

# Entropy and the Second Law of Thermodynamics

## 20-1 ENTROPY

### Learning Objectives

*After reading this module, you should be able to ...*

- 20.01 Identify the second law of thermodynamics: If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes; it never decreases.
- 20.02 Identify that entropy is a state function (the value for a particular state of the system does not depend on how that state is reached).
- 20.03 Calculate the change in entropy for a process by integrating the inverse of the temperature (in kelvins) with respect to the heat  $Q$  transferred during the process.
- 20.04 For a phase change with a constant temperature process, apply the relationship between the entropy change  $\Delta S$ , the total transferred heat  $Q$ , and the temperature  $T$  (in kelvins).

### Key Ideas

- An irreversible process is one that cannot be reversed by means of small changes in the environment. The direction in which an irreversible process proceeds is set by the change in entropy  $\Delta S$  of the system undergoing the process. Entropy  $S$  is a state property (or state function) of the system; that is, it depends only on the state of the system and not on the way in which the system reached that state. The entropy postulate states (in part): If an irreversible process occurs in a closed system, the entropy of the system always increases.
- The entropy change  $\Delta S$  for an irreversible process that takes a system from an initial state  $i$  to a final state  $f$  is exactly equal to the entropy change  $\Delta S$  for any reversible process that takes the system between those same two states. We can compute the latter (but not the former) with

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}.$$

Here  $Q$  is the energy transferred as heat to or from the system during the process, and  $T$  is the temperature of the system in kelvins during the process.

- For a reversible isothermal process, the expression for an entropy change reduces to

- 20.05 For a temperature change  $\Delta T$  that is small relative to the temperature  $T$ , apply the relationship between the entropy change  $\Delta S$ , the transferred heat  $Q$ , and the average temperature  $T_{\text{avg}}$  (in kelvins).
- 20.06 For an ideal gas, apply the relationship between the entropy change  $\Delta S$  and the initial and final values of the pressure and volume.
- 20.07 Identify that if a process is an irreversible one, the integration for the entropy change must be done for a reversible process that takes the system between the same initial and final states as the irreversible process.
- 20.08 For stretched rubber, relate the elastic force to the rate at which the rubber's entropy changes with the change in the stretching distance.

$$\Delta S = S_f - S_i = \frac{Q}{T}.$$

- When the temperature change  $\Delta T$  of a system is small relative to the temperature (in kelvins) before and after the process, the entropy change can be approximated as

$$\Delta S = S_f - S_i \approx \frac{Q}{T_{\text{avg}}},$$

where  $T_{\text{avg}}$  is the system's average temperature during the process.

- When an ideal gas changes reversibly from an initial state with temperature  $T_i$  and volume  $V_i$  to a final state with temperature  $T_f$  and volume  $V_f$ , the change  $\Delta S$  in the entropy of the gas is

$$\Delta S = S_f - S_i = nR \ln \frac{V_f}{V_i} + nC_V \ln \frac{T_f}{T_i}.$$

- The second law of thermodynamics, which is an extension of the entropy postulate, states: If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases. In equation form,

$$\Delta S \geq 0.$$

## What Is Physics?

Time has direction, the direction in which we age. We are accustomed to many one-way processes—that is, processes that can occur only in a certain sequence (the right way) and never in the reverse sequence (the wrong way). An egg is dropped onto a floor, a pizza is baked, a car is driven into a lamppost, large waves erode a sandy beach—these one-way processes are **irreversible**, meaning that they cannot be reversed by means of only small changes in their environment.

One goal of physics is to understand why time has direction and why one-way processes are irreversible. Although this physics might seem disconnected from the practical issues of everyday life, it is in fact at the heart of any engine, such as a car engine, because it determines how well an engine can run.

The key to understanding why one-way processes cannot be reversed involves a quantity known as *entropy*.

## Irreversible Processes and Entropy

The one-way character of irreversible processes is so pervasive that we take it for granted. If these processes were to occur *spontaneously* (on their own) in the wrong way, we would be astonished. Yet *none* of these wrong-way events would violate the law of conservation of energy.

For example, if you were to wrap your hands around a cup of hot coffee, you would be astonished if your hands got cooler and the cup got warmer. That is obviously the wrong way for the energy transfer, but the total energy of the closed system (*hands + cup of coffee*) would be the same as the total energy if the process had run in the right way. For another example, if you popped a helium balloon, you would be astonished if, later, all the helium molecules were to gather together in the original shape of the balloon. That is obviously the wrong way for molecules to spread, but the total energy of the closed system (*molecules + room*) would be the same as for the right way.

Thus, changes in energy within a closed system do not set the direction of irreversible processes. Rather, that direction is set by another property that we shall discuss in this chapter—the *change in entropy*  $\Delta S$  of the system. The change in entropy of a system is defined later in this module, but we can here state its central property, often called the *entropy postulate*:



If an irreversible process occurs in a *closed* system, the entropy  $S$  of the system always increases; it never decreases.

Entropy differs from energy in that entropy does *not* obey a conservation law. The *energy* of a closed system is conserved; it always remains constant. For irreversible processes, the *entropy* of a closed system always increases. Because of this property, the change in entropy is sometimes called “the arrow of time.” For example, we associate the explosion of a popcorn kernel with the forward direction of time and with an increase in entropy. The backward direction of time (a videotape run backwards) would correspond to the exploded popcorn reforming the original kernel. Because this backward process would result in an entropy decrease, it never happens.

There are two equivalent ways to define the change in entropy of a system: (1) in terms of the system’s temperature and the energy the system gains or loses as heat, and (2) by counting the ways in which the atoms or molecules that make up the system can be arranged. We use the first approach in this module and the second in Module 20-4.

## Change in Entropy

Let's approach this definition of *change in entropy* by looking again at a process that we described in Modules 18-5 and 19-9: the free expansion of an ideal gas. Figure 20-1a shows the gas in its initial equilibrium state *i*, confined by a closed stopcock to the left half of a thermally insulated container. If we open the stopcock, the gas rushes to fill the entire container, eventually reaching the final equilibrium state *f* shown in Fig. 20-1b. This is an irreversible process; all the molecules of the gas will never return to the left half of the container.

The *p-V* plot of the process, in Fig. 20-2, shows the pressure and volume of the gas in its initial state *i* and final state *f*. Pressure and volume are *state properties*, properties that depend only on the state of the gas and not on how it reached that state. Other state properties are temperature and energy. We now assume that the gas has still another state property—its entropy. Furthermore, we define the **change in entropy**  $S_f - S_i$  of a system during a process that takes the system from an initial state *i* to a final state *f* as

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} \quad (\text{change in entropy defined}). \quad (20-1)$$

Here  $Q$  is the energy transferred as heat to or from the system during the process, and  $T$  is the temperature of the system in kelvins. Thus, an entropy change depends not only on the energy transferred as heat but also on the temperature at which the transfer takes place. Because  $T$  is always positive, the sign of  $\Delta S$  is the same as that of  $Q$ . We see from Eq. 20-1 that the SI unit for entropy and entropy change is the joule per kelvin.

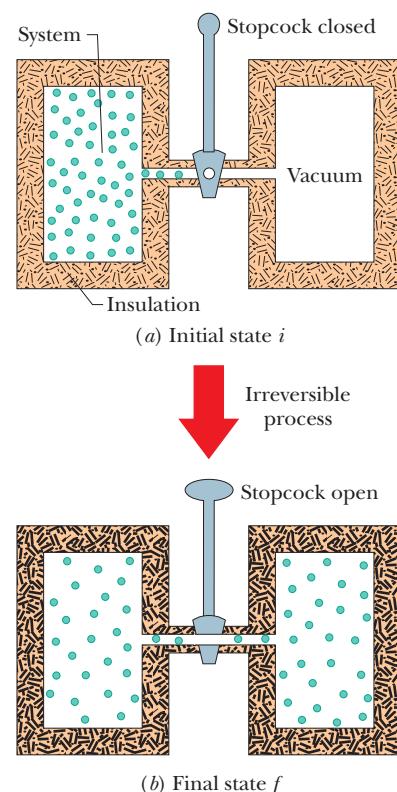
There is a problem, however, in applying Eq. 20-1 to the free expansion of Fig. 20-1. As the gas rushes to fill the entire container, the pressure, temperature, and volume of the gas fluctuate unpredictably. In other words, they do not have a sequence of well-defined equilibrium values during the intermediate stages of the change from initial state *i* to final state *f*. Thus, we cannot trace a pressure–volume path for the free expansion on the *p-V* plot of Fig. 20-2, and we cannot find a relation between  $Q$  and  $T$  that allows us to integrate as Eq. 20-1 requires.

However, if entropy is truly a state property, the difference in entropy between states *i* and *f* must depend *only on those states* and not at all on the way the system went from one state to the other. Suppose, then, that we replace the irreversible free expansion of Fig. 20-1 with a *reversible* process that connects states *i* and *f*. With a reversible process we can trace a pressure–volume path on a *p-V* plot, and we can find a relation between  $Q$  and  $T$  that allows us to use Eq. 20-1 to obtain the entropy change.

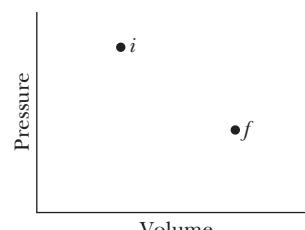
We saw in Module 19-9 that the temperature of an ideal gas does not change during a free expansion:  $T_i = T_f = T$ . Thus, points *i* and *f* in Fig. 20-2 must be on the same isotherm. A convenient replacement process is then a reversible isothermal expansion from state *i* to state *f*, which actually proceeds *along* that isotherm. Furthermore, because  $T$  is constant throughout a reversible isothermal expansion, the integral of Eq. 20-1 is greatly simplified.

Figure 20-3 shows how to produce such a reversible isothermal expansion. We confine the gas to an insulated cylinder that rests on a thermal reservoir maintained at the temperature  $T$ . We begin by placing just enough lead shot on the movable piston so that the pressure and volume of the gas are those of the initial state *i* of Fig. 20-1a. We then remove shot slowly (piece by piece) until the pressure and volume of the gas are those of the final state *f* of Fig. 20-1b. The temperature of the gas does not change because the gas remains in thermal contact with the reservoir throughout the process.

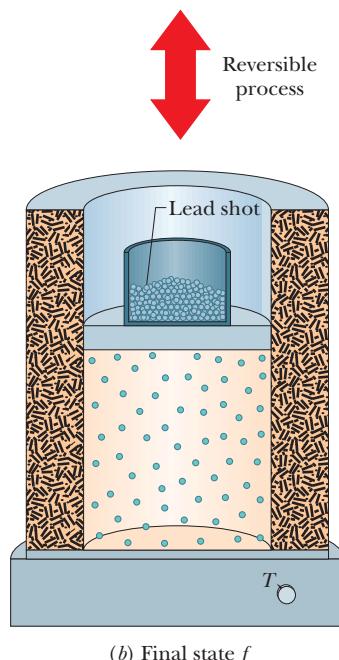
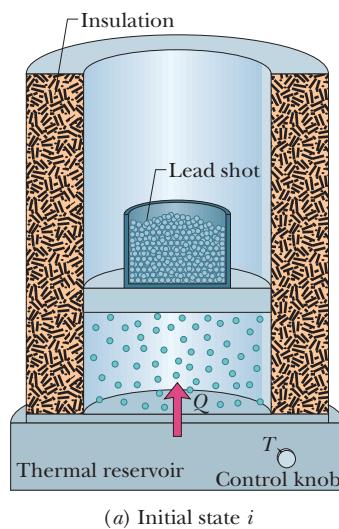
The reversible isothermal expansion of Fig. 20-3 is physically quite different from the irreversible free expansion of Fig. 20-1. However, *both processes have the same initial state and the same final state and thus must have the same change in*



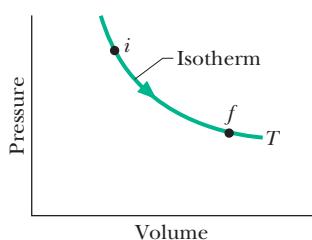
**Figure 20-1** The free expansion of an ideal gas. (a) The gas is confined to the left half of an insulated container by a closed stopcock. (b) When the stopcock is opened, the gas rushes to fill the entire container. This process is irreversible; that is, it does not occur in reverse, with the gas spontaneously collecting itself in the left half of the container.



**Figure 20-2** A *p-V* diagram showing the initial state *i* and the final state *f* of the free expansion of Fig. 20-1. The intermediate states of the gas cannot be shown because they are not equilibrium states.



**Figure 20-3** The isothermal expansion of an ideal gas, done in a reversible way. The gas has the same initial state  $i$  and same final state  $f$  as in the irreversible process of Figs. 20-1 and 20-2.



**Figure 20-4** A  $p$ - $V$  diagram for the reversible isothermal expansion of Fig. 20-3. The intermediate states, which are now equilibrium states, are shown.

entropy. Because we removed the lead shot slowly, the intermediate states of the gas are equilibrium states, so we can plot them on a  $p$ - $V$  diagram (Fig. 20-4).

To apply Eq. 20-1 to the isothermal expansion, we take the constant temperature  $T$  outside the integral, obtaining

$$\Delta S = S_f - S_i = \frac{1}{T} \int_i^f dQ.$$

Because  $\int dQ = Q$ , where  $Q$  is the total energy transferred as heat during the process, we have

$$\Delta S = S_f - S_i = \frac{Q}{T} \quad (\text{change in entropy, isothermal process}). \quad (20-2)$$

To keep the temperature  $T$  of the gas constant during the isothermal expansion of Fig. 20-3, heat  $Q$  must have been energy transferred *from* the reservoir *to* the gas. Thus,  $Q$  is positive and the entropy of the gas *increases* during the isothermal process and during the free expansion of Fig. 20-1.

To summarize:



To find the entropy change for an irreversible process, replace that process with any reversible process that connects the same initial and final states. Calculate the entropy change for this reversible process with Eq. 20-1.

When the temperature change  $\Delta T$  of a system is small relative to the temperature (in kelvins) before and after the process, the entropy change can be approximated as

$$\Delta S = S_f - S_i \approx \frac{Q}{T_{\text{avg}}}, \quad (20-3)$$

where  $T_{\text{avg}}$  is the average temperature of the system in kelvins during the process.



### Checkpoint 1

Water is heated on a stove. Rank the entropy changes of the water as its temperature rises (a) from 20°C to 30°C, (b) from 30°C to 35°C, and (c) from 80°C to 85°C, greatest first.

### Entropy as a State Function

We have assumed that entropy, like pressure, energy, and temperature, is a property of the state of a system and is independent of how that state is reached. That entropy is indeed a *state function* (as state properties are usually called) can be deduced only by experiment. However, we can prove it is a state function for the special and important case in which an ideal gas is taken through a reversible process.

