167)$$

The extremum is a maximum if the second derivative of S with respect to ϵ at $\epsilon = 0$ is negative. This derivative is

$$\frac{d^2S}{d\epsilon^2} = -\int_{-\alpha}^{\alpha} \frac{\eta^2}{\Theta_m^2}\ dx, \qquad \epsilon = 0 \qquad (4.168)$$

and hence if the extremum exists, it must be a maximum. Now our problem reduces to finding the function Θ_m such that Eq. (4.167) is satisfied, where $\eta(x)$ is arbitrary subject to Eq. (4.164). A sufficient condition that these equations be satisfied is that Θ_m be constant.

To show that constant Θ_m is the only solution, we assume that there is a function $1/\Theta_m$, continuous on the interval $[-\alpha,\alpha]$ but not constant, such that Eq. (4.167) is satisfied for all functions η restricted by Eq. (4.164). Because $1/\Theta_m$ is continuous and positive, there is a positive number M such that $1/\Theta_m > M$ on a subinterval I_1 of $[-\alpha,\alpha]$ having length δ. Moreover, there is a positive number m such that $1/\Theta_m < m$, where $m < M$, on another subinterval I_2 of length $\delta/2$. Because η is arbitrary subject to Eq. (4.164), we may take it to be as follows: $\eta(x) = 1$ when x is in I_1; $\eta(x) = -2$ when x is in I_2. This discontinuous function satisfies Eq. (4.164). With this choice of η, the integral in Eq. (4.167) becomes

$$\int_{-\alpha}^{\alpha} \frac{\eta(x)}{\Theta_m(x)}\ dx = \int_{I_1} \frac{1}{\Theta_m(x)}\ dx - 2\int_{I_2} \frac{1}{\Theta_m(x)}\ dx \qquad (4.169)$$

Because M is the minimum value of $1/\Theta_m$ on the interval I_1, we have

$$\int_{I_1} \frac{1}{\Theta_m}\, dx > M\delta \qquad (4.170)$$

and because m is the maximum value of $1/\Theta_m$ on the interval I_2, we have

$$\int_{I_2} \frac{1}{\Theta_m}\, dx < m\frac{\delta}{2} \qquad (4.171)$$

When the inequalities Eqs. (4.170) and (4.171) are combined with Eq. (4.169), the result is

$$\int_{-\alpha}^{\alpha} \frac{\eta}{\Theta_m}\, dx > (M-m)\,\delta > 0 \qquad (4.172)$$

But this contradicts our assumption that there is a function Θ_m, not constant (but continuous), such that Eq. (4.167) is satisfied for all arbitrary functions η restricted by Eq. (4.164). Hence our original assumption must have been false, and the only potential temperature that satisfies Eq. (4.167) is a constant. We owe this proof by contradiction to George Greaves, a mathematician at the University of Wales, Cardiff.

Thermodynamic Efficiency: The Carnot Cycle

The mass of the atmosphere per unit area of Earth's surface is approximately p_o/g, where p_o is the surface pressure and g is the acceleration due to gravity. If we take the average surface pressure to be about 1000 mb (10^5 Pa), the mass of the atmosphere (per unit area) is about 10^4 kg/m^2. The mean radius of the earth is about 6400 km, which corresponds to a surface area of about 5×10^{14} m^2, and hence the total mass of the atmosphere is about 5×10^{18} kg.

The specific heat capacity of air (at constant pressure) is about 1000 J/kg K. Thus every one-degree change in average temperature of the entire atmosphere corresponds to an enthalpy change of about 5×10^{21} J. This enthalpy change occurring over one year ($\sim 3 \times 10^7$ s) corresponds to about 2×10^{14} W, or 2×10^8 MW. A yearly change in the mean temperature of the atmosphere of only 0.1°C is equivalent to 20,000 1000-MW power plants. And this number pales in comparison with what we obtain when we consider temperature changes of the oceans, with 1000 times the mass and 4 times the specific heat capacity of the atmosphere.

