Thermodynamics is the study of heat and work. Heat is a transfer of energy due to a difference of temperature. Work is a transfer of energy by mechanical means, not due to a temperature difference. The first law of thermodynamics links the two in a general statement of energy conservation: the heat Q added to a system minus the net work W done by the system equals the change in internal energy ΔU of the system: $\Delta U = Q - W$.

There are many uses for a heat engine such as a modern coal-burning power plant, or a steam locomotive. The photograph shows a steam locomotive which produces steam that does work on a piston that moves linkage to turn locomotive wheels. The efficiency of any engine is limited by nature as described in the second law of thermodynamics. This great law is best stated in terms of a quantity called entropy, which is *not* conserved, but instead is constrained always to increase in any real process. Entropy is a measure of disorder. The second law of thermodynamics tells us that as time moves forward, the disorder in the universe increases. We also discuss practical matters such as heat engines, heat pumps, refrigerators, and air conditioners.

CHAPTER
15
The Laws of Thermodynamics

CONTENTS

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CHAPTER-OPENING QUESTION—Guess now!

Fossil-fuel electric generating plants produce "thermal pollution." Part of the heat produced by the burning fuel is not converted to electric energy. The reason for this waste is

(a) the efficiency is higher if some heat is allowed to escape.

(b) engineering technology has not yet reached the point where 100% waste heat recovery is possible.

(c) some waste heat *must* be produced: this is a fundamental property of nature when converting heat to useful work.

(d) the plants rely on fossil fuels, not nuclear fuel.

(e) None of the above.

Thermodynamics is the name we give to the study of processes in which energy is transferred as heat and as work.

In Chapter 6 we saw that work is done when energy is transferred from one object to another by mechanical means. In Chapter 14 we saw that heat is a transfer of energy from one object to a second one at a lower temperature. Thus, heat is much like work. To distinguish them, *heat* is defined as a *transfer of energy due to a difference in temperature*, whereas work is a transfer of energy that is not due to a temperature difference.

In discussing thermodynamics, we often refer to particular systems. A **system** is any object or set of objects that we wish to consider (see Section 14–4). Everything else in the universe is referred to as its "environment" or the "surroundings."

In this Chapter, we examine the two great laws of thermodynamics. The first law of thermodynamics relates work and heat transfers to the change in internal energy of a system, and is a general statement of the conservation of energy. The second law of thermodynamics expresses limits on the ability to do useful work, and is often stated in terms of *entropy*, which is a measure of disorder. Besides these two great laws, we also discuss some important related practical devices: heat engines, refrigerators, heat pumps, and air conditioners.

15–1 The First Law of Thermodynamics

In Section 14–2, we defined the internal energy of a system as the sum total of all the energy of the molecules within the system. Then the internal energy of a system should increase if work is done on the system, or if heat is added to it. Similarly the internal energy should decrease if heat flows out of the system or if work is done by the system on something in the surroundings.

Thus it is reasonable to extend conservation of energy and propose an important law: the change in internal energy of a closed system, ΔU, will be equal to the energy added to the system by heating minus the work done by the system on the surroundings. In equation form we write

$$\Delta U = Q - W \qquad (15\text{–}1)$$

FIRST LAW OF THERMODYNAMICS

where Q is the net heat *added* to the system and W is the net work done *by* the system. We must be careful and consistent in following the sign conventions for Q and W. Because W in Eq. 15–1 is the work done *by* the system, then if work is done *on* the system, W will be negative and U will increase. Similarly, Q is positive for heat added to the system, so if heat leaves the system, Q is negative. [Caution: Elsewhere you may sometimes encounter the opposite convention for W where W is defined as the work done *on* the system; in that case Eq. 15–1 is written as $\Delta U = Q + W$.]

⚠ CAUTION
Heat added is +
Heat lost is −
Work on system is −
Work by system is +

Equation 15–1 is known as the **first law of thermodynamics**. It is one of the great laws of physics, and its validity rests on experiments (such as Joule's) to which no exceptions have been seen. Since Q and W represent energy transferred into or out of the system, the internal energy changes accordingly. Thus, the first law of thermodynamics is a general statement of the *law of conservation of energy*.

Note that the conservation of energy law was not able to be formulated until the 1800s, because it depended on the interpretation of heat as a transfer of energy.