To make the process reversible, it is done slowly in a series of small steps, with the gas in an equilibrium state at the end of each step. For each small step, the energy transferred as heat to or from the gas is  $dQ$ , the work done by the gas is  $dW$ , and the change in internal energy is  $dE_{\text{int}}$ . These are related by the first law of thermodynamics in differential form (Eq. 18-27):

$$dE_{\text{int}} = dQ - dW.$$

Because the steps are reversible, with the gas in equilibrium states, we can use Eq. 18-24 to replace  $dW$  with  $p dV$  and Eq. 19-45 to replace  $dE_{\text{int}}$  with  $nC_V dT$ . Solving for  $dQ$  then leads to

$$dQ = p dV + nC_V dT.$$

Using the ideal gas law, we replace  $p$  in this equation with  $nRT/V$ . Then we divide each term in the resulting equation by  $T$ , obtaining

$$\frac{dQ}{T} = nR \frac{dV}{V} + nC_V \frac{dT}{T}.$$

Now let us integrate each term of this equation between an arbitrary initial state  $i$  and an arbitrary final state  $f$  to get

$$\int_i^f \frac{dQ}{T} = \int_i^f nR \frac{dV}{V} + \int_i^f nC_V \frac{dT}{T}.$$

The quantity on the left is the entropy change  $\Delta S (= S_f - S_i)$  defined by Eq. 20-1. Substituting this and integrating the quantities on the right yield

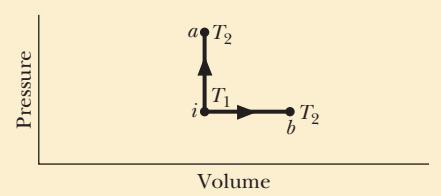
$$\Delta S = S_f - S_i = nR \ln \frac{V_f}{V_i} + nC_V \ln \frac{T_f}{T_i}. \quad (20-4)$$

Note that we did not have to specify a particular reversible process when we integrated. Therefore, the integration must hold for all reversible processes that take the gas from state  $i$  to state  $f$ . Thus, the change in entropy  $\Delta S$  between the initial and final states of an ideal gas depends only on properties of the initial state ( $V_i$  and  $T_i$ ) and properties of the final state ( $V_f$  and  $T_f$ );  $\Delta S$  does not depend on how the gas changes between the two states.



### Checkpoint 2

An ideal gas has temperature  $T_1$  at the initial state  $i$  shown in the  $p$ - $V$  diagram here. The gas has a higher temperature  $T_2$  at final states  $a$  and  $b$ , which it can reach along the paths shown. Is the entropy change along the path to state  $a$  larger than, smaller than, or the same as that along the path to state  $b$ ?



### Sample Problem 20.01 Entropy change of two blocks coming to thermal equilibrium

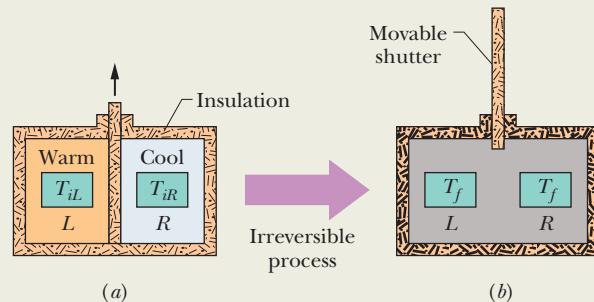
Figure 20-5a shows two identical copper blocks of mass  $m = 1.5 \text{ kg}$ : block  $L$  at temperature  $T_{iL} = 60^\circ\text{C}$  and block  $R$  at temperature  $T_{iR} = 20^\circ\text{C}$ . The blocks are in a thermally insulated box and are separated by an insulating shutter. When we lift the shutter, the blocks eventually come to the equilibrium temperature  $T_f = 40^\circ\text{C}$  (Fig. 20-5b). What is the net entropy change of the two-block system during this irreversible process? The specific heat of copper is  $386 \text{ J/kg}\cdot\text{K}$ .

#### KEY IDEA

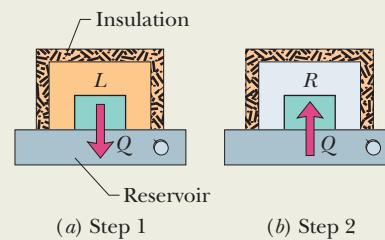
To calculate the entropy change, we must find a reversible process that takes the system from the initial state of Fig. 20-5a to the final state of Fig. 20-5b. We can calculate the net entropy change  $\Delta S_{\text{rev}}$  of the reversible process using Eq. 20-1, and then the entropy change for the irreversible process is equal to  $\Delta S_{\text{rev}}$ .

**Calculations:** For the reversible process, we need a thermal reservoir whose temperature can be changed slowly (say, by turning a knob). We then take the blocks through the following two steps, illustrated in Fig. 20-6.

**Step 1:** With the reservoir's temperature set at  $60^\circ\text{C}$ , put block  $L$  on the reservoir. (Since block and reservoir are at the same temperature, they are already in thermal equilib-



**Figure 20-5** (a) In the initial state, two copper blocks  $L$  and  $R$ , identical except for their temperatures, are in an insulating box and are separated by an insulating shutter. (b) When the shutter is removed, the blocks exchange energy as heat and come to a final state, both with the same temperature  $T_f$ .



**Figure 20-6** The blocks of Fig. 20-5 can proceed from their initial state to their final state in a reversible way if we use a reservoir with a controllable temperature (a) to extract heat reversibly from block  $L$  and (b) to add heat reversibly to block  $R$ .

rium.) Then slowly lower the temperature of the reservoir and the block to 40°C. As the block's temperature changes by each increment  $dT$  during this process, energy  $dQ$  is transferred as heat from the block to the reservoir. Using Eq. 18-14, we can write this transferred energy as  $dQ = mc dT$ , where  $c$  is the specific heat of copper. According to Eq. 20-1, the entropy change  $\Delta S_L$  of block  $L$  during the full temperature change from initial temperature  $T_{iL}$  ( $= 60^\circ\text{C} = 333\text{ K}$ ) to final temperature  $T_f$  ( $= 40^\circ\text{C} = 313\text{ K}$ ) is

$$\begin{aligned}\Delta S_L &= \int_i^f \frac{dQ}{T} = \int_{T_{iL}}^{T_f} \frac{mc dT}{T} = mc \int_{T_{iL}}^{T_f} \frac{dT}{T} \\ &= mc \ln \frac{T_f}{T_{iL}}.\end{aligned}$$

Inserting the given data yields

$$\begin{aligned}\Delta S_L &= (1.5\text{ kg})(386\text{ J/kg}\cdot\text{K}) \ln \frac{313\text{ K}}{333\text{ K}} \\ &= -35.86\text{ J/K}.\end{aligned}$$

**Step 2:** With the reservoir's temperature now set at 20°C,

put block  $R$  on the reservoir. Then slowly raise the temperature of the reservoir and the block to 40°C. With the same reasoning used to find  $\Delta S_L$ , you can show that the entropy change  $\Delta S_R$  of block  $R$  during this process is

$$\begin{aligned}\Delta S_R &= (1.5\text{ kg})(386\text{ J/kg}\cdot\text{K}) \ln \frac{313\text{ K}}{293\text{ K}} \\ &= +38.23\text{ J/K}.\end{aligned}$$

The net entropy change  $\Delta S_{\text{rev}}$  of the two-block system undergoing this two-step reversible process is then

$$\begin{aligned}\Delta S_{\text{rev}} &= \Delta S_L + \Delta S_R \\ &= -35.86\text{ J/K} + 38.23\text{ J/K} = 2.4\text{ J/K}.\end{aligned}$$

Thus, the net entropy change  $\Delta S_{\text{irrev}}$  for the two-block system undergoing the actual irreversible process is

$$\Delta S_{\text{irrev}} = \Delta S_{\text{rev}} = 2.4\text{ J/K}. \quad (\text{Answer})$$

This result is positive, in accordance with the entropy postulate.

### Sample Problem 20.02 Entropy change of a free expansion of a gas

Suppose 1.0 mol of nitrogen gas is confined to the left side of the container of Fig. 20-1a. You open the stopcock, and the volume of the gas doubles. What is the entropy change of the gas for this irreversible process? Treat the gas as ideal.

#### KEY IDEAS

- (1) We can determine the entropy change for the irreversible process by calculating it for a reversible process that provides the same change in volume. (2) The temperature of the gas does not change in the free expansion. Thus, the reversible process should be an isothermal expansion—namely, the one of Figs. 20-3 and 20-4.

**Calculations:** From Table 19-4, the energy  $Q$  added as heat to the gas as it expands isothermally at temperature  $T$  from an initial volume  $V_i$  to a final volume  $V_f$  is

$$Q = nRT \ln \frac{V_f}{V_i},$$

in which  $n$  is the number of moles of gas present. From Eq. 20-2 the entropy change for this reversible process in which the temperature is held constant is

$$\Delta S_{\text{rev}} = \frac{Q}{T} = \frac{nRT \ln(V_f/V_i)}{T} = nR \ln \frac{V_f}{V_i}.$$

Substituting  $n = 1.00\text{ mol}$  and  $V_f/V_i = 2$ , we find

$$\begin{aligned}\Delta S_{\text{rev}} &= nR \ln \frac{V_f}{V_i} = (1.00\text{ mol})(8.31\text{ J/mol}\cdot\text{K})(\ln 2) \\ &= +5.76\text{ J/K}.\end{aligned}$$

Thus, the entropy change for the free expansion (and for all other processes that connect the initial and final states shown in Fig. 20-2) is

$$\Delta S_{\text{irrev}} = \Delta S_{\text{rev}} = +5.76\text{ J/K}. \quad (\text{Answer})$$

Because  $\Delta S$  is positive, the entropy increases, in accordance with the entropy postulate.



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### The Second Law of Thermodynamics

Here is a puzzle. In the process of going from (a) to (b) in Fig. 20-3, the entropy change of the gas (our system) is positive. However, because the process is reversible, we can also go from (b) to (a) by, say, gradually adding lead shot to the piston, to restore the initial gas volume. To maintain a constant temperature, we need to remove energy as heat, but that means  $Q$  is negative and thus the entropy change is also. Doesn't this entropy decrease violate the entropy postulate: en-

tropy always increases? No, because the postulate holds only for irreversible processes in closed systems. Here, the process is *not* irreversible and the system is *not* closed (because of the energy transferred to and from the reservoir as heat).

However, if we include the reservoir, along with the gas, as part of the system, then we do have a closed system. Let's check the change in entropy of the enlarged system *gas + reservoir* for the process that takes it from (b) to (a) in Fig. 20-3. During this reversible process, energy is transferred as heat from the gas to the reservoir—that is, from one part of the enlarged system to another. Let  $|Q|$  represent the absolute value (or magnitude) of this heat. With Eq. 20-2, we can then calculate separately the entropy changes for the gas (which loses  $|Q|$ ) and the reservoir (which gains  $|Q|$ ). We get

$$\Delta S_{\text{gas}} = -\frac{|Q|}{T}$$

and

$$\Delta S_{\text{res}} = +\frac{|Q|}{T}.$$

The entropy change of the closed system is the sum of these two quantities: 0.

With this result, we can modify the entropy postulate to include both reversible and irreversible processes:



If a process occurs in a *closed* system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases.

Although entropy may decrease in part of a closed system, there will always be an equal or larger entropy increase in another part of the system, so that the entropy of the system as a whole never decreases. This fact is one form of the **second law of thermodynamics** and can be written as

$$\Delta S \geq 0 \quad (\text{second law of thermodynamics}), \quad (20-5)$$

where the greater-than sign applies to irreversible processes and the equals sign to reversible processes. Equation 20-5 applies only to closed systems.

In the real world almost all processes are irreversible to some extent because of friction, turbulence, and other factors, so the entropy of real closed systems undergoing real processes always increases. Processes in which the system's entropy remains constant are always idealizations.

### Force Due to Entropy

To understand why rubber resists being stretched, let's write the first law of thermodynamics

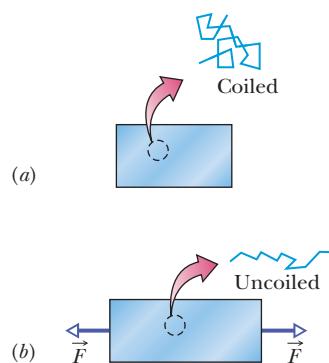
$$dE = dQ - dW$$

for a rubber band undergoing a small increase in length  $dx$  as we stretch it between our hands. The force from the rubber band has magnitude  $F$ , is directed inward, and does work  $dW = -F dx$  during length increase  $dx$ . From Eq. 20-2 ( $\Delta S = Q/T$ ), small changes in  $Q$  and  $S$  at constant temperature are related by  $dS = dQ/T$ , or  $dQ = T dS$ . So, now we can rewrite the first law as

$$dE = T dS + F dx. \quad (20-6)$$

To good approximation, the change  $dE$  in the internal energy of rubber is 0 if the total stretch of the rubber band is not very much. Substituting 0 for  $dE$  in Eq. 20-6 leads us to an expression for the force from the rubber band:

$$F = -T \frac{dS}{dx}. \quad (20-7)$$



**Figure 20-7** A section of a rubber band (a) unstretched and (b) stretched, and a polymer within it (a) coiled and (b) uncoiled.

This tells us that  $F$  is proportional to the rate  $dS/dx$  at which the rubber band's entropy changes during a small change  $dx$  in the rubber band's length. Thus, you can *feel* the effect of entropy on your hands as you stretch a rubber band.

To make sense of the relation between force and entropy, let's consider a simple model of the rubber material. Rubber consists of cross-linked polymer chains (long molecules with cross links) that resemble three-dimensional zig-zags (Fig. 20-7). When the rubber band is at its rest length, the polymers are coiled up in a spaghetti-like arrangement. Because of the large disorder of the molecules, this rest state has a high value of entropy. When we stretch a rubber band, we uncoil many of those polymers, aligning them in the direction of stretch. Because the alignment decreases the disorder, the entropy of the stretched rubber band is less. That is, the change  $dS/dx$  in Eq. 20-7 is a negative quantity because the entropy decreases with stretching. Thus, the force on our hands from the rubber band is due to the tendency of the polymers to return to their former disordered state and higher value of entropy.



## 20-2 ENTROPY IN THE REAL WORLD: ENGINES

### Learning Objectives

After reading this module, you should be able to . . .

**20.09** Identify that a heat engine is a device that extracts energy from its environment in the form of heat and does useful work and that in an *ideal* heat engine, all processes are reversible, with no wasteful energy transfers.

**20.10** Sketch a  $p$ - $V$  diagram for the cycle of a Carnot engine, indicating the direction of cycling, the nature of the processes involved, the work done during each process (including algebraic sign), the net work done in the cycle, and the heat transferred during each process (including algebraic sign).

**20.11** Sketch a Carnot cycle on a temperature–entropy diagram, indicating the heat transfers.

**20.12** Determine the net entropy change around a Carnot cycle.

**20.13** Calculate the efficiency  $\varepsilon_C$  of a Carnot engine in terms of the heat transfers and also in terms of the temperatures of the reservoirs.

**20.14** Identify that there are no perfect engines in which the energy transferred as heat  $Q$  from a high temperature reservoir goes entirely into the work  $W$  done by the engine.

**20.15** Sketch a  $p$ - $V$  diagram for the cycle of a Stirling engine, indicating the direction of cycling, the nature of the processes involved, the work done during each process (including algebraic sign), the net work done in the cycle, and the heat transfers during each process.

### Key Ideas

- An engine is a device that, operating in a cycle, extracts energy as heat  $|Q_H|$  from a high-temperature reservoir and does a certain amount of work  $|W|$ . The efficiency  $\varepsilon$  of any engine is defined as

$$\varepsilon = \frac{\text{energy we get}}{\text{energy we pay for}} = \frac{|W|}{|Q_H|}.$$

- In an ideal engine, all processes are reversible and no wasteful energy transfers occur due to, say, friction and turbulence.

- A Carnot engine is an ideal engine that follows the cycle of Fig. 20-9. Its efficiency is

$$\varepsilon_C = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_L}{T_H},$$

in which  $T_H$  and  $T_L$  are the temperatures of the high- and low-temperature reservoirs, respectively. Real engines always have an efficiency lower than that of a Carnot engine. Ideal engines that are not Carnot engines also have efficiencies lower than that of a Carnot engine.

- A perfect engine is an imaginary engine in which energy extracted as heat from the high-temperature reservoir is converted completely to work. Such an engine would violate the second law of thermodynamics, which can be restated as follows: No series of processes is possible whose sole result is the absorption of energy as heat from a thermal reservoir and the complete conversion of this energy to work.