Why do we bother to burn coal and oil in power plants when the atmosphere and oceans are vast reservoirs of energy? By lowering the temperature of the atmosphere a mere 0.1°C per year, we could generate a staggering amount of power and at the same time mitigate the effects of global warming. Why aren't engineers beavering away at schemes for extracting energy from the atmosphere and the oceans? Is this a consequence of a giant conspiracy among OPEC, oil-refining companies, the coal industry, and automobile manufacturers to deprive the world of breakthroughs that would release enormous quantities of cheap but hitherto untapped energy? Why is all the energy in the atmosphere and oceans, free for the asking, going to waste? Scandalous, is it not?

It is indeed true that according to the first law, the atmosphere and oceans are vast

reservoirs of energy, and this law places no restrictions on our ability to tap these reservoirs. The second law, unfortunately, throws cold water on grandiose schemes permitted by the first law. To show this, we must take a closer look at just what is meant by the efficiency of power generation.

Thermodynamic internal energy is disorganized energy, not in a form suitable for many activities in which humans engage. To get something useful to us, this disorganized energy must be transformed into organized energy. An automobile that bucked back and forth and sideways violently would possess kinetic energy but would not take its occupants anywhere. To be useful, the center of mass of the automobile must move mostly in one direction.

Let us consider the simplest conceptual device that transforms disorganized thermodynamic internal energy into organized energy capable of turning electric power generators, driving tractors, trucks, automobiles, airplanes, and an endless variety of machines, from giant steel mills to lawn mowers.

As our system we take a fixed mass of a working fluid, which could be a gas or a liquid. This system undergoes a *cycle*, by which is meant that its state changes in a series of processes such that the initial and final states are the same. The particular cycle of interest is made up of two isothermal and two adiabatic processes, all assumed to be reversible. To aid our thinking, it is helpful to represent this cycle on a pressure–volume (p–v) diagram (Fig. 4.9).

The system begins its cycle at point 1 and undergoes an isothermal compression at constant temperature T_{low}. We can imagine the system to be compressed while in contact with a reservoir at this temperature. At point 2, the system is further compressed, but this time adiabatically to point 3, where it then expands isothermally at temperature $T_{high} > T_{low}$. Again, this expansion may be imagined to occur while the system is in contact with a reservoir at this temperature. At point 4, the system is isolated from the reservoir and further expands adiabatically back to the starting point. And on and on forever.
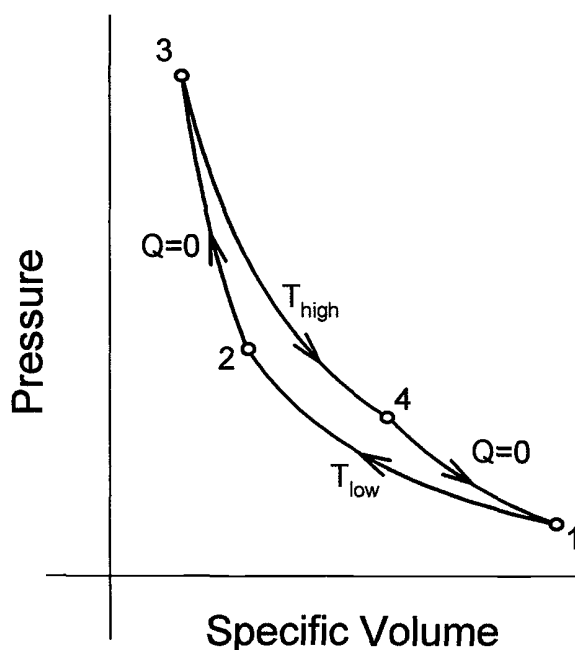

Figure 4.9 Carnot cycle undergone by an ideal gas. The cycle is illustrated by a closed curve in p–v space formed by the intersection of two isotherms (T_{high} and T_{low}) with two adiabats ($Q = 0$).