A given system does not "have" a certain amount of heat or work. Rather, work and heat are involved in *thermodynamic processes* that can change the system from one state to another; they are not characteristic of the state itself. Quantities which describe the state of a system, such as internal energy U, pressure P, volume V, temperature T, and mass m or number of moles n, are called **state variables**. Q and W are *not* state variables.

⚠ CAUTION
P, V, T, U, m, n are state variables. W and Q are not: a system does not have *an amount of heat or work*

EXAMPLE 15–1 **Using the first law.** 2500 J of heat is added to a system, and 1800 J of work is done on the system. What is the change in internal energy of the system?

APPROACH We apply the first law of thermodynamics, Eq. 15–1, to our system.

SOLUTION The heat added to the system is $Q = 2500$ J. The work W done *by* the system is -1800 J. Why the minus sign? Because 1800 J done *on* the system (as given) equals -1800 J done *by* the system, and it is the latter we need for the sign conventions we used for Eq. 15–1. Hence

$$\Delta U = 2500\text{ J} - (-1800\text{ J}) = 2500\text{ J} + 1800\text{ J} = 4300\text{ J}.$$

NOTE We did this calculation in detail to emphasize the importance of keeping careful track of signs. Both the heat and the work are inputs to the system, so we expect ΔU to be increased by both.

EXERCISE A What would be the internal energy change in Example 15–1 if 2500 J of heat is added to the system and 1800 J of work is done *by* the system (i.e., as output)?

*The First Law of Thermodynamics Extended

To write the first law of thermodynamics in a more complete form, consider a system that is moving so it has kinetic energy KE, and suppose there is also potential energy PE. Then the first law of thermodynamics would have to include these terms and would be written as

$$\Delta \text{KE} + \Delta \text{PE} + \Delta U = Q - W. \tag{15–2}$$

EXAMPLE 15–2 **Kinetic energy transformed to thermal energy.** A 3.0-g bullet traveling at a speed of 400 m/s enters a tree and exits the other side with a speed of 200 m/s. Where did the bullet's lost KE go, and how much energy was transferred?

APPROACH Take the bullet and tree as our system. No potential energy is involved. No work is done on (or by) the system by outside forces, nor is any heat added because no energy was transferred to or from the system due to a temperature difference. Thus the kinetic energy gets transformed into internal energy of the bullet and tree. This answers the first question.

SOLUTION In the first law of thermodynamics as written in Eq. 15–2, we are given $Q = W = \Delta \text{PE} = 0$, so we have

$$\Delta \text{KE} + \Delta U = 0$$

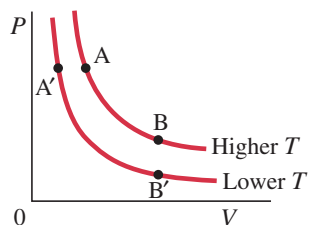or, using subscripts i and f for initial and final velocities,

$$\Delta U = -\Delta \text{KE} = -(\text{KE}_f - \text{KE}_i) = \tfrac{1}{2}m(v_i^2 - v_f^2)$$
$$= \tfrac{1}{2}(3.0 \times 10^{-3}\,\text{kg})\big[(400\,\text{m/s})^2 - (200\,\text{m/s})^2\big] = 180\,\text{J}.$$

NOTE The internal energy of the bullet and tree both increase, as both experience a rise in temperature. If we had chosen the bullet alone as our system, work would be done on it and heat transfer would occur.
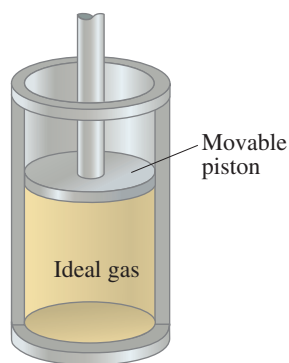
15–2 Thermodynamic Processes and the First Law

Let us analyze some thermodynamic processes in light of the first law of thermodynamics.

Isothermal Processes $(\Delta T = 0)$

To begin, we choose a very simple system: a fixed mass of an ideal gas enclosed in a container fitted with a movable piston as shown in Fig. 15–1.