### Entropy in the Real World: Engines

A **heat engine**, or more simply, an **engine**, is a device that extracts energy from its environment in the form of heat and does useful work. At the heart of every engine is a *working substance*. In a steam engine, the working substance is water,

in both its vapor and its liquid form. In an automobile engine the working substance is a gasoline–air mixture. If an engine is to do work on a sustained basis, the working substance must operate in a *cycle*; that is, the working substance must pass through a closed series of thermodynamic processes, called *strokes*, returning again and again to each state in its cycle. Let us see what the laws of thermodynamics can tell us about the operation of engines.

### A Carnot Engine

We have seen that we can learn much about real gases by analyzing an ideal gas, which obeys the simple law  $pV = nRT$ . Although an ideal gas does not exist, any real gas approaches ideal behavior if its density is low enough. Similarly, we can study real engines by analyzing the behavior of an **ideal engine**.



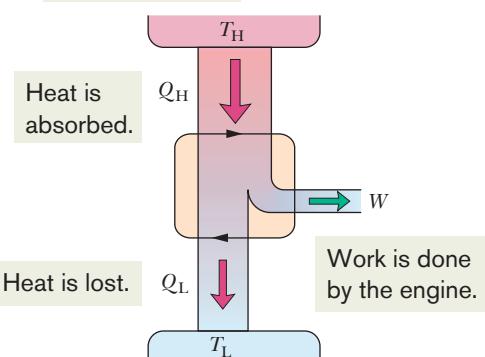
In an ideal engine, all processes are reversible and no wasteful energy transfers occur due to, say, friction and turbulence.

We shall focus on a particular ideal engine called a **Carnot engine** after the French scientist and engineer N. L. Sadi Carnot (pronounced “car-no”), who first proposed the engine’s concept in 1824. This ideal engine turns out to be the best (in principle) at using energy as heat to do useful work. Surprisingly, Carnot was able to analyze the performance of this engine before the first law of thermodynamics and the concept of entropy had been discovered.

Figure 20-8 shows schematically the operation of a Carnot engine. During each cycle of the engine, the working substance absorbs energy  $|Q_H|$  as heat from a thermal reservoir at constant temperature  $T_H$  and discharges energy  $|Q_L|$  as heat to a second thermal reservoir at a constant lower temperature  $T_L$ .

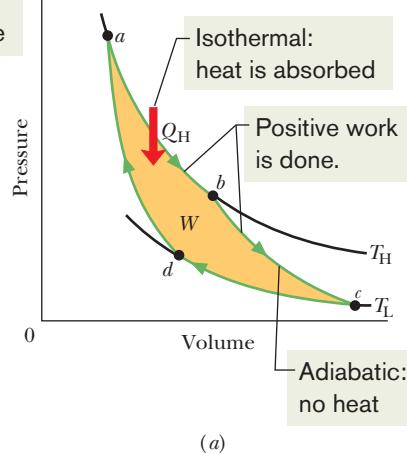
Figure 20-9 shows a *p*-*V* plot of the *Carnot cycle*—the cycle followed by the working substance. As indicated by the arrows, the cycle is traversed in the clockwise direction. Imagine the working substance to be a gas, confined to an insulating cylinder with a weighted, movable piston. The cylinder may be placed at will on either of the two thermal reservoirs, as in Fig. 20-6, or on an insulating slab. Figure 20-9a shows that, if we place the cylinder in contact with the high-temperature reservoir at temperature  $T_H$ , heat  $|Q_H|$  is transferred *to* the working substance *from* this reservoir as the gas undergoes an isothermal *expansion* from volume  $V_a$  to volume  $V_b$ . Similarly, with the working substance in contact with the low-temperature reservoir at temperature  $T_L$ , heat  $|Q_L|$  is transferred *from*

Schematic of a Carnot engine

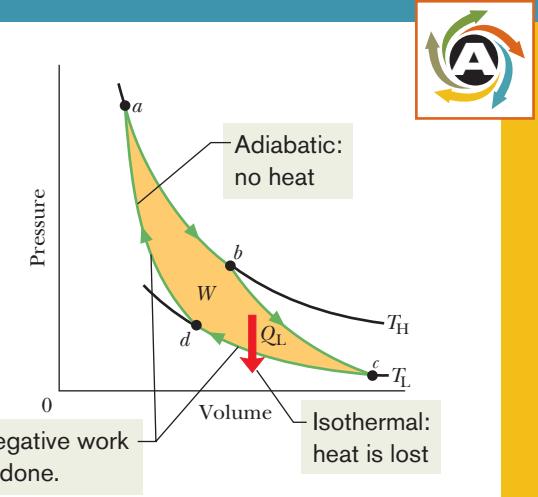


**Figure 20-8** The elements of a Carnot engine. The two black arrowheads on the central loop suggest the working substance operating in a cycle, as if on a *p*-*V* plot. Energy  $|Q_H|$  is transferred as heat from the high-temperature reservoir at temperature  $T_H$  to the working substance. Energy  $|Q_L|$  is transferred as heat from the working substance to the low-temperature reservoir at temperature  $T_L$ . Work  $W$  is done by the engine (actually by the working substance) on something in the environment.

Stages of a Carnot engine



**Figure 20-9** A pressure–volume plot of the cycle followed by the working substance of the Carnot engine in Fig. 20-8. The cycle consists of two isothermal (*ab* and *cd*) and two adiabatic processes (*bc* and *da*). The shaded area enclosed by the cycle is equal to the work  $W$  per cycle done by the Carnot engine.



the working substance *to* the low-temperature reservoir as the gas undergoes an isothermal compression from volume  $V_c$  to volume  $V_d$  (Fig. 20-9b).

In the engine of Fig. 20-8, we assume that heat transfers to or from the working substance can take place *only* during the isothermal processes *ab* and *cd* of Fig. 20-9. Therefore, processes *bc* and *da* in that figure, which connect the two isotherms at temperatures  $T_H$  and  $T_L$ , must be (reversible) adiabatic processes; that is, they must be processes in which no energy is transferred as heat. To ensure this, during processes *bc* and *da* the cylinder is placed on an insulating slab as the volume of the working substance is changed.

During the processes *ab* and *bc* of Fig. 20-9*a*, the working substance is expanding and thus doing positive work as it raises the weighted piston. This work is represented in Fig. 20-9*a* by the area under curve *abc*. During the processes *cd* and *da* (Fig. 20-9*b*), the working substance is being compressed, which means that it is doing negative work on its environment or, equivalently, that its environment is doing work on it as the loaded piston descends. This work is represented by the area under curve *cda*. The *net work per cycle*, which is represented by  $W$  in both Figs. 20-8 and 20-9, is the difference between these two areas and is a positive quantity equal to the area enclosed by cycle *abcd* in Fig. 20-9. This work  $W$  is performed on some outside object, such as a load to be lifted.

Equation 20-1 ( $\Delta S = \int dQ/T$ ) tells us that any energy transfer as heat must involve a change in entropy. To see this for a Carnot engine, we can plot the Carnot cycle on a temperature–entropy ( $T$ - $S$ ) diagram as in Fig. 20-10. The lettered points *a*, *b*, *c*, and *d* there correspond to the lettered points in the  $p$ - $V$  diagram in Fig. 20-9. The two horizontal lines in Fig. 20-10 correspond to the two isothermal processes of the cycle. Process *ab* is the isothermal expansion of the cycle. As the working substance (reversibly) absorbs energy  $|Q_H|$  as heat at constant temperature  $T_H$  during the expansion, its entropy increases. Similarly, during the isothermal compression *cd*, the working substance (reversibly) loses energy  $|Q_L|$  as heat at constant temperature  $T_L$ , and its entropy decreases.

The two vertical lines in Fig. 20-10 correspond to the two adiabatic processes of the Carnot cycle. Because no energy is transferred as heat during the two processes, the entropy of the working substance is constant during them.

**The Work** To calculate the net work done by a Carnot engine during a cycle, let us apply Eq. 18-26, the first law of thermodynamics ( $\Delta E_{\text{int}} = Q - W$ ), to the working substance. That substance must return again and again to any arbitrarily selected state in the cycle. Thus, if  $X$  represents any state property of the working substance, such as pressure, temperature, volume, internal energy, or entropy, we must have  $\Delta X = 0$  for every cycle. It follows that  $\Delta E_{\text{int}} = 0$  for a complete cycle of the working substance. Recalling that  $Q$  in Eq. 18-26 is the *net* heat transfer per cycle and  $W$  is the *net* work, we can write the first law of thermodynamics for the Carnot cycle as

$$W = |Q_H| - |Q_L|. \quad (20-8)$$

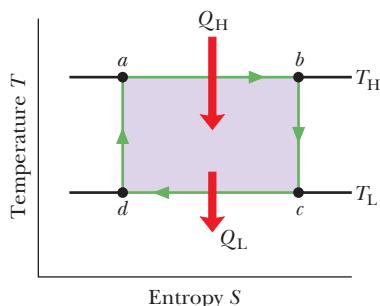
**Entropy Changes** In a Carnot engine, there are *two* (and only two) reversible energy transfers as heat, and thus two changes in the entropy of the working substance—one at temperature  $T_H$  and one at  $T_L$ . The net entropy change per cycle is then

$$\Delta S = \Delta S_H + \Delta S_L = \frac{|Q_H|}{T_H} - \frac{|Q_L|}{T_L}. \quad (20-9)$$

Here  $\Delta S_H$  is positive because energy  $|Q_H|$  is *added* to the working substance as heat (an increase in entropy) and  $\Delta S_L$  is negative because energy  $|Q_L|$  is *removed* from the working substance as heat (a decrease in entropy). Because entropy is a state function, we must have  $\Delta S = 0$  for a complete cycle. Putting  $\Delta S = 0$  in Eq. 20-9 requires that

$$\frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}. \quad (20-10)$$

Note that, because  $T_H > T_L$ , we must have  $|Q_H| > |Q_L|$ ; that is, more energy is



**Figure 20-10** The Carnot cycle of Fig. 20-9 plotted on a temperature–entropy diagram. During processes *ab* and *cd* the temperature remains constant. During processes *bc* and *da* the entropy remains constant.

extracted as heat from the high-temperature reservoir than is delivered to the low-temperature reservoir.

We shall now derive an expression for the efficiency of a Carnot engine.

### Efficiency of a Carnot Engine

The purpose of any engine is to transform as much of the extracted energy  $Q_H$  into work as possible. We measure its success in doing so by its **thermal efficiency**  $\varepsilon$ , defined as the work the engine does per cycle (“energy we get”) divided by the energy it absorbs as heat per cycle (“energy we pay for”):

$$\varepsilon = \frac{\text{energy we get}}{\text{energy we pay for}} = \frac{|W|}{|Q_H|} \quad (\text{efficiency, any engine}). \quad (20-11)$$

For a Carnot engine we can substitute for  $W$  from Eq. 20-8 to write Eq. 20-11 as

$$\varepsilon_C = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|}. \quad (20-12)$$

Using Eq. 20-10 we can write this as

$$\varepsilon_C = 1 - \frac{T_L}{T_H} \quad (\text{efficiency, Carnot engine}), \quad (20-13)$$

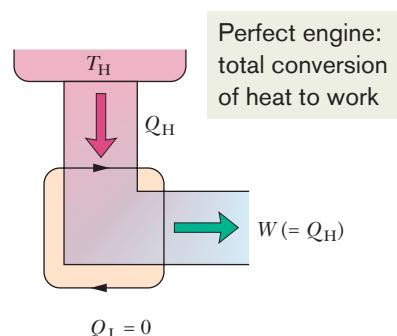
where the temperatures  $T_L$  and  $T_H$  are in kelvins. Because  $T_L < T_H$ , the Carnot engine necessarily has a thermal efficiency less than unity—that is, less than 100%. This is indicated in Fig. 20-8, which shows that only part of the energy extracted as heat from the high-temperature reservoir is available to do work, and the rest is delivered to the low-temperature reservoir. We shall show in Module 20-3 that no real engine can have a thermal efficiency greater than that calculated from Eq. 20-13.

Inventors continually try to improve engine efficiency by reducing the energy  $|Q_L|$  that is “thrown away” during each cycle. The inventor’s dream is to produce the *perfect engine*, diagrammed in Fig. 20-11, in which  $|Q_L|$  is reduced to zero and  $|Q_H|$  is converted completely into work. Such an engine on an ocean liner, for example, could extract energy as heat from the water and use it to drive the propellers, with no fuel cost. An automobile fitted with such an engine could extract energy as heat from the surrounding air and use it to drive the car, again with no fuel cost. Alas, a perfect engine is only a dream: Inspection of Eq. 20-13 shows that we can achieve 100% engine efficiency (that is,  $\varepsilon = 1$ ) only if  $T_L = 0$  or  $T_H \rightarrow \infty$ , impossible requirements. Instead, experience gives the following alternative version of the second law of thermodynamics, which says in short, *there are no perfect engines*:

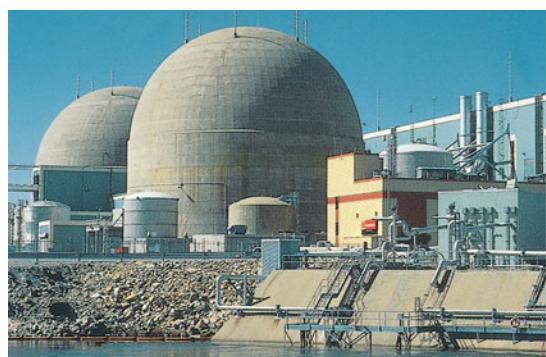


No series of processes is possible whose sole result is the transfer of energy as heat from a thermal reservoir and the complete conversion of this energy to work.

To summarize: The thermal efficiency given by Eq. 20-13 applies only to Carnot engines. Real engines, in which the processes that form the engine cycle are not reversible, have lower efficiencies. If your car were powered by a Carnot engine, it would have an efficiency of about 55% according to Eq. 20-13; its actual efficiency is probably about 25%. A nuclear power plant (Fig. 20-12), taken in its entirety, is an engine. It extracts energy as heat from a reactor core, does work by means of a turbine, and discharges energy as heat to a nearby river. If the power plant operated as a Carnot engine, its efficiency would be about 40%; its actual efficiency is about 30%. In designing engines of any type, there is simply no way to beat the efficiency limitation imposed by Eq. 20-13.

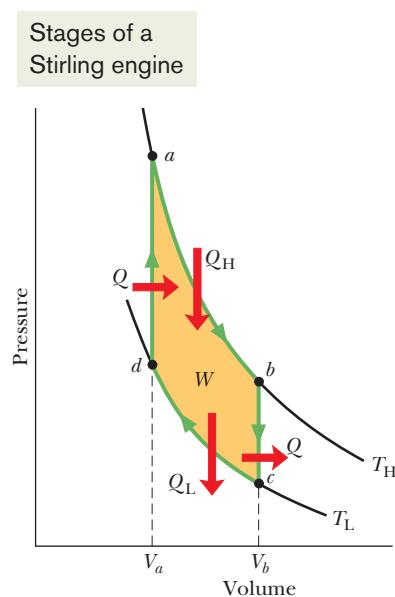


**Figure 20-11** The elements of a perfect engine—that is, one that converts heat  $Q_H$  from a high-temperature reservoir directly to work  $W$  with 100% efficiency.



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**Figure 20-12** The North Anna nuclear power plant near Charlottesville, Virginia, which generates electric energy at the rate of 900 MW. At the same time, by design, it discards energy into the nearby river at the rate of 2100 MW. This plant and all others like it throw away more energy than they deliver in useful form. They are real counterparts of the ideal engine of Fig. 20-8.



**Figure 20-13** A  $p$ - $V$  plot for the working substance of an ideal Stirling engine, with the working substance assumed for convenience to be an ideal gas.