Because the process is cyclic, the total working is, from the first law, the negative of the total heating:

$$W_{tot} = -Q_{tot} \tag{4.173}$$

The total heating in the isothermal process between states 1 and 2 must be negative in order to maintain constant temperature in a compression. Thus for this process

$$Q_{low} = -\int_1^2 Q \, dt \tag{4.174}$$

where Q_{low} is positive. For the high-temperature isothermal process we have

$$Q_{high} = -\int_3^4 Q \, dt \tag{4.175}$$

where Q_{high} is positive. Two of the processes are adiabatic, and hence do not contribute to the total heating. The total heating over the cycle is

$$Q_{tot} = Q_{high} - Q_{low} \tag{4.176}$$

which, from Eq. (4.174), yields

$$W_{tot} = -(Q_{high} - Q_{low}) \tag{4.177}$$

Negative total working means that work is done by the system, which is certainly necessary if the cycle represents the operation of an engine.

What is the efficiency of this cyclic process? The answer depends on what is meant by efficiency. And it also depends on the desired output of the engine. We have to agree that this desired output is W_{tot}. To maintain a reservoir at an elevated temperature requires doing something that results in the expenditure of resources, for example, burning coal or gasoline or oil. Once a fuel has been burned, it cannot be burned again. The most economical use of fuels results when W_{tot} is as large as possible relative to Q_{high}. The low-temperature reservoir need not cost anything: It could be the atmosphere or a large body of water. We may define the efficiency of this thermodynamic engine as the ratio of the desired result, the magnitude of W_{tot}, divided by what it costs in energy units:

$$\eta = \frac{|W_{tot}|}{Q_{high}} = \frac{Q_{high} - Q_{low}}{Q_{high}} \tag{4.178}$$

The efficiency in the form of Eq. (4.178) is not expressed in terms of readily measurable thermodynamic variables. So let us go a step further.

Because entropy is a state variable, the change in entropy of the system is zero in a cycle. This total zero entropy change is made up of separate entropy changes:

$$\Delta S = \Delta S_{12} + \Delta S_{23} + \Delta S_{34} + \Delta S_{41} = 0 \tag{4.179}$$

Neither of the two reversible adiabatic processes contributes to the total entropy change. The entropy change in the low-temperature isothermal process is

$$\Delta S_{12} = \int_1^2 \frac{Q}{T_{low}} \, dt = -\frac{Q_{low}}{T_{low}} \tag{4.180}$$

The entropy change in the high-temperature isothermal process is

$$\Delta S_{34} = \int_3^4 \frac{Q}{T_{high}}\, dt = \frac{Q_{high}}{T_{high}}$$

(4.181)

From Eqs. (4.179), (4.180), and (4.181) it follows that

$$\frac{Q_{low}}{T_{low}} = \frac{Q_{high}}{T_{high}}$$

(4.182)

With Eq. (4.182), the efficiency Eq. (4.178) becomes

$$\eta = 1 - \frac{T_{low}}{T_{high}}$$

(4.183)

This efficiency is often called the *thermodynamic* or *Carnot efficiency*, and the corresponding cycle is called the *Carnot cycle*.

All the separate processes in the cycle were taken to be reversible. Real processes are irreversible. We showed previously that in at least one irreversible process (free expansion) work was required to restore the system to its original state. This result, together with our intuitive feelings about entropy gained from having considered its behavior, lead us to postulate that the Carnot efficiency Eq. (4.183) for an idealized cycle is greater than that for any real cycle operating between the same two temperature limits. And in fact, no one has ever constructed an engine more efficient than permitted by Eq. (4.183), which sets an upper limit to the efficiency of a thermodynamic engine that transforms disorganized energy into organized energy. The practical utility of the Carnot efficiency is that it puts an end to fruitless searches for a substance or cycle that will yield high efficiencies. The Carnot efficiency is independent of the working fluid and the cyclic process it undergoes.