First we consider an idealized process, such as adding heat or doing work, that is carried out at constant temperature. Such a process is called an **isothermal** process (from the Greek meaning "same temperature"). If the system is an ideal gas, then $PV = nRT$ (Eq. 13–3), so for a fixed amount of gas kept at constant temperature, $PV = $ constant. Thus a graph of pressure P vs. volume V, a **PV diagram**, would follow a curve like AB in Fig. 15–2 for an isothermal process. Each point on the curve, such as point A, represents the state of the system at a given moment—that is, its pressure P and volume V. At a lower temperature, another isothermal process would be represented by a curve like A′ B′ in Fig. 15–2 (the product $PV = nRT = $ constant is less when T is less). The curves shown in Fig. 15–2 are referred to as *isotherms*.

We assume the gas is in contact with a **heat reservoir** (a body whose mass is so large that, ideally, its temperature does not change significantly when heat is exchanged with our system). We also assume that a process of compression (volume decrease) or expansion (volume increase) is done very slowly, so that the process can be considered a *series of equilibrium states* all at the same constant temperature.[†]

[†]If a gas expands or is compressed quickly, there is turbulence and different parts of the gas in its container would be at different pressures and temperatures.

FIGURE 15–1 An ideal gas in a cylinder fitted with a movable piston.

Movable piston

Ideal gas

FIGURE 15–2 *PV* diagram for an ideal gas undergoing isothermal processes at two different temperatures.

If the gas is initially in a state represented by point A in Fig. 15–2, and an amount of heat Q is added to the system, the pressure and volume will change and the state of the system will be represented by another point, B, on the diagram. If the temperature is to remain constant, the gas will expand and do an amount of work W on the environment (it exerts a force on the piston in Fig. 15–1 and moves it through a distance). The temperature and mass are kept constant so, from Eq. 14–1, the internal energy does not change: $\Delta U = \frac{3}{2} nR \, \Delta T = 0$. Hence, by the first law of thermodynamics, Eq. 15–1, $\Delta U = Q - W = 0$, so $W = Q$: the work done by the gas in an isothermal process equals the heat added to the gas.

Adiabatic Processes ($Q = 0$)

An **adiabatic** process is one in which no heat is allowed to flow into or out of the system: $Q = 0$. This situation can occur if the system is extremely well insulated, or the process happens so quickly that heat—which flows slowly—has no time to flow in or out. The very rapid expansion of gases in an internal combustion engine is one example of a process that is very nearly adiabatic. An adiabatic expansion of an ideal gas done very slowly can be represented by a curve like that labeled AC in Fig. 15–3. Since $Q = 0$, we have from Eq. 15–1 that $\Delta U = -W$. When a gas expands, it does work and W is positive, so the internal energy decreases; hence the temperature decreases as well (because $\Delta U = \frac{3}{2} nR \, \Delta T$). This is seen in Fig. 15–3 where the product PV ($= nRT$) is less at point C than at point B. (Compare to curve AB for an isothermal process, in which $\Delta U = 0$ and $\Delta T = 0$.) In the reverse operation, an adiabatic compression (going from C to A, for example), work is done *on* the gas, and hence the internal energy increases and the temperature rises. In a diesel engine, the fuel–air mixture is rapidly compressed adiabatically by a factor of 15 or more; the temperature rise is so great that the mixture ignites spontaneously, without spark plugs.
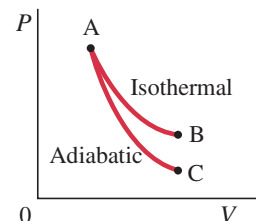

FIGURE 15–3 *PV* diagram for adiabatic (AC) and isothermal (AB) processes on an ideal gas.

Isobaric and Isovolumetric Processes

Isothermal and adiabatic processes are just two possible processes that can occur. Two other simple thermodynamic processes are illustrated on the *PV* diagrams of Fig. 15–4: (a) an **isobaric** process is one in which the pressure is kept constant, so the process is represented by a straight horizontal line on the *PV* diagram (Fig. 15–4a); (b) an **isovolumetric** (or *isochoric*) process is one in which the volume does not change (Fig. 15–4b). In these, and in all other processes, the first law of thermodynamics holds.

FIGURE 15–4 (a) Isobaric ("same pressure") process. (b) Isovolumetric ("same volume") process.