### Stirling Engine

Equation 20-13 applies not to all ideal engines but only to those that can be represented as in Fig. 20-9—that is, to Carnot engines. For example, Fig. 20-13 shows the operating cycle of an ideal **Stirling engine**. Comparison with the Carnot cycle of Fig. 20-9 shows that each engine has isothermal heat transfers at temperatures  $T_H$  and  $T_L$ . However, the two isotherms of the Stirling engine cycle are connected, not by adiabatic processes as for the Carnot engine but by constant-volume processes. To increase the temperature of a gas at constant volume reversibly from  $T_L$  to  $T_H$  (process  $da$  of Fig. 20-13) requires a transfer of energy as heat to the working substance from a thermal reservoir whose temperature can be varied smoothly between those limits. Also, a reverse transfer is required in process  $bc$ . Thus, reversible heat transfers (and corresponding entropy changes) occur in all four of the processes that form the cycle of a Stirling engine, not just two processes as in a Carnot engine. Thus, the derivation that led to Eq. 20-13 does not apply to an ideal Stirling engine. More important, the efficiency of an ideal Stirling engine is lower than that of a Carnot engine operating between the same two temperatures. Real Stirling engines have even lower efficiencies.

The Stirling engine was developed in 1816 by Robert Stirling. This engine, long neglected, is now being developed for use in automobiles and spacecraft. A Stirling engine delivering 5000 hp (3.7 MW) has been built. Because they are quiet, Stirling engines are used on some military submarines.



### Checkpoint 3

Three Carnot engines operate between reservoir temperatures of (a) 400 and 500 K, (b) 600 and 800 K, and (c) 400 and 600 K. Rank the engines according to their thermal efficiencies, greatest first.



### Sample Problem 20.03 Carnot engine, efficiency, power, entropy changes

Imagine a Carnot engine that operates between the temperatures  $T_H = 850$  K and  $T_L = 300$  K. The engine performs 1200 J of work each cycle, which takes 0.25 s.

(a) What is the efficiency of this engine?

#### KEY IDEA

The efficiency  $\varepsilon$  of a Carnot engine depends only on the ratio  $T_L/T_H$  of the temperatures (in kelvins) of the thermal reservoirs to which it is connected.

**Calculation:** Thus, from Eq. 20-13, we have

$$\varepsilon = 1 - \frac{T_L}{T_H} = 1 - \frac{300 \text{ K}}{850 \text{ K}} = 0.647 \approx 65\%. \quad (\text{Answer})$$

(b) What is the average power of this engine?

#### KEY IDEA

The average power  $P$  of an engine is the ratio of the work  $W$  it does per cycle to the time  $t$  that each cycle takes.

**Calculation:** For this Carnot engine, we find

$$P = \frac{W}{t} = \frac{1200 \text{ J}}{0.25 \text{ s}} = 4800 \text{ W} = 4.8 \text{ kW}. \quad (\text{Answer})$$

(c) How much energy  $|Q_H|$  is extracted as heat from the high-temperature reservoir every cycle?

#### KEY IDEA

The efficiency  $\varepsilon$  is the ratio of the work  $W$  that is done per cycle to the energy  $|Q_H|$  that is extracted as heat from the high-temperature reservoir per cycle ( $\varepsilon = W/|Q_H|$ ).

**Calculation:** Here we have

$$|Q_H| = \frac{W}{\varepsilon} = \frac{1200 \text{ J}}{0.647} = 1855 \text{ J}. \quad (\text{Answer})$$

(d) How much energy  $|Q_L|$  is delivered as heat to the low-temperature reservoir every cycle?

#### KEY IDEA

For a Carnot engine, the work  $W$  done per cycle is equal to the difference in the energy transfers as heat:  $|Q_H| - |Q_L|$ , as in Eq. 20-8.

**Calculation:** Thus, we have

$$|Q_L| = |Q_H| - W \\ = 1855 \text{ J} - 1200 \text{ J} = 655 \text{ J}. \quad (\text{Answer})$$

(e) By how much does the entropy of the working substance change as a result of the energy transferred to it from the high-temperature reservoir? From it to the low-temperature reservoir?

### KEY IDEA

The entropy change  $\Delta S$  during a transfer of energy as heat  $Q$  at constant temperature  $T$  is given by Eq. 20-2 ( $\Delta S = Q/T$ ).

**Calculations:** Thus, for the *positive* transfer of energy  $Q_H$  from the high-temperature reservoir at  $T_H$ , the change in the

### Sample Problem 20.04 Impossibly efficient engine

An inventor claims to have constructed an engine that has an efficiency of 75% when operated between the boiling and freezing points of water. Is this possible?

### KEY IDEA

The efficiency of a real engine must be less than the efficiency of a Carnot engine operating between the same two temperatures.



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entropy of the working substance is

$$\Delta S_H = \frac{Q_H}{T_H} = \frac{1855 \text{ J}}{850 \text{ K}} = +2.18 \text{ J/K.} \quad (\text{Answer})$$

Similarly, for the *negative* transfer of energy  $Q_L$  to the low-temperature reservoir at  $T_L$ , we have

$$\Delta S_L = \frac{Q_L}{T_L} = \frac{-655 \text{ J}}{300 \text{ K}} = -2.18 \text{ J/K.} \quad (\text{Answer})$$

Note that the net entropy change of the working substance for one cycle is zero, as we discussed in deriving Eq. 20-10.

**Calculation:** From Eq. 20-13, we find that the efficiency of a Carnot engine operating between the boiling and freezing points of water is

$$\varepsilon = 1 - \frac{T_L}{T_H} = 1 - \frac{(0 + 273) \text{ K}}{(100 + 273) \text{ K}} = 0.268 \approx 27\%.$$

Thus, for the given temperatures, the claimed efficiency of 75% for a real engine (with its irreversible processes and wasteful energy transfers) is impossible.

## 20-3 REFRIGERATORS AND REAL ENGINES

### Learning Objectives

After reading this module, you should be able to . . .

**20.16** Identify that a refrigerator is a device that uses work to transfer energy from a low-temperature reservoir to a high-temperature reservoir, and that an ideal refrigerator is one that does this with reversible processes and no wasteful losses.

**20.17** Sketch a *p*-*V* diagram for the cycle of a Carnot refrigerator, indicating the direction of cycling, the nature of the processes involved, the work done during each process (including algebraic sign), the net work done in the cycle,

### Key Ideas

● A refrigerator is a device that, operating in a cycle, has work  $W$  done on it as it extracts energy  $|Q_L|$  as heat from a low-temperature reservoir. The coefficient of performance  $K$  of a refrigerator is defined as

$$K = \frac{\text{what we want}}{\text{what we pay for}} = \frac{|Q_L|}{|W|}.$$

● A Carnot refrigerator is a Carnot engine operating in reverse. Its coefficient of performance is

$$K_C = \frac{|Q_L|}{|Q_H| - |Q_L|} = \frac{T_L}{T_H - T_L}.$$

and the heat transferred during each process (including algebraic sign).

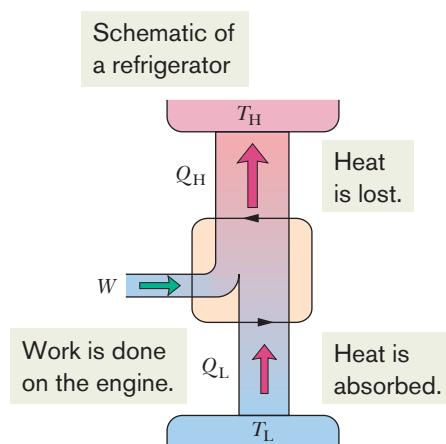
**20.18** Apply the relationship between the coefficient of performance  $K$  and the heat exchanges with the reservoirs and the temperatures of the reservoirs.

**20.19** Identify that there is no ideal refrigerator in which all of the energy extracted from the low-temperature reservoir is transferred to the high-temperature reservoir.

**20.20** Identify that the efficiency of a real engine is less than that of the ideal Carnot engine.

● A perfect refrigerator is an entirely imaginary refrigerator in which energy extracted as heat from the low-temperature reservoir is somehow converted completely to heat discharged to the high-temperature reservoir without any need for work.

● A perfect refrigerator would violate the second law of thermodynamics, which can be restated as follows: No series of processes is possible whose sole result is the transfer of energy as heat from a reservoir at a given temperature to a reservoir at a higher temperature (without work being involved).



**Figure 20-14** The elements of a refrigerator. The two black arrowheads on the central loop suggest the working substance operating in a cycle, as if on a  $p$ - $V$  plot. Energy is transferred as heat  $Q_L$  to the working substance from the low-temperature reservoir. Energy is transferred as heat  $Q_H$  to the high-temperature reservoir from the working substance. Work  $W$  is done on the refrigerator (on the working substance) by something in the environment.

## Entropy in the Real World: Refrigerators

A **refrigerator** is a device that uses work in order to transfer energy from a low-temperature reservoir to a high-temperature reservoir as the device continuously repeats a set series of thermodynamic processes. In a household refrigerator, for example, work is done by an electrical compressor to transfer energy from the food storage compartment (a low-temperature reservoir) to the room (a high-temperature reservoir).

Air conditioners and heat pumps are also refrigerators. For an air conditioner, the low-temperature reservoir is the room that is to be cooled and the high-temperature reservoir is the warmer outdoors. A heat pump is an air conditioner that can be operated in reverse to heat a room; the room is the high-temperature reservoir, and heat is transferred to it from the cooler outdoors.

Let us consider an *ideal refrigerator*:



In an ideal refrigerator, all processes are reversible and no wasteful energy transfers occur as a result of, say, friction and turbulence.

Figure 20-14 shows the basic elements of an ideal refrigerator. Note that its operation is the reverse of how the Carnot engine of Fig. 20-8 operates. In other words, all the energy transfers, as either heat or work, are reversed from those of a Carnot engine. We can call such an ideal refrigerator a **Carnot refrigerator**.

The designer of a refrigerator would like to extract as much energy  $|Q_L|$  as possible from the low-temperature reservoir (what we want) for the least amount of work  $|W|$  (what we pay for). A measure of the efficiency of a refrigerator, then, is

$$K = \frac{\text{what we want}}{\text{what we pay for}} = \frac{|Q_L|}{|W|} \quad (\text{coefficient of performance, any refrigerator}), \quad (20-14)$$

where  $K$  is called the *coefficient of performance*. For a Carnot refrigerator, the first law of thermodynamics gives  $|W| = |Q_H| - |Q_L|$ , where  $|Q_H|$  is the magnitude of the energy transferred as heat to the high-temperature reservoir. Equation 20-14 then becomes

$$K_C = \frac{|Q_L|}{|Q_H| - |Q_L|}. \quad (20-15)$$

Because a Carnot refrigerator is a Carnot engine operating in reverse, we can combine Eq. 20-10 with Eq. 20-15; after some algebra we find

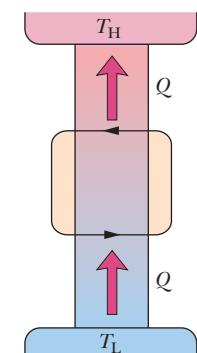
$$K_C = \frac{T_L}{T_H - T_L} \quad (\text{coefficient of performance, Carnot refrigerator}). \quad (20-16)$$

For typical room air conditioners,  $K \approx 2.5$ . For household refrigerators,  $K \approx 5$ . Perversely, the value of  $K$  is higher the closer the temperatures of the two reservoirs are to each other. That is why heat pumps are more effective in temperate climates than in very cold climates.

It would be nice to own a refrigerator that did not require some input of work—that is, one that would run without being plugged in. Figure 20-15 represents another “inventor’s dream,” a **perfect refrigerator** that transfers energy as heat  $Q$  from a cold reservoir to a warm reservoir without the need for work. Because the unit operates in cycles, the entropy of the working substance does not change during a complete cycle. The entropies of the two reservoirs, however, do change: The entropy change for the cold reservoir is  $-|Q|/T_L$ , and that for the warm reservoir is  $+|Q|/T_H$ . Thus, the net entropy change for the entire system is

$$\Delta S = -\frac{|Q|}{T_L} + \frac{|Q|}{T_H}.$$

Perfect refrigerator:  
total transfer of heat  
from cold to hot  
without any work



**Figure 20-15** The elements of a perfect refrigerator—that is, one that transfers energy from a low-temperature reservoir to a high-temperature reservoir without any input of work.

Because  $T_H > T_L$ , the right side of this equation is negative and thus the net change in entropy per cycle for the closed system *refrigerator + reservoirs* is also negative. Because such a decrease in entropy violates the second law of thermodynamics (Eq. 20-5), a perfect refrigerator does not exist. (If you want your refrigerator to operate, you must plug it in.)

Here, then, is another way to state the second law of thermodynamics:



No series of processes is possible whose sole result is the transfer of energy as heat from a reservoir at a given temperature to a reservoir at a higher temperature.

In short, *there are no perfect refrigerators*.



#### Checkpoint 4

You wish to increase the coefficient of performance of an ideal refrigerator. You can do so by (a) running the cold chamber at a slightly higher temperature, (b) running the cold chamber at a slightly lower temperature, (c) moving the unit to a slightly warmer room, or (d) moving it to a slightly cooler room. The magnitudes of the temperature changes are to be the same in all four cases. List the changes according to the resulting coefficients of performance, greatest first.

## The Efficiencies of Real Engines

Let  $\varepsilon_C$  be the efficiency of a Carnot engine operating between two given temperatures. Here we prove that no real engine operating between those temperatures can have an efficiency greater than  $\varepsilon_C$ . If it could, the engine would violate the second law of thermodynamics.

Let us assume that an inventor, working in her garage, has constructed an engine  $X$ , which she claims has an efficiency  $\varepsilon_X$  that is greater than  $\varepsilon_C$ :

$$\varepsilon_X > \varepsilon_C \quad (\text{a claim}). \quad (20-17)$$

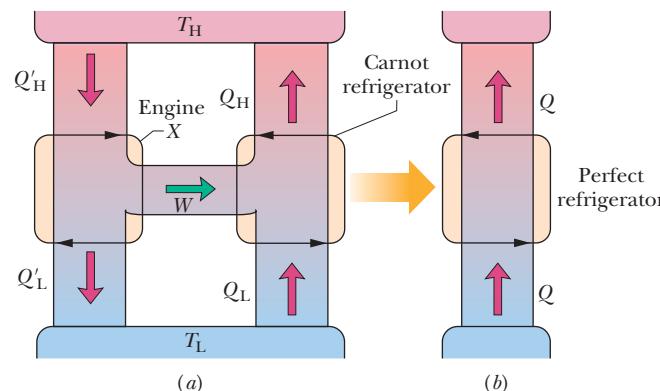
Let us couple engine  $X$  to a Carnot refrigerator, as in Fig. 20-16a. We adjust the strokes of the Carnot refrigerator so that the work it requires per cycle is just equal to that provided by engine  $X$ . Thus, no (external) work is performed on or by the combination *engine + refrigerator* of Fig. 20-16a, which we take as our system.

If Eq. 20-17 is true, from the definition of efficiency (Eq. 20-11), we must have

$$\frac{|W|}{|Q'_H|} > \frac{|W|}{|Q_H|},$$

where the prime refers to engine  $X$  and the right side of the inequality is the efficiency of the Carnot refrigerator when it operates as an engine. This inequality requires that

$$|Q_H| > |Q'_H|. \quad (20-18)$$



**Figure 20-16** (a) Engine  $X$  drives a Carnot refrigerator. (b) If, as claimed, engine  $X$  is more efficient than a Carnot engine, then the combination shown in (a) is equivalent to the perfect refrigerator shown here. This violates the second law of thermodynamics, so we conclude that engine  $X$  *cannot* be more efficient than a Carnot engine.