If only the good die young, Sadi Léonard Nicolas Carnot (b. Paris, 1796; d. 1832) must have been very good. Dispatched to an early grave by cholera, Carnot lived not more than 2 years longer than Mozart, another candle that burned briefly but brightly. Unlike Mozart, Carnot's fame was almost entirely posthumous. During his life he published but one short monograph, *Reflections on the Motive Power of Fire and on Machines Fitted to Develop this Power*, which received favorable initial reviews (1824) and then was mostly forgotten for 10 years until Clapeyron (whom we shall meet in Chapter 5) resuscitated it, putting Carnot's mostly qualitative arguments in a more analytical form. Yet although Clapeyron was himself a steam engine engineer, and surely understood and appreciated the implications of Carnot's work for engineering practice, neither Clapeyron nor any other French engineers were markedly influenced by it. Only when this work was resuscitated for a second time in the middle of the nineteenth century by William Thomson (later Lord Kelvin) and Rudolf Clausius were the originality and profundity of Carnot's ideas fully appreciated, by then too late for him to enjoy the fruits of fame even though he would have been comfortably middle-aged. Carnot's monograph, which he took pains to make accessible to as wide an audience as possible, still repays reading today even though its theoretical underpinning is the officially discredited caloric theory according to which heat is a weightless fluid that can be neither created nor destroyed.

The *p*–*v* diagram Fig. 4.9 provides a graphical means of visualizing the work done

by a thermodynamic engine in a cyclic process. From the definition of the rate of working in a reversible process we have

$$w_{tot} = \int_1^2 p \frac{dv}{dt} \, dt + \int_2^3 p \frac{dv}{dt} \, dt + \int_3^4 p \frac{dv}{dt} \, dt + \int_4^1 p \frac{dv}{dt} \, dt \qquad (4.184)$$

where w_{tot} is the (positive) work done per cycle per unit mass of working substance. Equation (4.184) is often written compactly as

$$w_{tot} = \oint p \, dv \qquad (4.185)$$

where the circle intersecting the integral sign denotes integration around a cycle (in a clockwise sense for w_{tot} to be positive). According to Eq. (4.184) or (4.185) the work done in any cyclic process is proportional to the area enclosed by the closed curve representing the process on a p–v diagram.

Now we have all that is necessary to answer the question posed at the beginning of this section: Why can't we extract energy from the atmosphere and oceans? The naive answer is that they would have to serve as both high- and low-temperature reservoirs. According to Eq. (4.183), the Carnot efficiency of an engine operating between these two reservoirs would be zero. Reality, although bleak, is not quite this bleak. There are finite temperature differences in both the atmosphere and the oceans. For example, the difference between the surface air temperature and that at 5 km might be 30–40 K. For an average temperature of 300 K, the corresponding Carnot efficiency is about 10%, the maximum attainable. A real engine exploiting this temperature difference would be less efficient. Similarly for the oceans. From the surface to a depth of about 1 km, the temperature may decrease by about 20 K, which corresponds to a Carnot efficiency less than 10%. It also has been pointed out by G. F. R. Ellis that the clear night sky is a low-temperature reservoir. The equivalent blackbody temperature of the clear sky often is taken to be about 250 K. If the mean surface temperature is 280 K, a 30 K difference could be exploited, but the associated Carnot efficiency would be low.

Devices could be constructed to exploit natural temperature differences. But how? This could be done only with turbines and pipes made of steel or aluminum, which would have to be designed, built, and maintained. Given the low Carnot efficiency of such devices, the investment in resources is not likely to yield a sufficient return. Schemes for generating power by exploiting ocean temperature differences have been promoted for over half a century. These schemes even have inspired their own acronym: OTEC (Ocean Thermal Energy Conversion). Presumably, adherents of OTEC hope to break the back of OPEC, but this happy event has yet to occur, and we suspect that at least part of the reason is the fundamental limit imposed by the Carnot efficiency.

Entropic Derivation of the Dry Adiabatic Lapse Rate

In Section 3.4 we derived the dry adiabatic lapse rate by means of the Poisson relations and the hydrostatic equation. The process underlying this derivation was adiabatic and reversible, and hence isentropic. Thus we should be able to derive the dry

adiabatic lapse rate by invoking conservation of entropy. We shall do so as a prelude to obtaining the moist adiabatic lapse rate in Section 6.5.