(a) Isobaric   (b) Isovolumetric
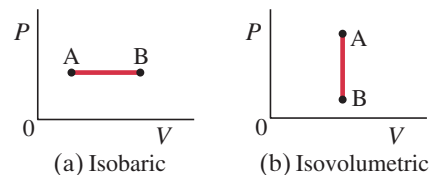
Work Done in Volume Changes

It is often valuable to calculate the work done in a process. If the pressure is kept constant during a process (isobaric), the work done is easily calculated. For example, if the gas in Fig. 15–5 expands very slowly against the piston, the work done by the gas to raise the piston is the force F times the distance d. But the force is just the pressure P of the gas times the area A of the piston, $F = PA$. Thus,

$$W = Fd = PAd.$$

Note that $Ad = \Delta V$, the change in volume of the gas, so

$$W = P \, \Delta V. \qquad \text{[constant pressure]} \quad \textbf{(15–3)}$$

Equation 15–3 also holds if the gas is *compressed* at constant pressure, in which case ΔV is negative (since V decreases); W is then negative, which indicates that work is done *on* the gas. Equation 15–3 is also valid for liquids and solids, as long as the pressure is constant during the process.

In an isovolumetric process (Fig. 15–4b) the volume does not change, so no work is done, $W = 0$.

FIGURE 15–5 Work is done on the piston when the gas expands, moving the piston a distance d.
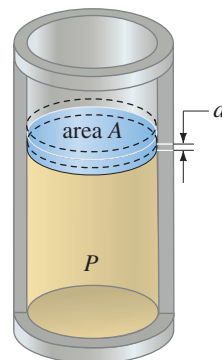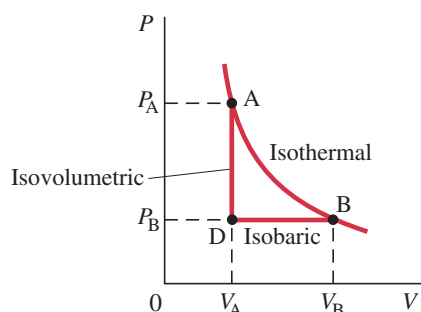
FIGURE 15–6 *PV* diagram for different processes (see the text), where the system changes from A to B.

Figure 15–6 shows the isotherm AB we saw in Fig. 15–2 as well as another possible process represented by the path ADB. In going from A to D, the gas does no work since the volume does not change. But in going from D to B, the gas does work equal to $P_B(V_B - V_A)$, and this is the total work done in the process ADB.

If the pressure varies during a process, such as for the isothermal process AB in Fig. 15–6 (and Fig. 15–2), Eq. 15–3 cannot be used directly to determine the work. A rough estimate can be obtained, however, by using an "average" value for *P* in Eq. 15–3. More accurately, the work done is equal to the area under the *PV* curve. This is obvious when the pressure is constant: as Fig. 15–7a shows, the shaded area is just $P_B(V_B - V_A)$, and this is the work done. Similarly, the work done during an isothermal process is equal to the shaded area shown in Fig. 15–7b. The calculation of work done in this case can be carried out using calculus, or by estimating the area on graph paper.

(a)   (b)
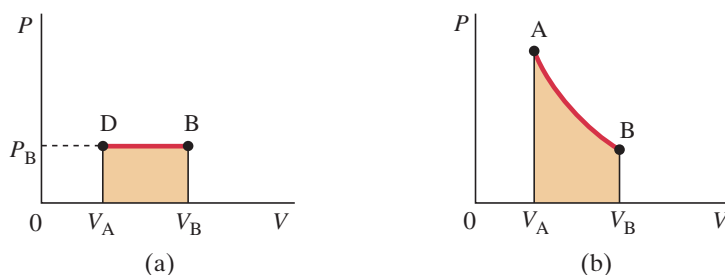
FIGURE 15–7 Work done by a gas is equal to the area under the *PV* curve.

| CONCEPTUAL EXAMPLE 15–3 | **Work in isothermal and adiabatic processes.** In Fig. 15–3 we saw the *PV* diagrams for a gas expanding in two ways, isothermally and adiabatically. The initial volume V_A was the same in each case, and the final volumes were the same $(V_B = V_C)$. In which process was more work done by the gas?