Because the work done by engine  $X$  is equal to the work done on the Carnot refrigerator, we have, from the first law of thermodynamics as given by Eq. 20-8,

$$|Q_H| - |Q_L| = |Q'_H| - |Q'_L|,$$

which we can write as

$$|Q_H| - |Q'_H| = |Q_L| - |Q'_L| = Q. \quad (20-19)$$

Because of Eq. 20-18, the quantity  $Q$  in Eq. 20-19 must be positive.

Comparison of Eq. 20-19 with Fig. 20-16 shows that the net effect of engine  $X$  and the Carnot refrigerator working in combination is to transfer energy  $Q$  as heat from a low-temperature reservoir to a high-temperature reservoir without the requirement of work. Thus, the combination acts like the perfect refrigerator of Fig. 20-15, whose existence is a violation of the second law of thermodynamics.

Something must be wrong with one or more of our assumptions, and it can only be Eq. 20-17. We conclude that *no real engine can have an efficiency greater than that of a Carnot engine when both engines work between the same two temperatures*. At most, the real engine can have an efficiency equal to that of a Carnot engine. In that case, the real engine is a Carnot engine.

## 20-4 A STATISTICAL VIEW OF ENTROPY

### Learning Objectives

After reading this module, you should be able to . . .

**20.21** Explain what is meant by the configurations of a system of molecules.

**20.22** Calculate the multiplicity of a given configuration.

**20.23** Identify that all microstates are equally probable but

the configurations with more microstates are more probable than the other configurations.

**20.24** Apply Boltzmann's entropy equation to calculate the entropy associated with a multiplicity.

### Key Ideas

- The entropy of a system can be defined in terms of the possible distributions of its molecules. For identical molecules, each possible distribution of molecules is called a microstate of the system. All equivalent microstates are grouped into a configuration of the system. The number of microstates in a configuration is the multiplicity  $W$  of the configuration.

- For a system of  $N$  molecules that may be distributed between the two halves of a box, the multiplicity is given by

$$W = \frac{N!}{n_1! n_2!},$$

in which  $n_1$  is the number of molecules in one half of the box and  $n_2$  is the number in the other half. A basic assumption of statistical mechanics is that all the microstates are equally probable.

Thus, configurations with a large multiplicity occur most often. When  $N$  is very large (say,  $N = 10^{22}$  molecules or more), the molecules are nearly always in the configuration in which  $n_1 = n_2$ .

- The multiplicity  $W$  of a configuration of a system and the entropy  $S$  of the system in that configuration are related by Boltzmann's entropy equation:

$$S = k \ln W,$$

where  $k = 1.38 \times 10^{-23}$  J/K is the Boltzmann constant.

- When  $N$  is very large (the usual case), we can approximate  $\ln N!$  with Stirling's approximation:

$$\ln N! \approx N(\ln N) - N.$$

### A Statistical View of Entropy

In Chapter 19 we saw that the macroscopic properties of gases can be explained in terms of their microscopic, or molecular, behavior. Such explanations are part of a study called **statistical mechanics**. Here we shall focus our attention on a single problem, one involving the distribution of gas molecules between the two halves of an insulated box. This problem is reasonably simple to analyze, and it allows us to use statistical mechanics to calculate the entropy change for the free expansion of an ideal gas. You will see that statistical mechanics leads to the same entropy change as we would find using thermodynamics.

Figure 20-17 shows a box that contains six identical (and thus indistinguishable) molecules of a gas. At any instant, a given molecule will be in either the left or the right half of the box; because the two halves have equal volumes, the molecule has the same likelihood, or probability, of being in either half.

Table 20-1 shows the seven possible *configurations* of the six molecules, each configuration labeled with a Roman numeral. For example, in configuration I, all six molecules are in the left half of the box ( $n_1 = 6$ ) and none are in the right half ( $n_2 = 0$ ). We see that, in general, a given configuration can be achieved in a number of different ways. We call these different arrangements of the molecules *microstates*. Let us see how to calculate the number of microstates that correspond to a given configuration.

Suppose we have  $N$  molecules, distributed with  $n_1$  molecules in one half of the box and  $n_2$  in the other. (Thus  $n_1 + n_2 = N$ .) Let us imagine that we distribute the molecules “by hand,” one at a time. If  $N = 6$ , we can select the first molecule in six independent ways; that is, we can pick any one of the six molecules. We can pick the second molecule in five ways, by picking any one of the remaining five molecules; and so on. The total number of ways in which we can select all six molecules is the product of these independent ways, or  $6 \times 5 \times 4 \times 3 \times 2 \times 1 = 720$ . In mathematical shorthand we write this product as  $6! = 720$ , where  $6!$  is pronounced “six factorial.” Your hand calculator can probably calculate factorials. For later use you will need to know that  $0! = 1$ . (Check this on your calculator.)

However, because the molecules are indistinguishable, these 720 arrangements are not all different. In the case that  $n_1 = 4$  and  $n_2 = 2$  (which is configuration III in Table 20-1), for example, the order in which you put four molecules in one half of the box does not matter, because after you have put all four in, there is no way that you can tell the order in which you did so. The number of ways in which you can order the four molecules is  $4! = 24$ . Similarly, the number of ways in which you can order two molecules for the other half of the box is simply  $2! = 2$ . To get the number of *different* arrangements that lead to the (4, 2) split of configuration III, we must divide 720 by 24 and also by 2. We call the resulting quantity, which is the number of microstates that correspond to a given configuration, the *multiplicity W* of that configuration. Thus, for configuration III,

$$W_{\text{III}} = \frac{6!}{4! 2!} = \frac{720}{24 \times 2} = 15.$$

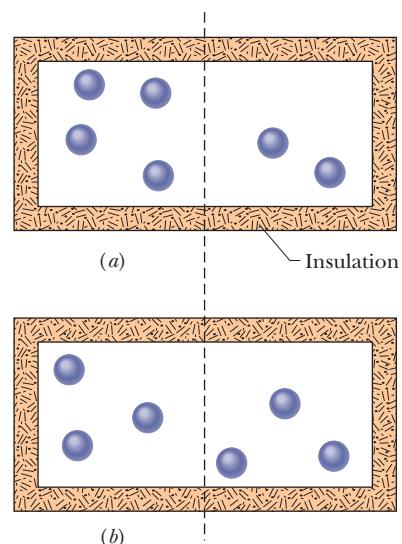
Thus, Table 20-1 tells us there are 15 independent microstates that correspond to configuration III. Note that, as the table also tells us, the total number of microstates for six molecules distributed over the seven configurations is 64.

Extrapolating from six molecules to the general case of  $N$  molecules, we have

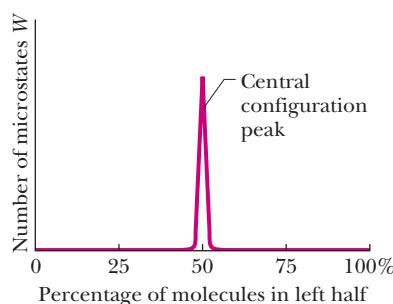
$$W = \frac{N!}{n_1! n_2!} \quad (\text{multiplicity of configuration}). \quad (20-20)$$

**Table 20-1 Six Molecules in a Box**

Configuration Label		Multiplicity W (number of microstates)		Calculation of W (Eq. 20-20)	Entropy $10^{-23}$ J/K (Eq. 20-21)
	$n_1$	$n_2$			
I	6	0	1	$6!/(6! 0!) = 1$	0
II	5	1	6	$6!/(5! 1!) = 6$	2.47
III	4	2	15	$6!/(4! 2!) = 15$	3.74
IV	3	3	20	$6!/(3! 3!) = 20$	4.13
V	2	4	15	$6!/(2! 4!) = 15$	3.74
VI	1	5	6	$6!/(1! 5!) = 6$	2.47
VII	0	6	1	$6!/(0! 6!) = 1$	0
		Total = 64			



**Figure 20-17** An insulated box contains six gas molecules. Each molecule has the same probability of being in the left half of the box as in the right half. The arrangement in (a) corresponds to configuration III in Table 20-1, and that in (b) corresponds to configuration IV.



**Figure 20-18** For a large number of molecules in a box, a plot of the number of microstates that require various percentages of the molecules to be in the left half of the box. Nearly all the microstates correspond to an approximately equal sharing of the molecules between the two halves of the box; those microstates form the *central configuration peak* on the plot. For  $N \approx 10^{22}$ , the central configuration peak is much too narrow to be drawn on this plot.

You should verify the multiplicities for all the configurations in Table 20-1. The basic assumption of statistical mechanics is that



All microstates are equally probable.

In other words, if we were to take a great many snapshots of the six molecules as they jostle around in the box of Fig. 20-17 and then count the number of times each microstate occurred, we would find that all 64 microstates would occur equally often. Thus the system will spend, on average, the same amount of time in each of the 64 microstates.

Because all microstates are equally probable but different configurations have different numbers of microstates, the configurations are *not* all equally probable. In Table 20-1 configuration IV, with 20 microstates, is the *most probable configuration*, with a probability of  $20/64 = 0.313$ . This result means that the system is in configuration IV 31.3% of the time. Configurations I and VII, in which all the molecules are in one half of the box, are the least probable, each with a probability of  $1/64 = 0.016$  or 1.6%. It is not surprising that the most probable configuration is the one in which the molecules are evenly divided between the two halves of the box, because that is what we expect at thermal equilibrium. However, it *is* surprising that there is *any* probability, however small, of finding all six molecules clustered in half of the box, with the other half empty.

For large values of  $N$  there are extremely large numbers of microstates, but nearly all the microstates belong to the configuration in which the molecules are divided equally between the two halves of the box, as Fig. 20-18 indicates. Even though the measured temperature and pressure of the gas remain constant, the gas is churning away endlessly as its molecules “visit” all probable microstates with equal probability. However, because so few microstates lie outside the very narrow central configuration peak of Fig. 20-18, we might as well assume that the gas molecules are always divided equally between the two halves of the box. As we shall see, this is the configuration with the greatest entropy.

### Sample Problem 20.05 Microstates and multiplicity

Suppose that there are 100 indistinguishable molecules in the box of Fig. 20-17. How many microstates are associated with the configuration  $n_1 = 50$  and  $n_2 = 50$ , and with the configuration  $n_1 = 100$  and  $n_2 = 0$ ? Interpret the results in terms of the relative probabilities of the two configurations.

#### KEY IDEA

The multiplicity  $W$  of a configuration of indistinguishable molecules in a closed box is the number of independent microstates with that configuration, as given by Eq. 20-20.

**Calculations:** Thus, for the  $(n_1, n_2)$  configuration  $(50, 50)$ ,

$$\begin{aligned} W &= \frac{N!}{n_1! n_2!} = \frac{100!}{50! 50!} \\ &= \frac{9.33 \times 10^{157}}{(3.04 \times 10^{64})(3.04 \times 10^{64})} \\ &= 1.01 \times 10^{29}. \end{aligned} \quad (\text{Answer})$$

Similarly, for the configuration  $(100, 0)$ , we have

$$W = \frac{N!}{n_1! n_2!} = \frac{100!}{100! 0!} = \frac{1}{0!} = \frac{1}{1} = 1. \quad (\text{Answer})$$

**The meaning:** Thus, a 50–50 distribution is more likely than a 100–0 distribution by the enormous factor of about  $1 \times 10^{29}$ . If you could count, at one per nanosecond, the number of microstates that correspond to the 50–50 distribution, it would take you about  $3 \times 10^{12}$  years, which is about 200 times longer than the age of the universe. Keep in mind that the 100 molecules used in this sample problem is a very small number. Imagine what these calculated probabilities would be like for a mole of molecules, say about  $N = 10^{24}$ . Thus, you need never worry about suddenly finding all the air molecules clustering in one corner of your room, with you gasping for air in another corner. So, you can breathe easy because of the physics of entropy.



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## Probability and Entropy

In 1877, Austrian physicist Ludwig Boltzmann (the Boltzmann of Boltzmann's constant  $k$ ) derived a relationship between the entropy  $S$  of a configuration of a gas and the multiplicity  $W$  of that configuration. That relationship is

$$S = k \ln W \quad (\text{Boltzmann's entropy equation}). \quad (20-21)$$

This famous formula is engraved on Boltzmann's tombstone.

It is natural that  $S$  and  $W$  should be related by a logarithmic function. The total entropy of two systems is the *sum* of their separate entropies. The probability of occurrence of two independent systems is the *product* of their separate probabilities. Because  $\ln ab = \ln a + \ln b$ , the logarithm seems the logical way to connect these quantities.

Table 20-1 displays the entropies of the configurations of the six-molecule system of Fig. 20-17, computed using Eq. 20-21. Configuration IV, which has the greatest multiplicity, also has the greatest entropy.

When you use Eq. 20-20 to calculate  $W$ , your calculator may signal "OVERFLOW" if you try to find the factorial of a number greater than a few hundred. Instead, you can use **Stirling's approximation** for  $\ln N!$ :

$$\ln N! \approx N(\ln N) - N \quad (\text{Stirling's approximation}). \quad (20-22)$$

The Stirling of this approximation was an English mathematician and not the Robert Stirling of engine fame.



### Checkpoint 5

A box contains 1 mol of a gas. Consider two configurations: (a) each half of the box contains half the molecules and (b) each third of the box contains one-third of the molecules. Which configuration has more microstates?



### Sample Problem 20.06 Entropy change of free expansion using microstates

In Sample Problem 20.01, we showed that when  $n$  moles of an ideal gas doubles its volume in a free expansion, the entropy increase from the initial state  $i$  to the final state  $f$  is  $S_f - S_i = nR \ln 2$ . Derive this increase in entropy by using statistical mechanics.

#### KEY IDEA

We can relate the entropy  $S$  of any given configuration of the molecules in the gas to the multiplicity  $W$  of microstates for that configuration, using Eq. 20-21 ( $S = k \ln W$ ).

**Calculations:** We are interested in two configurations: the final configuration  $f$  (with the molecules occupying the full volume of their container in Fig. 20-1b) and the initial configuration  $i$  (with the molecules occupying the left half of the container). Because the molecules are in a closed container, we can calculate the multiplicity  $W$  of their microstates with Eq. 20-20. Here we have  $N$  molecules in the  $n$  moles of the gas. Initially, with the molecules all in the left

half of the container, their  $(n_1, n_2)$  configuration is  $(N, 0)$ . Then, Eq. 20-20 gives their multiplicity as

$$W_i = \frac{N!}{N! 0!} = 1.$$

Finally, with the molecules spread through the full volume, their  $(n_1, n_2)$  configuration is  $(N/2, N/2)$ . Then, Eq. 20-20 gives their multiplicity as

$$W_f = \frac{N!}{(N/2)! (N/2)!}.$$

From Eq. 20-21, the initial and final entropies are

$$S_i = k \ln W_i = k \ln 1 = 0$$

and

$$S_f = k \ln W_f = k \ln(N!) - 2k \ln[(N/2)!]. \quad (20-23)$$

In writing Eq. 20-23, we have used the relation

$$\ln \frac{a}{b^2} = \ln a - 2 \ln b.$$

Now, applying Eq. 20-22 to evaluate Eq. 20-23, we find that

$$\begin{aligned} S_f &= k \ln(N!) - 2k \ln[(N/2)!] \\ &= k[N(\ln N) - N] - 2k[(N/2) \ln(N/2) - (N/2)] \\ &= k[N(\ln N) - N - N \ln(N/2) + N] \\ &= k[N(\ln N) - N(\ln N - \ln 2)] = Nk \ln 2. \end{aligned} \quad (20-24)$$

From Eq. 19-8 we can substitute  $nR$  for  $Nk$ , where  $R$  is the universal gas constant. Equation 20-24 then becomes

$$S_f = nR \ln 2.$$

The change in entropy from the initial state to the final is



Additional examples, video, and practice available at WileyPLUS

thus

$$\begin{aligned} S_f - S_i &= nR \ln 2 - 0 \\ &= nR \ln 2, \end{aligned} \quad (\text{Answer})$$

which is what we set out to show. In the first sample problem of this chapter we calculated this entropy increase for a free expansion with thermodynamics by finding an equivalent reversible process and calculating the entropy change for *that* process in terms of temperature and heat transfer. In this sample problem, we calculate the same increase in entropy with statistical mechanics using the fact that the system consists of molecules. In short, the two, very different approaches give the same answer.