The specific entropy s of an ideal gas can be expressed as a function of the two intensive thermodynamic variables, temperature and pressure:

$$s = c_p \ln T - R \ln p \tag{4.186}$$

where additive constants are omitted. The total entropy of a parcel of dry air mixed with water vapor is therefore

$$S = S_d + S_v = M_d c_{pd} \ln T - R_d M_d \ln p_d + M_v c_{pv} \ln T - R_v M_v \ln e \tag{4.187}$$

Conservation of the entropy of the parcel in ascent (or descent) requires that

$$\frac{d}{dz}(S_d + S_v) = 0 \tag{4.188}$$

from which follows

$$\frac{1}{T}\frac{dT}{dz}(M_d c_{pd} + M_v c_{pv}) - \frac{1}{p_d}\frac{dp_d}{dz}R_d M_d - \frac{1}{e}\frac{de}{dz}R_v M_v = 0 \tag{4.189}$$

Both the dry air and the water vapor components of the parcel obey the ideal gas law

$$p_d = \rho_d R_d T, \qquad e = \rho_v R_v T \tag{4.190}$$

We also have

$$M_d = \rho_d V, \qquad M_v = \rho_v V \tag{4.191}$$

where V is the volume of the parcel. If Eqs. (4.188)–(4.190) are combined

$$\frac{1}{T}\frac{dT}{dz}(M_d c_{pd} + M_v c_{pv}) - \frac{V}{T}\frac{dp}{dz} = 0 \tag{4.192}$$

where $p = p_d + e$. The density ρ of the parcel is

$$\rho = \frac{M_d + M_v}{V} \tag{4.193}$$

and its specific heat capacity at constant pressure is

$$c_p = \frac{M_d c_{pd} + M_v c_{pv}}{M_d + M_v} \tag{4.194}$$

Equations (4.190)–(4.192) and the hydrostatic equation then yield

$$\frac{dT}{dz} = -\frac{g}{c_p} \tag{4.195}$$

in accordance with what we obtained previously when we were innocent of any knowledge of entropy. This gives us confidence that entropy conservation sometimes can take us where we want to go.

In this derivation of the dry adiabatic lapse rate, for which, by definition, water vapor does not condense, separating the water vapor and dry air components was not

necessary. We would have obtained the same result if we had expressed the entropy of a parcel in terms of the average properties (specific heat capacity and gas constant) and total pressure of air. But water vapor in the atmosphere can and does condense, and when we allow for this, treating water vapor and dry air as separate components becomes necessary because the vapor can be transformed into liquid water or ice, the specific entropies of which are not equal to that of the vapor phase.

SELECTED REFERENCES AND SUGGESTIONS FOR FURTHER READING

A rebuttal by Neil Postman to our complaint at the beginning of this chapter about how the term entropy has been mangled by popular use is in *The End of Education* (Knopf, 1995), p. 77: "The physicists describe all this [entropy] in mathematical codes and do not always appreciate the ways in which the rest of us employ their ideas of entropy and negentropy. Still, the universe is as much our business as theirs . . ."

Two books devoted exclusively to entropy are Henry A. Bent, *The Second Law* (Oxford U. P., 1965) and J. D. Fast, *Entropy,* 2nd Ed. (Gordon and Breach, 1968).

For criticisms of the now-widespread and hence virtually ineradicable notion that entropy is synonymous with disorder, see Kark K. Darrow, 1944: The concept of entropy. *American Journal of Physics,* Vol. 12, pp. 183–96; M. L. McGlashan, 1966: The use and misuse of the laws of thermodynamics. *Journal of Chemical Education,* Vol. 43, pp. 226–32; P. G. Wright, 1970: Entropy and disorder. *Contemporary Physics,* Vol. 11, pp. 581–88.

The relation between potential temperature and entropy was first pointed out by Louis Bauer, 1908: On the relationship between "Potential Temperature" and "Entropy." *Physical Review,* Vol. 26, pp. 177–83.