RESPONSE Our system is the gas. More work was done by the gas in the isothermal process, which we can see in two simple ways by looking at Fig. 15–3. First, the "average" pressure was higher during the isothermal process AB, so $W = P_{av} \Delta V$ was greater (ΔV is the same for both processes). Second, we can look at the area under each curve as we showed in Fig. 15–7b: the area under curve AB, which represents the work done, is greater (because curve AB is higher) than the area under AC in Fig. 15–3.

EXERCISE B Is the work done by the gas in process ADB of Fig. 15–6 greater than, less than, or equal to the work done in the isothermal process AB?

Table 15–1 gives a brief summary of the processes we have discussed. Many other types of processes can occur, but these "simple" ones are useful and can be dealt with by fairly simple means.

TABLE 15–1 Simple Thermodynamic Processes and the First Law

Process	What is constant:	The first law, $\Delta U = Q - W$, predicts:
Isothermal	T = constant	$\Delta T = 0$ makes $\Delta U = 0$, so $Q = W$
Isobaric	P = constant	$Q = \Delta U + W = \Delta U + P\,\Delta V$
Isovolumetric	V = constant	$\Delta V = 0$ makes $W = 0$, so $Q = \Delta U$
Adiabatic	$Q = 0$	$\Delta U = -W$

EXAMPLE 15–4 **First law in isobaric and isovolumetric processes.** An ideal gas is slowly compressed at a constant pressure of 2.0 atm from 10.0 L to 2.0 L. This process is represented in Fig. 15–8 as the path B to D. (In this process, some heat flows out of the gas and the temperature drops.) Heat is then added to the gas, holding the volume constant, and the pressure and temperature are allowed to rise (line DA) until the temperature reaches its original value $(T_A = T_B)$. In the process BDA, calculate (a) the total work done by the gas, and (b) the total heat flow into the gas.

APPROACH (a) Work is done only in the compression process BD. In process DA, the volume is constant so $\Delta V = 0$ and no work is done (Eq. 15–3). (b) We use the first law of thermodynamics, Eq. 15–1.

SOLUTION (a) During the compression BD, the pressure is $2.0 \text{ atm} = 2(1.01 \times 10^5 \text{ N/m}^2)$ and the work done is $(1 \text{ L} = 10^3 \text{ cm}^3 = 10^{-3} \text{ m}^3)$

$$W = P\,\Delta V$$
$$= (2.02 \times 10^5 \text{ N/m}^2)[(2.0 \times 10^{-3} \text{ m}^3) - (10.0 \times 10^{-3} \text{ m}^3)]$$
$$= -1.6 \times 10^3 \text{ J}.$$

The total work done by the gas is $-1.6 \times 10^3 \text{ J}$, where the minus sign means that $+1.6 \times 10^3 \text{ J}$ of work is done on the gas.

(b) Because the temperature at the beginning and at the end of process BDA is the same, there is no change in internal energy: $\Delta U = 0$. From the first law of thermodynamics we have

$$0 = \Delta U = Q - W,$$

so

$$Q = W = -1.6 \times 10^3 \text{ J}.$$

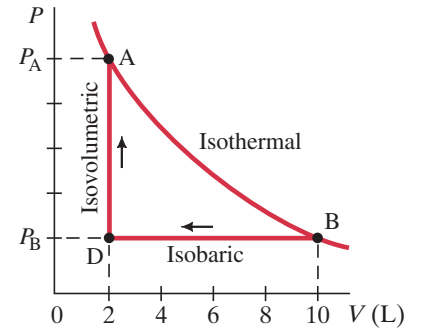Because Q is negative, 1600 J of heat flows out of the gas for the whole process, BDA.

FIGURE 15–8 Example 15–4.

EXERCISE C In Example 15–4, if the heat lost from the gas in the process BD is $8.4 \times 10^3 \text{ J}$, what is the change in internal energy of the gas during process BD?

EXAMPLE 15–5 **Work done in an engine.** In an engine, 0.25 mol of an ideal monatomic gas in the cylinder expands rapidly and adiabatically against the piston. In the process, the temperature of the gas drops from 1150 K to 400 K. How much work does the gas do?