## Review & Summary

**One-Way Processes** An **irreversible process** is one that cannot be reversed by means of small changes in the environment. The direction in which an irreversible process proceeds is set by the *change in entropy*  $\Delta S$  of the system undergoing the process. Entropy  $S$  is a *state property* (or *state function*) of the system; that is, it depends only on the state of the system and not on the way in which the system reached that state. The *entropy postulate* states (in part): *If an irreversible process occurs in a closed system, the entropy of the system always increases.*

**Calculating Entropy Change** The **entropy change**  $\Delta S$  for an irreversible process that takes a system from an initial state  $i$  to a final state  $f$  is exactly equal to the entropy change  $\Delta S$  for *any reversible process* that takes the system between those same two states. We can compute the latter (but not the former) with

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}. \quad (20-1)$$

Here  $Q$  is the energy transferred as heat to or from the system during the process, and  $T$  is the temperature of the system in kelvins during the process.

For a reversible isothermal process, Eq. 20-1 reduces to

$$\Delta S = S_f - S_i = \frac{Q}{T}. \quad (20-2)$$

When the temperature change  $\Delta T$  of a system is small relative to the temperature (in kelvins) before and after the process, the entropy change can be approximated as

$$\Delta S = S_f - S_i \approx \frac{Q}{T_{\text{avg}}}, \quad (20-3)$$

where  $T_{\text{avg}}$  is the system's average temperature during the process.

When an ideal gas changes reversibly from an initial state with temperature  $T_i$  and volume  $V_i$  to a final state with temperature  $T_f$  and volume  $V_f$ , the change  $\Delta S$  in the entropy of the gas is

$$\Delta S = S_f - S_i = nR \ln \frac{V_f}{V_i} + nC_V \ln \frac{T_f}{T_i}. \quad (20-4)$$

**The Second Law of Thermodynamics** This law, which is an extension of the entropy postulate, states: *If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases.* In equation form,

$$\Delta S \geq 0. \quad (20-5)$$

**Engines** An **engine** is a device that, operating in a cycle, extracts energy as heat  $|Q_H|$  from a high-temperature reservoir and does a certain amount of work  $|W|$ . The *efficiency*  $\epsilon$  of any engine is defined as

$$\epsilon = \frac{\text{energy we get}}{\text{energy we pay for}} = \frac{|W|}{|Q_H|}. \quad (20-11)$$

In an **ideal engine**, all processes are reversible and no wasteful energy transfers occur due to, say, friction and turbulence. A **Carnot engine** is an ideal engine that follows the cycle of Fig. 20-9. Its efficiency is

$$\epsilon_C = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_L}{T_H}, \quad (20-12, 20-13)$$

in which  $T_H$  and  $T_L$  are the temperatures of the high- and low-temperature reservoirs, respectively. Real engines always have an efficiency lower than that given by Eq. 20-13. Ideal engines that are not Carnot engines also have lower efficiencies.

A **perfect engine** is an imaginary engine in which energy extracted as heat from the high-temperature reservoir is converted completely to work. Such an engine would violate the second law of thermodynamics, which can be restated as follows: No series of processes is possible whose sole result is the absorption of energy as heat from a thermal reservoir and the complete conversion of this energy to work.

**Refrigerators** A **refrigerator** is a device that, operating in a cycle, has work  $W$  done on it as it extracts energy  $|Q_L|$  as heat from a low-temperature reservoir. The coefficient of performance  $K$  of a refrigerator is defined as

$$K = \frac{\text{what we want}}{\text{what we pay for}} = \frac{|Q_L|}{|W|}. \quad (20-14)$$

A **Carnot refrigerator** is a Carnot engine operating in reverse.

For a Carnot refrigerator, Eq. 20-14 becomes

$$K_C = \frac{|Q_L|}{|Q_H| - |Q_L|} = \frac{T_L}{T_H - T_L}. \quad (20-15, 20-16)$$

A *perfect refrigerator* is an imaginary refrigerator in which energy extracted as heat from the low-temperature reservoir is converted completely to heat discharged to the high-temperature reservoir, without any need for work. Such a refrigerator would violate the second law of thermodynamics, which can be restated as follows: No series of processes is possible whose sole result is the transfer of energy as heat from a reservoir at a given temperature to a reservoir at a higher temperature.

**Entropy from a Statistical View** The entropy of a system can be defined in terms of the possible distributions of its molecules. For identical molecules, each possible distribution of molecules is called a **microstate** of the system. All equivalent microstates are grouped into

## Questions

- 1 Point *i* in Fig. 20-19 represents the initial state of an ideal gas at temperature  $T$ . Taking algebraic signs into account, rank the entropy changes that the gas undergoes as it moves, successively and reversibly, from point *i* to points *a*, *b*, *c*, and *d*, greatest first.

- 2 In four experiments, blocks *A* and *B*, starting at different initial temperatures, were brought together in an insulating box and allowed to reach a common final temperature. The entropy changes for the blocks in the four experiments had the following values (in joules per kelvin), but not necessarily in the order given. Determine which values for *A* go with which values for *B*.

Block	Values			
<i>A</i>	8	5	3	9
<i>B</i>	-3	-8	-5	-2

- 3 A gas, confined to an insulated cylinder, is compressed adiabatically to half its volume. Does the entropy of the gas increase, decrease, or remain unchanged during this process?

- 4 An ideal monatomic gas at initial temperature  $T_0$  (in kelvins) expands from initial volume  $V_0$  to volume  $2V_0$  by each of the five processes indicated in the *T-V* diagram of Fig. 20-20. In which process is the expansion

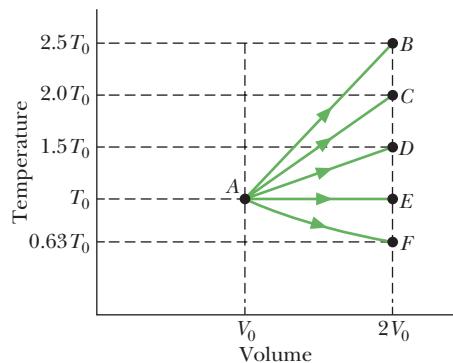


Figure 20-20  
Question 4.

a **configuration** of the system. The number of microstates in a configuration is the **multiplicity**  $W$  of the configuration.

For a system of  $N$  molecules that may be distributed between the two halves of a box, the multiplicity is given by

$$W = \frac{N!}{n_1! n_2!}, \quad (20-20)$$

in which  $n_1$  is the number of molecules in one half of the box and  $n_2$  is the number in the other half. A basic assumption of **statistical mechanics** is that all the microstates are equally probable. Thus, configurations with a large multiplicity occur most often.

The multiplicity  $W$  of a configuration of a system and the entropy  $S$  of the system in that configuration are related by Boltzmann's entropy equation:

$$S = k \ln W, \quad (20-21)$$

where  $k = 1.38 \times 10^{-23}$  J/K is the Boltzmann constant.

sion (a) isothermal, (b) isobaric (constant pressure), and (c) adiabatic? Explain your answers. (d) In which processes does the entropy of the gas decrease?

- 5 In four experiments, 2.5 mol of hydrogen gas undergoes reversible isothermal expansions, starting from the same volume but at different temperatures. The corresponding *p-V* plots are shown in Fig. 20-21. Rank the situations according to the change in the entropy of the gas, greatest first.

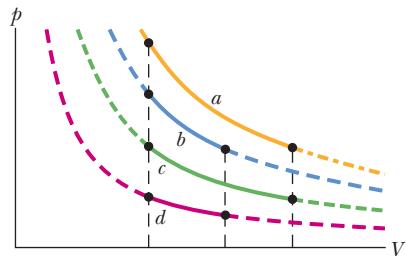


Figure 20-21 Question 5.

- 6 A box contains 100 atoms in a configuration that has 50 atoms in each half of the box. Suppose that you could count the different microstates associated with this configuration at the rate of 100 billion states per second, using a supercomputer. Without written calculation, guess how much computing time you would need: a day, a year, or much more than a year.

- 7 Does the entropy per cycle increase, decrease, or remain the same for (a) a Carnot engine, (b) a real engine, and (c) a perfect engine (which is, of course, impossible to build)?

- 8 Three Carnot engines operate between temperature limits of (a) 400 and 500 K, (b) 500 and 600 K, and (c) 400 and 600 K. Each engine extracts the same amount of energy per cycle from the high-temperature reservoir. Rank the magnitudes of the work done by the engines per cycle, greatest first.

- 9 An inventor claims to have invented four engines, each of which operates between constant-temperature reservoirs at 400 and 300 K. Data on each engine, per cycle of operation, are: engine A,  $Q_H = 200$  J,  $Q_L = -175$  J, and  $W = 40$  J; engine B,  $Q_H = 500$  J,  $Q_L = -200$  J, and  $W = 400$  J; engine C,  $Q_H = 600$  J,  $Q_L = -200$  J, and  $W = 400$  J; engine D,  $Q_H = 100$  J,  $Q_L = -90$  J, and  $W = 10$  J. Of the first and second laws of thermodynamics, which (if either) does each engine violate?

- 10 Does the entropy per cycle increase, decrease, or remain the same for (a) a Carnot refrigerator, (b) a real refrigerator, and (c) a perfect refrigerator (which is, of course, impossible to build)?



## Problems

Tutoring problem available (at instructor's discretion) in *WileyPLUS* and WebAssign

Worked-out solution available in Student Solutions Manual



Number of dots indicates level of problem difficulty

Additional information available in *The Flying Circus of Physics* and at [flyingcircusofphysics.com](http://flyingcircusofphysics.com)

Worked-out solution is at



Interactive solution is at

<http://www.wiley.com/college/halliday>**Module 20-1 Entropy**

- 1 SSM** Suppose 4.00 mol of an ideal gas undergoes a reversible isothermal expansion from volume  $V_1$  to volume  $V_2 = 2.00V_1$  at temperature  $T = 400\text{ K}$ . Find (a) the work done by the gas and (b) the entropy change of the gas. (c) If the expansion is reversible and adiabatic instead of isothermal, what is the entropy change of the gas?

- 2** An ideal gas undergoes a reversible isothermal expansion at  $77.0^\circ\text{C}$ , increasing its volume from 1.30 L to 3.40 L. The entropy change of the gas is  $22.0\text{ J/K}$ . How many moles of gas are present?

- 3 ILW** A 2.50 mol sample of an ideal gas expands reversibly and isothermally at  $360\text{ K}$  until its volume is doubled. What is the increase in entropy of the gas?

- 4** How much energy must be transferred as heat for a reversible isothermal expansion of an ideal gas at  $132^\circ\text{C}$  if the entropy of the gas increases by  $46.0\text{ J/K}$ ?

- 5 ILW** Find (a) the energy absorbed as heat and (b) the change in entropy of a 2.00 kg block of copper whose temperature is increased reversibly from  $25.0^\circ\text{C}$  to  $100^\circ\text{C}$ . The specific heat of copper is  $386\text{ J/kg}\cdot\text{K}$ .

- 6** (a) What is the entropy change of a 12.0 g ice cube that melts completely in a bucket of water whose temperature is just above the freezing point of water? (b) What is the entropy change of a 5.00 g spoonful of water that evaporates completely on a hot plate whose temperature is slightly above the boiling point of water?

- 7 ILW** A 50.0 g block of copper whose temperature is  $400\text{ K}$  is placed in an insulating box with a 100 g block of lead whose temperature is  $200\text{ K}$ . (a) What is the equilibrium temperature of the two-block system? (b) What is the change in the internal energy of the system between the initial state and the equilibrium state? (c) What is the change in the entropy of the system? (See Table 18-3.)

- 8** At very low temperatures, the molar specific heat  $C_V$  of many solids is approximately  $C_V = AT^3$ , where  $A$  depends on the particular substance. For aluminum,  $A = 3.15 \times 10^{-5}\text{ J/mol}\cdot\text{K}^4$ . Find the entropy change for 4.00 mol of aluminum when its temperature is raised from  $5.00\text{ K}$  to  $10.0\text{ K}$ .

- 9** A 10 g ice cube at  $-10^\circ\text{C}$  is placed in a lake whose temperature is  $15^\circ\text{C}$ . Calculate the change in entropy of the cube–lake system as the ice cube comes to thermal equilibrium with the lake. The specific heat of ice is  $2220\text{ J/kg}\cdot\text{K}$ . (*Hint:* Will the ice cube affect the lake temperature?)

- 10** A 364 g block is put in contact with a thermal reservoir. The block is initially at a lower temperature than the reservoir. Assume that the consequent transfer of energy as heat from the reservoir to the block is reversible. Figure 20-22

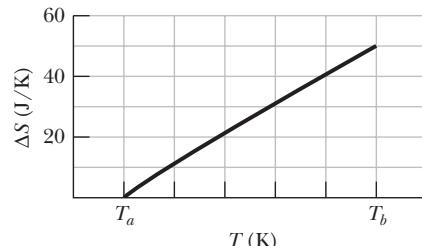


Figure 20-22 Problem 10.

gives the change in entropy  $\Delta S$  of the block until thermal equilibrium is reached. The scale of the horizontal axis is set by  $T_a = 280\text{ K}$  and  $T_b = 380\text{ K}$ . What is the specific heat of the block?

- 11 SSM WWW** In an experiment, 200 g of aluminum (with a specific heat of  $900\text{ J/kg}\cdot\text{K}$ ) at  $100^\circ\text{C}$  is mixed with 50.0 g of water at  $20.0^\circ\text{C}$ , with the mixture thermally isolated. (a) What is the equilibrium temperature? What are the entropy changes of (b) the aluminum, (c) the water, and (d) the aluminum–water system?

- 12** A gas sample undergoes a reversible isothermal expansion. Figure 20-23 gives the change  $\Delta S$  in entropy of the gas versus the final volume  $V_f$  of the gas. The scale of the vertical axis is set by  $\Delta S_s = 64\text{ J/K}$ . How many moles are in the sample?

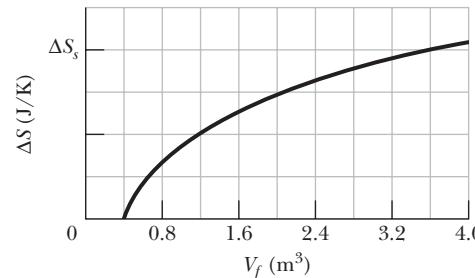


Figure 20-23 Problem 12.

- 13** In the irreversible process of Fig. 20-5, let the initial temperatures of the identical blocks  $L$  and  $R$  be  $305.5$  and  $294.5\text{ K}$ , respectively, and let  $215\text{ J}$  be the energy that must be transferred between the blocks in order to reach equilibrium. For the reversible processes of Fig. 20-6, what is  $\Delta S$  for (a) block  $L$ , (b) its reservoir, (c) block  $R$ , (d) its reservoir, (e) the two-block system, and (f) the system of the two blocks and the two reservoirs?

- 14** (a) For 1.0 mol of a monatomic ideal gas taken through the cycle in Fig. 20-24, where  $V_1 = 4.00V_0$ , what is  $W/p_0V_0$  as the gas goes from state  $a$  to state  $c$  along path  $abc$ ? What is  $\Delta E_{\text{int}}/p_0V_0$  in going (b) from  $b$  to  $c$  and (c) through one full cycle? What is  $\Delta S$  in going (d) from  $b$  to  $c$  and (e) through one full cycle?