One of the two papers in which what is now called the Brunt–Väisälä frequency is derived is that by David Brunt, 1927: The period of simple vertical oscillations in the atmosphere. *Quarterly Journal of the Royal Meteorological Society,* Vol. 53, pp. 30–32.

Our discussion of entropy maximization in the atmosphere was inspired by F. K. Ball, 1956: Energy changes involved in disturbing a dry atmosphere. *Quarterly Journal of the Royal Meteorological Society,* Vol. 82, pp. 15–29.

A translation by R. H. Thurston of Carnot's monograph under the title *Reflections on the Motive Power of Heat* was published by The American Society of Mechanical Engineers in 1943.

For a sketch of the life of Sadi Carnot, see James F. Challey's entry in the *Dictionary of Scientific Biography.* An insightful article on Carnot's work is by F. C. Frank, 1966: Reflections on Sadi Carnot. *Physics Education,* Vol. 1, pp. 11–18. The curious lack of impact Carnot's monograph had on the work of steam engine engineers, even Clapeyron, who did as much as anyone to bring Carnot's ideas to a wider audience, is discussed by Milton Kerker, 1960: Sadi Carnot and the steam engine engineers. *Isis,* Vol. 51, pp. 257–70.

For the use of the night sky as a low-temperature reservoir, see G. F. R. Ellis, 1979: Utilization of low-grade thermal energy by using the clear night sky as a heat sink. *American Journal of Physics*, Vol. 47, pp. 1010–11.

Ocean thermal energy conversion (OTEC) is discussed by Roger H. Charlier and John R. Justus, *Ocean Energies: Environmental, Economic and Technological Aspects of Alternative Energy Sources* (Elsevier, 1993).

PROBLEMS

1. The boilers for the earliest steam engines were not much different from ordinary tea kettles. Estimate the maximum efficiency of such steam engines.

2. Suppose that you want to increase the efficiency of an engine operating between two temperatures, T_{low} and T_{high}. You have two choices: You can decrease T_{low} by a given amount ΔT or you can increase T_{high} by the same amount. Which would you choose in order to obtain the greatest increase in efficiency? *Hint:* This question is easy to answer by applying simple calculus.

3. In Chapter 1 we asserted without explanation that the so-called energy crisis is really an entropy crisis. You now should be able to explain what we meant by this. Please do so.

4. The atmosphere has been likened to a giant thermodynamic engine in which disorganized energy is transformed into the organized kinetic energy of the winds. The general circulation of the atmosphere is driven by temperature differences between the polar and equatorial regions. Estimate the maximum efficiency of the atmospheric engine. Do this for both summer and winter in the Northern Hemisphere. On the basis of your calculations, what would you predict for the relative strength of winds in summer and winter? Keep in mind that in the equatorial region there are no seasonal changes comparable to those at mid-latitudes.

5. The specific entropy (entropy per unit mass) of liquid water is greater than that of solid water (ice) at the same temperature. This is true at 0°C, and would also be true at any temperature. That is, the entropy of ice at, say, −20°C is less than that of liquid water at −20°C. Why, therefore, doesn't ice in surroundings at −20°C spontaneously melt? What is special about 0°C from a thermodynamic point of view? What is wanted here is an argument based on the *proper* use of the second law of thermodynamics. *Hints:* The enthalpy of water is greater than that of ice at the same temperature. You may assume that this enthalpy difference is approximately independent of temperature. Assume that this hypothetical melting of cold ice takes place at constant pressure in surroundings at constant temperature. You may also assume that the entropy difference between ice and water is approximately independent of temperature.

6. Many years ago one of the authors used to drive regularly through Yuma, Arizona. Outside town he would pass a strange orange grove. Scattered among the

orange trees were large towers onto which were mounted propellers driven by engines. The scene was that of a flight of silent airplanes mysteriously hovering over the orange grove.