APPROACH We take the gas as our system (the piston is part of the surroundings). The pressure is not constant, so we can't use Eq. 15–3 ($W = P\,\Delta V$). Instead, we can use the first law of thermodynamics to find W because we can determine ΔU (from ΔT) and $Q = 0$ (the process is adiabatic).

SOLUTION We determine ΔU from Eq. 14–1 for the internal energy of an ideal monatomic gas, using subscripts f and i for final and initial states:

$$\Delta U = U_f - U_i = \tfrac{3}{2}nR(T_f - T_i)$$
$$= \tfrac{3}{2}(0.25 \text{ mol})(8.314 \text{ J/mol}\cdot\text{K})(400 \text{ K} - 1150 \text{ K})$$
$$= -2300 \text{ J}.$$

Then, from the first law of thermodynamics, Eq. 15–1, the work done by the gas is

$$W = Q - \Delta U = 0 - (-2300 \text{ J}) = 2300 \text{ J}.$$

EXAMPLE 15–6 ΔU **for boiling water to steam.** Determine the change in internal energy of 1.00 liter of water (mass 1.00 kg) at 100°C when it is fully boiled from liquid to gas, which results in 1671 liters of steam at 100°C. Assume the process is done at atmospheric pressure.

APPROACH Our system is the water. The heat required here does not result in a temperature change; rather, a change in phase occurs. We can determine the heat Q required using the latent heat of water, as in Section 14–5. Work too will be done: $W = P\,\Delta V$. The first law of thermodynamics will then give us ΔU.

SOLUTION The latent heat of vaporization of water (Table 14–3) is $L_V = 22.6 \times 10^5$ J/kg. So the heat input required for this process is (Eq. 14–4)

$$Q = mL = (1.00\,\text{kg})(22.6 \times 10^5\,\text{J/kg}) = 22.6 \times 10^5\,\text{J}.$$

The work done by the water is (Eq. 15–3 since P is constant)

$$W = P\,\Delta V = (1.01 \times 10^5\,\text{N/m}^2)\big[(1671 \times 10^{-3}\,\text{m}^3) - (1 \times 10^{-3}\,\text{m}^3)\big]$$
$$= 1.69 \times 10^5\,\text{J},$$

where we used $1\,\text{atm} = 1.01 \times 10^5\,\text{N/m}^2$ and $1\,\text{L} = 10^3\,\text{cm}^3 = 10^{-3}\,\text{m}^3$. Then

$$\Delta U = Q - W = (22.6 \times 10^5\,\text{J}) - (1.7 \times 10^5\,\text{J}) = 20.9 \times 10^5\,\text{J}.$$

NOTE Most of the heat added goes to increasing the internal energy of the water (increasing molecular energy to overcome the attraction that held the molecules close together in the liquid state). Only a small part ($< 10\%$) goes into doing work.

NOTE Equation 14–1, $U = \frac{3}{2}nRT$, would tell us that $\Delta U = 0$ here because $\Delta T = 0$. Yet we determined that $\Delta U = 21 \times 10^5$ J. What is wrong? Equation 14–1 applies only to an ideal monatomic gas, not to liquid water.

*15–3 Human Metabolism and the First Law

Human beings and other animals do work. Work is done when a person walks or runs, or lifts a heavy object. Work requires energy. Energy is also needed for growth—to make new cells, and to replace old cells that have died. A great many energy-transforming processes occur within an organism, and they are referred to as *metabolism*.

We can apply the first law of thermodynamics,

$$\Delta U = Q - W,$$

FIGURE 15–9 Bike rider getting an input of energy.

to an organism: say, the human body. Work W is done by the body in its various activities; if this is not to result in a decrease in the body's internal energy (and temperature), energy must somehow be added to compensate. The body's internal energy is not maintained by a flow of heat Q into the body, however. Normally, the body is at a higher temperature than its surroundings, so heat usually flows *out* of the body. Even on a very hot day when heat is absorbed, the body has no way of utilizing this heat to support its vital processes. What then is the source of energy that allows us to do work? It is the internal energy (chemical potential energy) stored in foods (Fig. 15–9). In a closed system, the internal energy changes only as a result of heat flow or work done. In an open system, such as a human, internal energy itself can flow into or out of the system. When we eat food, we are bringing internal energy into our bodies directly, which thus increases the total internal energy U in our bodies. This energy eventually goes into work and heat flow from the body according to the first law.