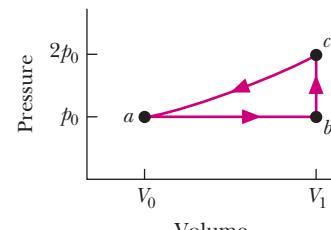


Figure 20-24 Problem 14.

- 15** A mixture of 1773 g of water and 227 g of ice is in an initial equilibrium state at  $0.000^\circ\text{C}$ . The mixture is then, in a reversible process, brought to a second equilibrium state where the water–ice ratio, by mass, is  $1.00:1.00$  at  $0.000^\circ\text{C}$ . (a) Calculate the entropy change of the system during this process. (The heat of fusion for water is  $333\text{ kJ/kg}$ .) (b) The system is then returned to the initial equilibrium state in an irreversible process (say, by using a Bunsen burner). Calculate the entropy change of the system during this process. (c) Are your answers consistent with the second law of thermodynamics?

**••16 GO** An 8.0 g ice cube at  $-10^{\circ}\text{C}$  is put into a Thermos flask containing  $100\text{ cm}^3$  of water at  $20^{\circ}\text{C}$ . By how much has the entropy of the cube–water system changed when equilibrium is reached? The specific heat of ice is  $2220\text{ J/kg}\cdot\text{K}$ .

**••17** In Fig. 20-25, where  $V_{23} = 3.00V_1$ ,  $n$  moles of a diatomic ideal gas are taken through the cycle with the molecules rotating but not oscillating. What are (a)  $p_2/p_1$ , (b)  $p_3/p_1$ , and (c)  $T_3/T_1$ ? For path  $1 \rightarrow 2$ , what are (d)  $W/nRT_1$ , (e)  $Q/nRT_1$ , (f)  $\Delta E_{\text{int}}/nRT_1$ , and (g)  $\Delta S/nR$ ? For path  $2 \rightarrow 3$ , what are (h)  $W/nRT_1$ , (i)  $Q/nRT_1$ , (j)  $\Delta E_{\text{int}}/nRT_1$ , (k)  $\Delta S/nR$ ? For path  $3 \rightarrow 1$ , what are (l)  $W/nRT_1$ , (m)  $Q/nRT_1$ , (n)  $\Delta E_{\text{int}}/nRT_1$ , and (o)  $\Delta S/nR$ ?

**••18 GO** A 2.0 mol sample of an ideal monatomic gas undergoes the reversible process shown in Fig. 20-26. The scale of the vertical axis is set by  $T_s = 400.0\text{ K}$  and the scale of the horizontal axis is set by  $S_s = 20.0\text{ J/K}$ . (a) How much energy is absorbed as heat by the gas? (b) What is the change in the internal energy of the gas? (c) How much work is done by the gas?

**••19** Suppose 1.00 mol of a monatomic ideal gas is taken from initial pressure  $p_1$  and volume  $V_1$  through two steps: (1) an isothermal expansion to volume  $2.00V_1$  and (2) a pressure increase to  $2.00p_1$  at constant volume. What is  $Q/p_1V_1$  for (a) step 1 and (b) step 2? What is  $W/p_1V_1$  for (c) step 1 and (d) step 2? For the full process, what are (e)  $\Delta E_{\text{int}}/p_1V_1$  and (f)  $\Delta S$ ? The gas is returned to its initial state and again taken to the same final state but now through these two steps: (1) an isothermal compression to pressure  $2.00p_1$  and (2) a volume increase to  $2.00V_1$  at constant pressure. What is  $Q/p_1V_1$  for (g) step 1 and (h) step 2? What is  $W/p_1V_1$  for (i) step 1 and (j) step 2? For the full process, what are (k)  $\Delta E_{\text{int}}/p_1V_1$  and (l)  $\Delta S$ ?

**••20** Expand 1.00 mol of an monatomic gas initially at  $5.00\text{ kPa}$  and  $600\text{ K}$  from initial volume  $V_i = 1.00\text{ m}^3$  to final volume  $V_f = 2.00\text{ m}^3$ . At any instant during the expansion, the pressure  $p$  and volume  $V$  of the gas are related by  $p = 5.00 \exp[(V_i - V)/a]$ , with  $p$  in kilopascals,  $V_i$  and  $V$  in cubic meters, and  $a = 1.00\text{ m}^3$ . What are the final (a) pressure and (b) temperature of the gas? (c) How much work is done by the gas during the expansion? (d) What is  $\Delta S$  for the expansion? (Hint: Use two simple reversible processes to find  $\Delta S$ .)

**••21 GO** Energy can be removed from water as heat at and even below the normal freezing point ( $0.0^{\circ}\text{C}$  at atmospheric pressure) without causing the water to freeze; the water is then said to be *supercooled*. Suppose a 1.00 g water drop is supercooled until its temperature is that of the surrounding air, which is at  $-5.00^{\circ}\text{C}$ . The drop then suddenly and irreversibly freezes, transferring energy to the air as heat. What is the entropy change for the drop? (Hint: Use a three-step reversible process as if the water were taken through the normal freezing point.) The specific heat of ice is  $2220\text{ J/kg}\cdot\text{K}$ .

**••22 GO** An insulated Thermos contains 130 g of water at  $80.0^{\circ}\text{C}$ . You put in a 12.0 g ice cube at  $0^{\circ}\text{C}$  to form a system of

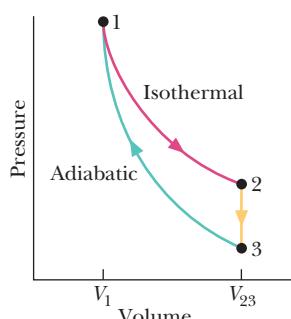


Figure 20-25 Problem 17.

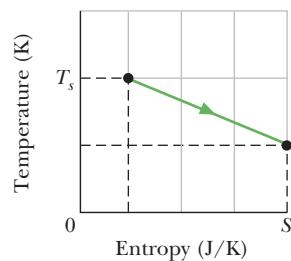


Figure 20-26 Problem 18.

*ice + original water.* (a) What is the equilibrium temperature of the system? What are the entropy changes of the water that was originally the ice cube (b) as it melts and (c) as it warms to the equilibrium temperature? (d) What is the entropy change of the original water as it cools to the equilibrium temperature? (e) What is the net entropy change of the *ice + original water* system as it reaches the equilibrium temperature?

### Module 20-2 Entropy in the Real World: Engines

**•23** A Carnot engine whose low-temperature reservoir is at  $17^{\circ}\text{C}$  has an efficiency of 40%. By how much should the temperature of the high-temperature reservoir be increased to increase the efficiency to 50%?

**•24** A Carnot engine absorbs 52 kJ as heat and exhausts 36 kJ as heat in each cycle. Calculate (a) the engine's efficiency and (b) the work done per cycle in kilojoules.

**•25** A Carnot engine has an efficiency of 22.0%. It operates between constant-temperature reservoirs differing in temperature by  $75.0\text{ }^{\circ}\text{C}$ . What is the temperature of the (a) lower-temperature and (b) higher-temperature reservoir?

**•26** In a hypothetical nuclear fusion reactor, the fuel is deuterium gas at a temperature of  $7 \times 10^8\text{ K}$ . If this gas could be used to operate a Carnot engine with  $T_L = 100^{\circ}\text{C}$ , what would be the engine's efficiency? Take both temperatures to be exact and report your answer to seven significant figures.

**•27 SSM WWW** A Carnot engine operates between  $235^{\circ}\text{C}$  and  $115^{\circ}\text{C}$ , absorbing  $6.30 \times 10^4\text{ J}$  per cycle at the higher temperature. (a) What is the efficiency of the engine? (b) How much work per cycle is this engine capable of performing?

**•28** In the first stage of a two-stage Carnot engine, energy is absorbed as heat  $Q_1$  at temperature  $T_1$ , work  $W_1$  is done, and energy is expelled as heat  $Q_2$  at a lower temperature  $T_2$ . The second stage absorbs that energy as heat  $Q_2$ , does work  $W_2$ , and expels energy as heat  $Q_3$  at a still lower temperature  $T_3$ . Prove that the efficiency of the engine is  $(T_1 - T_3)/T_1$ .

**•29 GO** Figure 20-27 shows a reversible cycle through which 1.00 mol of a monatomic ideal gas is taken. Assume that  $p = 2p_0$ ,  $V = 2V_0$ ,  $p_0 = 1.01 \times 10^5\text{ Pa}$ , and  $V_0 = 0.0225\text{ m}^3$ . Calculate (a) the work done during the cycle, (b) the energy added as heat during stroke  $abc$ , and (c) the efficiency of the cycle. (d) What is the efficiency of a Carnot engine operating between the highest and lowest temperatures that occur in the cycle? (e) Is this greater than or less than the efficiency calculated in (c)?

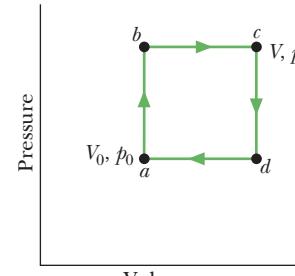


Figure 20-27 Problem 29.

**•30** A 500 W Carnot engine operates between constant-temperature reservoirs at  $100^{\circ}\text{C}$  and  $60.0^{\circ}\text{C}$ . What is the rate at which energy is (a) taken in by the engine as heat and (b) exhausted by the engine as heat?

**•31** The efficiency of a particular car engine is 25% when the engine does 8.2 kJ of work per cycle. Assume the process is reversible. What are (a) the energy the engine gains per cycle as heat  $Q_{\text{gain}}$  from the fuel combustion and (b) the energy the engine loses per cycle as heat  $Q_{\text{lost}}$ ? If a tune-up increases the efficiency to 31%, what are (c)  $Q_{\text{gain}}$  and (d)  $Q_{\text{lost}}$  at the same work value?

- 32 GO** A Carnot engine is set up to produce a certain work  $W$  per cycle. In each cycle, energy in the form of heat  $Q_H$  is transferred to the working substance of the engine from the higher-temperature thermal reservoir, which is at an adjustable temperature  $T_H$ . The lower-temperature thermal reservoir is maintained at temperature  $T_L = 250\text{ K}$ . Figure 20-28 gives  $Q_H$  for a range of  $T_H$ . The scale of the vertical axis is set by  $Q_{Hs} = 6.0\text{ kJ}$ . If  $T_H$  is set at  $550\text{ K}$ , what is  $Q_H$ ?

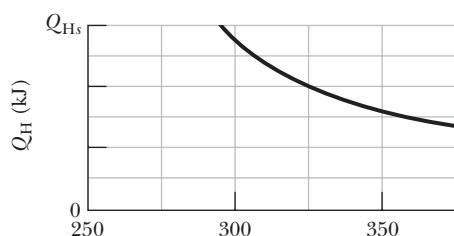


Figure 20-28 Problem 32.

- 33 SSM ILW** Figure 20-29 shows a reversible cycle through which  $1.00\text{ mol}$  of a monatomic ideal gas is taken. Volume  $V_c = 8.00V_b$ . Process  $bc$  is an adiabatic expansion, with  $p_b = 10.0\text{ atm}$  and  $V_b = 1.00 \times 10^{-3}\text{ m}^3$ . For the cycle, find (a) the energy added to the gas as heat, (b) the energy leaving the gas as heat, (c) the net work done by the gas, and (d) the efficiency of the cycle.

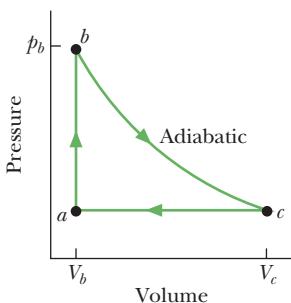


Figure 20-29 Problem 33.

- 34 GO** An ideal gas ( $1.0\text{ mol}$ ) is the working substance in an engine that operates on the cycle shown in Fig. 20-30. Processes  $BC$  and  $DA$  are reversible and adiabatic. (a) Is the gas monatomic, diatomic, or polyatomic? (b) What is the engine efficiency?

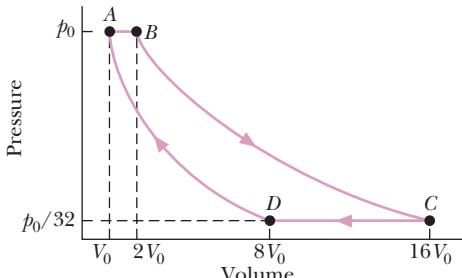


Figure 20-30 Problem 34.

- 35** The cycle in Fig. 20-31 represents the operation of a gasoline internal combustion engine. Volume  $V_3 = 4.00V_1$ . Assume the gasoline-air intake mixture is an ideal gas with  $\gamma = 1.30$ . What are the ratios (a)  $T_2/T_1$ , (b)  $T_3/T_1$ , (c)  $T_4/T_1$ , (d)  $p_3/p_1$ , and (e)  $p_4/p_1$ ? (f) What is the engine efficiency?

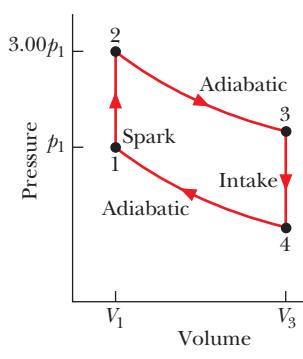


Figure 20-31 Problem 35.

### Module 20-3 Refrigerators and Real Engines

- 36** How much work must be done by a Carnot refrigerator to transfer  $1.0\text{ J}$

as heat (a) from a reservoir at  $7.0^\circ\text{C}$  to one at  $27^\circ\text{C}$ , (b) from a reservoir at  $-73^\circ\text{C}$  to one at  $27^\circ\text{C}$ , (c) from a reservoir at  $-173^\circ\text{C}$  to one at  $27^\circ\text{C}$ , and (d) from a reservoir at  $-223^\circ\text{C}$  to one at  $27^\circ\text{C}$ ?

- 37 SSM** A heat pump is used to heat a building. The external temperature is less than the internal temperature. The pump's coefficient of performance is 3.8, and the heat pump delivers  $7.54\text{ MJ}$  as heat to the building each hour. If the heat pump is a Carnot engine working in reverse, at what rate must work be done to run it?

- 38** The electric motor of a heat pump transfers energy as heat from the outdoors, which is at  $-5.0^\circ\text{C}$ , to a room that is at  $17^\circ\text{C}$ . If the heat pump were a Carnot heat pump (a Carnot engine working in reverse), how much energy would be transferred as heat to the room for each joule of electric energy consumed?

- 39 SSM** A Carnot air conditioner takes energy from the thermal energy of a room at  $70^\circ\text{F}$  and transfers it as heat to the outdoors, which is at  $96^\circ\text{F}$ . For each joule of electric energy required to operate the air conditioner, how many joules are removed from the room?

- 40** To make ice, a freezer that is a reverse Carnot engine extracts  $42\text{ kJ}$  as heat at  $-15^\circ\text{C}$  during each cycle, with coefficient of performance 5.7. The room temperature is  $30.3^\circ\text{C}$ . How much (a) energy per cycle is delivered as heat to the room and (b) work per cycle is required to run the freezer?

- 41 ILW** An air conditioner operating between  $93^\circ\text{F}$  and  $70^\circ\text{F}$  is rated at  $4000\text{ Btu/h}$  cooling capacity. Its coefficient of performance is 27% of that of a Carnot refrigerator operating between the same two temperatures. What horsepower is required of the air conditioner motor?

- 42** The motor in a refrigerator has a power of  $200\text{ W}$ . If the freezing compartment is at  $270\text{ K}$  and the outside air is at  $300\text{ K}$ , and assuming the efficiency of a Carnot refrigerator, what is the maximum amount of energy that can be extracted as heat from the freezing compartment in  $10.0\text{ min}$ ?