The purpose of these propellers (huge fans) is to prevent frost damage on clear, cool nights. During such nights, air near the surface is cooled as the ground cools because of net longwave radiation. Since air higher in the atmosphere may be relatively unaffected by surface cooling, air near the surface can become very stable. How are fans used to keep the air near the surface warmer than it would be otherwise? At first glance, this seems crazy: Aren't fans used for cooling?

To show that these fans can yield the desired results, you must support your arguments with calculations. Consider a situation where at sunset air temperature near the surface is 10°C and the lowest several hundred meters of the atmosphere is well mixed. At sunrise, many hours later, air near the surface has cooled to −5°C while the air temperature at 50 m and above is unchanged (you may assume that temperature varies linearly with height between the surface and 50 m). Now turn on the fans. Can this result in a surface temperature above freezing? *Hints:* This is a potential temperature problem. Do not be disturbed if your simple analysis leads to a temperature discontinuity. This corresponds to a very thin inversion layer.

7. In his delightful book *The Simple Science of Flight* Henk Tennekes asserts on pp. 117–18 that "The colder the air the better. The efficiency of jet engines improves as the difference between the intake temperature and the combustion chamber increases . . . This fact has far-reaching consequences for jetliners. The coldest air is found in the lower stratosphere, about 10 kilometers . . . The temperature there is about 55°C below zero." Estimate the change in efficiency of jet engines as a consequence of flying at 10 km instead of, say, at 3 km. You will have to guess or look up the temperatures in the combustion chamber of a jet engine. Keep in mind that if the intake air is colder at the higher altitude, so will be the air in the combustion chamber.

8. We are so accustomed to thinking of energy as being conserved and entropy as increasing that we may lose sight of the fact that the converse is possible. In what kind of a general process is the entropy of a system conserved but its internal energy is not? This is a simple and straightforward question, not a trick.

9. You may have encountered the assertion that according to the second law of thermodynamics you cannot unscramble an egg. Yet with a bit of thought you should be able to devise a very simple method for unscrambling an egg. After you have done so, try to reconcile the supposedly impossible unscrambling of an egg with the second law of thermodynamics.

10. A refrigerator is the reverse of an engine: Work is done *on* rather than *by* the working fluid in a refrigerator. Devise an efficiency for a refrigerator. Keep in mind that such an efficiency (for refrigerators called *coefficient of performance*) is the ratio of what is desired to what this costs (in energy). After you have obtained this efficiency for any refrigerator, determine what it is for an ideal

Carnot refrigerator (one that operates on a Carnot cycle). Estimate the Carnot coefficient of performance for a typical refrigerator. If you express the Carnot coefficient of performance as a function of the Carnot efficiency, a striking difference between the two becomes obvious. Discuss and interpret.

11. The so-called heat pump is essentially a refrigerator. In winter a heat pump functions as a heater, the low-temperature reservoir being the outside environment, the high-temperature reservoir being the inside of a house. In summer, a heat pump functions as an air conditioner, the low-temperature reservoir being the inside of a house, the high-temperature reservoir being its outside environment. Obtain an expression for the coefficients of performance of a heat pump acting as a heater and as an air conditioner. Estimate values for these coefficients of performance. See the previous problem.

12. You sometimes encounter assertions that a refrigerator "transfers heat from a cold body to a hot body" (in seeming defiance of the second law of thermodynamics). Is this assertion literally true? *Hint:* The easiest way to answer this question is to consider carefully each step of a Carnot cycle on a *p–v* diagram. For simplicity, take the working fluid to be an ideal gas. Ask yourself if at any point of the cycle energy is transferred from a cold to a hot body by virtue of direct interaction between the two.

13. The author of a newspaper article on heat pumps (see Problem 20 in Chapter 1) asserts that "new models are so efficient they produce up to four units of heat for every one unit of electricity they use." This statement seems false but is in fact true. Convince yourself that it is true (see Problem 11) but misleading. Someone reading this article and taking it at face value might conclude that burning fuel oil (or natural gas) to heat a house in winter is madness. Why burn oil when you can use a heat pump and get four times as much heating? This statement is true but incomplete. Please discuss.