The metabolic rate is the rate at which internal energy is transformed within the body. It is usually specified in kcal/h or in watts. Typical metabolic rates for a variety of human activities are given in Table 15–2 (top of next page) for an "average" 65-kg adult.

EXAMPLE 15–7 **Energy transformation in the body.** How much energy is transformed in 24 h by a 65-kg person who spends 8.0 h sleeping, 1.0 h at moderate physical labor, 4.0 h in light activity, and 11.0 h working at a desk or relaxing?

APPROACH The energy transformed during each activity equals the metabolic rate (Table 15–2) multiplied by the time.

SOLUTION Table 15–2 gives the metabolic rate in watts (J/s). Since there are 3600 s in an hour, the total energy transformed is

$$\left[\begin{array}{l}(8.0\,\text{h})(70\,\text{J/s}) + (1.0\,\text{h})(460\,\text{J/s}) \\ + (4.0\,\text{h})(230\,\text{J/s}) + (11.0\,\text{h})(115\,\text{J/s})\end{array}\right](3600\,\text{s/h}) = 1.15 \times 10^7\,\text{J}.$$

NOTE Since $4.186 \times 10^3\,\text{J} = 1\,\text{kcal}$, this is equivalent to 2800 kcal; a food intake of 2800 Cal would compensate for this energy output. A 65-kg person who wanted to lose weight would have to eat less than 2800 Cal a day, or increase his or her level of activity. Exercise beats *any* diet technique.

TABLE 15–2 Metabolic Rates
(65-kg human)

Activity	Metabolic Rate (approximate)	
	kcal/h	watts
Sleeping	60	70
Sitting upright	100	115
Light activity (eating, dressing, household chores)	200	230
Moderate work (tennis, walking)	400	460
Running (15 km/h)	1000	1150
Bicycling (race)	1100	1270

15–4 The Second Law of Thermodynamics—Introduction

The first law of thermodynamics states that energy is conserved. There are, however, many processes we can imagine that conserve energy but are not observed to occur in nature. For example, when a hot object is placed in contact with a cold object, heat flows from the hotter one to the colder one, never spontaneously from colder to hotter. If heat were to leave the colder object and pass to the hotter one, energy could still be conserved. Yet it does not happen spontaneously.[†] As a second example, consider what happens when you drop a rock and it hits the ground. The initial potential energy of the rock changes to kinetic energy as the rock falls. When the rock hits the ground, this energy in turn is transformed into internal energy of the rock and the ground in the vicinity of the impact; the molecules move faster and the temperature rises slightly. But have you seen the reverse happen—a rock at rest on the ground suddenly rise up in the air because the thermal energy of molecules is transformed into kinetic energy of the rock as a whole? Energy could be conserved in this process, yet we never see it happen.

There are many other examples of processes that occur in nature but whose reverse does not. Here are two more. (1) If you put a layer of salt in a jar and cover it with a layer of similar-sized grains of pepper, when you shake it you get a thorough mixture. But no matter how long you shake it, the mixture does not separate into two layers again. (2) Coffee cups and glasses break spontaneously if you drop them. But they do not go back together spontaneously (Fig. 15–10).

The first law of thermodynamics (conservation of energy) would not be violated if any of these processes occurred in reverse. To explain this lack of reversibility, scientists in the latter half of the nineteenth century formulated a new principle known as the second law of thermodynamics.

[†]By spontaneously, we mean by itself without input of work of some sort. (A refrigerator does move heat from a cold environment to a warmer one, but only because its motor does work—Section 15–6.)

(a) Initial state. (b) Later: cup reassembles and rises up. (c) Later still: cup lands on table.

FIGURE 15–10 Have you ever observed this process, a broken cup spontaneously reassembling and rising up onto a table? This process could conserve energy. But it never happens.

The **second law of thermodynamics** is a statement about which processes occur in nature and which do not. It can be stated in a variety of ways, all of which are equivalent. One statement, due to R. J. E. Clausius (1822–1888), is that

heat can flow spontaneously from a hot object to a cold object; heat will not flow spontaneously from a cold object to a hot object.

Since this statement applies to one particular process, it is not obvious how it applies to other processes. A more general statement is needed that will include other possible processes in a more obvious way.