- 43 GO** Figure 20-32 represents a Carnot engine that works between temperatures  $T_1 = 400\text{ K}$  and  $T_2 = 150\text{ K}$  and drives a Carnot refrigerator that works between temperatures  $T_3 = 325\text{ K}$  and  $T_4 = 225\text{ K}$ . What is the ratio  $Q_3/Q_1$ ?

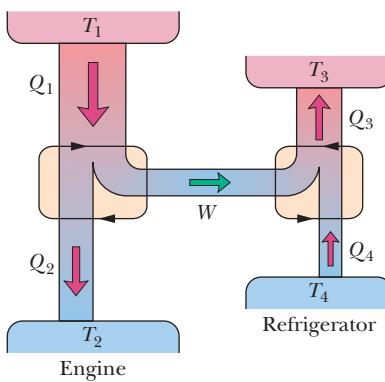


Figure 20-32 Problem 43.

- 44** (a) During each cycle, a Carnot engine absorbs  $750\text{ J}$  as heat from a high-temperature reservoir at  $360\text{ K}$ , with the low-temperature reservoir at  $280\text{ K}$ . How much work is done per cycle? (b) The engine is then made to work in reverse to function as a Carnot refrigerator between those same two reservoirs. During each cycle, how much work is required to remove  $1200\text{ J}$  as heat from the low-temperature reservoir?

### Module 20-4 A Statistical View of Entropy

- 45** Construct a table like Table 20-1 for eight molecules.

- 46** A box contains  $N$  identical gas molecules equally divided between its two halves. For  $N = 50$ , what are (a) the multiplicity  $W$  of the central configuration, (b) the total number of microstates, and (c) the percentage of the time the system spends in the central configuration? For  $N = 100$ , what are (d)  $W$  of the central configura-

tion, (e) the total number of microstates, and (f) the percentage of the time the system spends in the central configuration? For  $N = 200$ , what are (g)  $W$  of the central configuration, (h) the total number of microstates, and (i) the percentage of the time the system spends in the central configuration? (j) Does the time spent in the central configuration increase or decrease with an increase in  $N$ ?

**•••47 SSM WWW** A box contains  $N$  gas molecules. Consider the box to be divided into three equal parts. (a) By extension of Eq. 20-20, write a formula for the multiplicity of any given configuration. (b) Consider two configurations: configuration  $A$  with equal numbers of molecules in all three thirds of the box, and configuration  $B$  with equal numbers of molecules in each half of the box divided into two equal parts rather than three. What is the ratio  $W_A/W_B$  of the multiplicity of configuration  $A$  to that of configuration  $B$ ? (c) Evaluate  $W_A/W_B$  for  $N = 100$ . (Because 100 is not evenly divisible by 3, put 34 molecules into one of the three box parts of configuration  $A$  and 33 in each of the other two parts.)

### Additional Problems

**48** Four particles are in the insulated box of Fig. 20-17. What are (a) the least multiplicity, (b) the greatest multiplicity, (c) the least entropy, and (d) the greatest entropy of the four-particle system?

**49** A cylindrical copper rod of length 1.50 m and radius 2.00 cm is insulated to prevent heat loss through its curved surface. One end is attached to a thermal reservoir fixed at 300°C; the other is attached to a thermal reservoir fixed at 30.0°C. What is the rate at which entropy increases for the rod–reservoirs system?

**50** Suppose 0.550 mol of an ideal gas is isothermally and reversibly expanded in the four situations given below. What is the change in the entropy of the gas for each situation?

Situation	(a)	(b)	(c)	(d)
Temperature (K)	250	350	400	450
Initial volume (cm <sup>3</sup> )	0.200	0.200	0.300	0.300
Final volume (cm <sup>3</sup> )	0.800	0.800	1.20	1.20

**51 SSM** As a sample of nitrogen gas ( $N_2$ ) undergoes a temperature increase at constant volume, the distribution of molecular speeds increases. That is, the probability distribution function  $P(v)$  for the molecules spreads to higher speed values, as suggested in Fig. 19-8b. One way to report the spread in  $P(v)$  is to measure the difference  $\Delta v$  between the most probable speed  $v_p$  and the rms speed  $v_{rms}$ . When  $P(v)$  spreads to higher speeds,  $\Delta v$  increases. Assume that the gas is ideal and the  $N_2$  molecules rotate but do not oscillate. For 1.5 mol, an initial temperature of 250 K, and a final temperature of 500 K, what are (a) the initial difference  $\Delta v_i$ , (b) the final difference  $\Delta v_f$ , and (c) the entropy change  $\Delta S$  for the gas?

**52** Suppose 1.0 mol of a monatomic ideal gas initially at 10 L and 300 K is heated at constant volume to 600 K, allowed to expand isothermally to its initial pressure, and finally compressed at constant pressure to its original volume, pressure, and temperature. During the cycle, what are (a) the net energy entering the system (the gas) as heat and (b) the net work done by the gas? (c) What is the efficiency of the cycle?

**53 GO** Suppose that a deep shaft were drilled in Earth's crust near one of the poles, where the surface temperature is –40°C, to a depth where the temperature is 800°C. (a) What is the theoretical limit to the efficiency of an engine operating between these

temperatures? (b) If all the energy released as heat into the low-temperature reservoir were used to melt ice that was initially at –40°C, at what rate could liquid water at 0°C be produced by a 100 MW power plant (treat it as an engine)? The specific heat of ice is 2220 J/kg·K; water's heat of fusion is 333 kJ/kg. (Note that the engine can operate only between 0°C and 800°C in this case. Energy exhausted at –40°C cannot warm anything above –40°C.)

**54** What is the entropy change for 3.20 mol of an ideal monatomic gas undergoing a reversible increase in temperature from 380 K to 425 K at constant volume?

**55** A 600 g lump of copper at 80.0°C is placed in 70.0 g of water at 10.0°C in an insulated container. (See Table 18-3 for specific heats.) (a) What is the equilibrium temperature of the copper–water system? What entropy changes do (b) the copper, (c) the water, and (d) the copper–water system undergo in reaching the equilibrium temperature?

**56** Figure 20-33 gives the force magnitude  $F$  versus stretch distance  $x$  for a rubber band, with the scale of the  $F$  axis set by  $F_s = 1.50 \text{ N}$  and the scale of the  $x$  axis set by  $x_s = 3.50 \text{ cm}$ . The temperature is 2.00°C. When the rubber band is stretched by  $x = 1.70 \text{ cm}$ , at what rate does the entropy of the rubber band change during a small additional stretch?

**57** The temperature of 1.00 mol of a monatomic ideal gas is raised reversibly from 300 K to 400 K, with its volume kept constant. What is the entropy change of the gas?

**58** Repeat Problem 57, with the pressure now kept constant.

**59 SSM** A 0.600 kg sample of water is initially ice at temperature –20°C. What is the sample's entropy change if its temperature is increased to 40°C?

**60** A three-step cycle is undergone by 3.4 mol of an ideal diatomic gas: (1) the temperature of the gas is increased from 200 K to 500 K at constant volume; (2) the gas is then isothermally expanded to its original pressure; (3) the gas is then contracted at constant pressure back to its original volume. Throughout the cycle, the molecules rotate but do not oscillate. What is the efficiency of the cycle?

**61** An inventor has built an engine X and claims that its efficiency  $\epsilon_X$  is greater than the efficiency  $\epsilon$  of an ideal engine operating between the same two temperatures. Suppose you couple engine X to an ideal refrigerator (Fig. 20-34a) and adjust the cycle

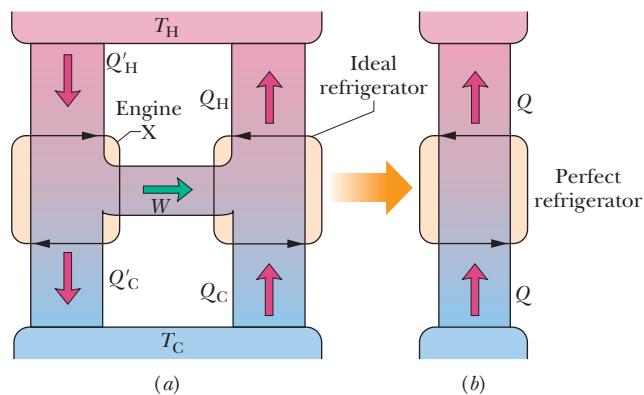


Figure 20-34 Problem 61.

of engine X so that the work per cycle it provides equals the work per cycle required by the ideal refrigerator. Treat this combination as a single unit and show that if the inventor's claim were true (if  $\varepsilon_X > \varepsilon$ ), the combined unit would act as a perfect refrigerator (Fig. 20-34b), transferring energy as heat from the low-temperature reservoir to the high-temperature reservoir without the need for work.

**62** Suppose 2.00 mol of a diatomic gas is taken reversibly around the cycle shown in the  $T$ - $S$  diagram of Fig. 20-35, where  $S_1 = 6.00 \text{ J/K}$  and  $S_2 = 8.00 \text{ J/K}$ . The molecules do not rotate or oscillate. What is the energy transferred as heat  $Q$  for (a) path  $1 \rightarrow 2$ , (b) path  $2 \rightarrow 3$ , and (c) the full cycle? (d) What is the work  $W$  for the isothermal process? The volume  $V_1$  in state 1 is  $0.200 \text{ m}^3$ . What is the volume in (e) state 2 and (f) state 3?

What is the change  $\Delta E_{\text{int}}$  for (g) path  $1 \rightarrow 2$ , (h) path  $2 \rightarrow 3$ , and (i) the full cycle? (Hint: (h) can be done with one or two lines of calculation using Module 19-7 or with a page of calculation using Module 19-9.) (j) What is the work  $W$  for the adiabatic process?

**63** A three-step cycle is undergone reversibly by 4.00 mol of an ideal gas: (1) an adiabatic expansion that gives the gas 2.00 times its initial volume, (2) a constant-volume process, (3) an isothermal compression back to the initial state of the gas. We do not know whether the gas is monatomic or diatomic; if it is diatomic, we do not know whether the molecules are rotating or oscillating. What are the entropy changes for (a) the cycle, (b) process 1, (c) process 3, and (d) process 2?

**64** (a) A Carnot engine operates between a hot reservoir at 320 K and a cold one at 260 K. If the engine absorbs 500 J as heat per cycle at the hot reservoir, how much work per cycle does it deliver? (b) If the engine working in reverse functions as a refrigerator between the same two reservoirs, how much work per cycle must be supplied to remove 1000 J as heat from the cold reservoir?

**65** A 2.00 mol diatomic gas initially at 300 K undergoes this cycle: It is (1) heated at constant volume to 800 K, (2) then allowed to expand isothermally to its initial pressure, (3) then compressed at constant pressure to its initial state. Assuming the gas molecules neither rotate nor oscillate, find (a) the net energy transferred as heat to the gas, (b) the net work done by the gas, and (c) the efficiency of the cycle.

**66** An ideal refrigerator does 150 J of work to remove 560 J as heat from its cold compartment. (a) What is the refrigerator's coefficient of performance? (b) How much heat per cycle is exhausted to the kitchen?

**67** Suppose that 260 J is conducted from a constant-temperature reservoir at 400 K to one at (a) 100 K, (b) 200 K, (c) 300 K, and (d) 360 K. What is the net change in entropy  $\Delta S_{\text{net}}$  of the reservoirs in each case? (e) As the temperature difference of the two reservoirs decreases, does  $\Delta S_{\text{net}}$  increase, decrease, or remain the same?

**68** An apparatus that liquefies helium is in a room maintained at 300 K. If the helium in the apparatus is at 4.0 K, what is the minimum ratio  $Q_{\text{to}}/Q_{\text{from}}$ , where  $Q_{\text{to}}$  is the energy delivered as heat to the room and  $Q_{\text{from}}$  is the energy removed as heat from the helium?

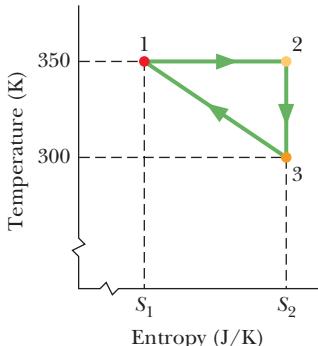


Figure 20-35 Problem 62.

**69 GO** A brass rod is in thermal contact with a constant-temperature reservoir at 130°C at one end and a constant-temperature reservoir at 24.0°C at the other end. (a) Compute the total change in entropy of the rod-reservoirs system when 5030 J of energy is conducted through the rod, from one reservoir to the other. (b) Does the entropy of the rod change?

**70** A 45.0 g block of tungsten at 30.0°C and a 25.0 g block of silver at -120°C are placed together in an insulated container. (See Table 18-3 for specific heats.) (a) What is the equilibrium temperature? What entropy changes do (b) the tungsten, (c) the silver, and (d) the tungsten-silver system undergo in reaching the equilibrium temperature?

**71** A box contains  $N$  molecules. Consider two configurations: configuration *A* with an equal division of the molecules between the two halves of the box, and configuration *B* with 60.0% of the molecules in the left half of the box and 40.0% in the right half. For  $N = 50$ , what are (a) the multiplicity  $W_A$  of configuration *A*, (b) the multiplicity  $W_B$  of configuration *B*, and (c) the ratio  $f_{B/A}$  of the time the system spends in configuration *B* to the time it spends in configuration *A*? For  $N = 100$ , what are (d)  $W_A$ , (e)  $W_B$ , and (f)  $f_{B/A}$ ? For  $N = 200$ , what are (g)  $W_A$ , (h)  $W_B$ , and (i)  $f_{B/A}$ ? (j) With increasing  $N$ , does  $f$  increase, decrease, or remain the same?

**72** Calculate the efficiency of a fossil-fuel power plant that consumes 380 metric tons of coal each hour to produce useful work at the rate of 750 MW. The heat of combustion of coal (the heat due to burning it) is 28 MJ/kg.

**73 SSM** A Carnot refrigerator extracts 35.0 kJ as heat during each cycle, operating with a coefficient of performance of 4.60. What are (a) the energy per cycle transferred as heat to the room and (b) the work done per cycle?

**74** A Carnot engine whose high-temperature reservoir is at 400 K has an efficiency of 30.0%. By how much should the temperature of the low-temperature reservoir be changed to increase the efficiency to 40.0%?

**75 SSM** System *A* of three particles and system *B* of five particles are in insulated boxes like that in Fig. 20-17. What is the least multiplicity  $W$  of (a) system *A* and (b) system *B*? What is the greatest multiplicity  $W$  of (c) *A* and (d) *B*? What is the greatest entropy of (e) *A* and (f) *B*?

**76** Figure 20-36 shows a Carnot cycle on a  $T$ - $S$  diagram, with a scale set by  $S_s = 0.60 \text{ J/K}$ . For a full cycle, find (a) the net heat transfer and (b) the net work done by the system.

**77** Find the relation between the efficiency of a reversible ideal heat engine and the coefficient of performance of the reversible refrigerator obtained by running the engine backwards.

**78** A Carnot engine has a power of 500 W. It operates between heat reservoirs at 100°C and 60.0°C. Calculate (a) the rate of heat input and (b) the rate of exhaust heat output.

**79** In a real refrigerator, the low-temperature coils are at -13°C, and the compressed gas in the condenser is at 26°C. What is the theoretical coefficient of performance?

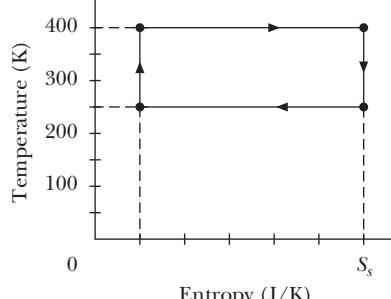


Figure 20-36 Problem 76.