The development of a general statement of the second law of thermodynamics was based partly on the study of heat engines. A **heat engine** is any device that changes thermal energy into mechanical work, such as a steam engine or an automobile engine. We now examine heat engines, both from a practical point of view and to show their importance in developing the second law of thermodynamics.

15–5 Heat Engines

It is easy to produce thermal energy by doing work—for example, by simply rubbing your hands together briskly, or indeed by any frictional process. But to get work from thermal energy is more difficult, and a practical device to do so was invented only about 1700 with the development of the steam engine.

The basic idea behind any heat engine is that mechanical energy can be obtained from thermal energy only when heat is allowed to flow from a high temperature to a low temperature. In the process, some of the heat can then be transformed to mechanical work, as diagrammed schematically in Fig. 15–11. Useful heat engines run in a repeating *cycle*: that is, the system returns repeatedly to its starting point, and thus can run continuously. In each cycle the change in internal energy of the system is $\Delta U = 0$ because it returns to the starting state. Thus a heat input Q_H at a high temperature T_H is partly transformed into work W and partly exhausted as heat Q_L at a lower temperature T_L (Fig. 15–11). By conservation of energy, $Q_H = W + Q_L$. The high and low temperatures, T_H and T_L, are called the **operating temperatures** of the engine. Note carefully that we are now using a new (and intuitive) sign convention for heat engines: we take Q_H, Q_L, and W as always positive. The direction of each energy transfer is shown by the arrow on the applicable diagram, such as Fig. 15–11.

FIGURE 15–11 Schematic diagram of energy transfers for a heat engine.
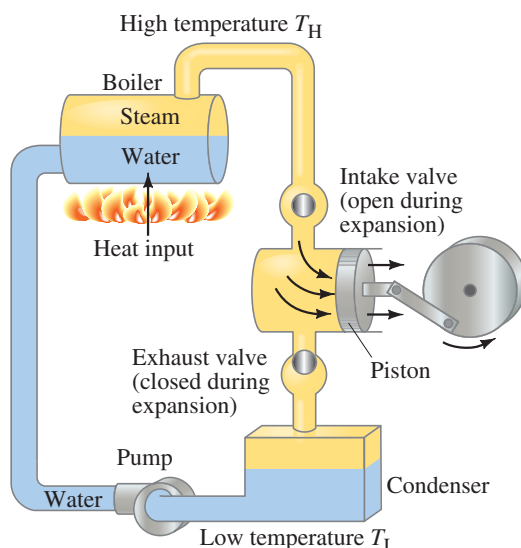
🏃 **PHYSICS APPLIED**
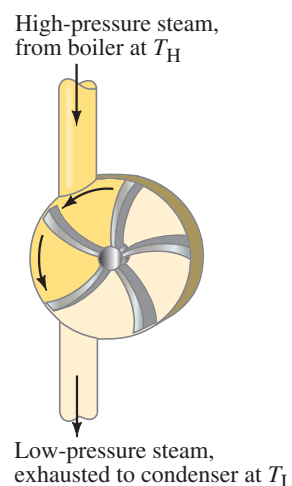*Engines*

Steam Engine and Internal Combustion Engine

The operation of a steam engine is shown in Fig. 15–12. Steam engines are of two main types, each using steam heated by combustion of coal, oil, or gas, or by nuclear energy.

**FIGURE 15–12** Steam engines.

(a) Reciprocating type

(b) Turbine (boiler and condenser not shown)

In a reciprocating engine, Fig. 15–12a, the heated steam passes through the intake valve and expands against a piston, forcing it to move. As the piston returns to its original position, it forces the gases out the exhaust valve which opens. A steam turbine, Fig. 15–12b, is very similar except that the reciprocating piston is replaced by a rotating turbine that resembles a paddlewheel with many sets of blades. Most of our electricity today is generated using steam turbines.[†] The material that is heated and cooled, steam in this case, is called the **working substance**. In an old-time steam engine (see page 412), the high temperature is obtained by burning coal, oil, or other fuel to heat the steam.

In an internal combustion engine (used in most automobiles), the high temperature is achieved by burning the gasoline–air mixture in the cylinder itself (ignited by the spark plug), as described in Fig. 15–13.
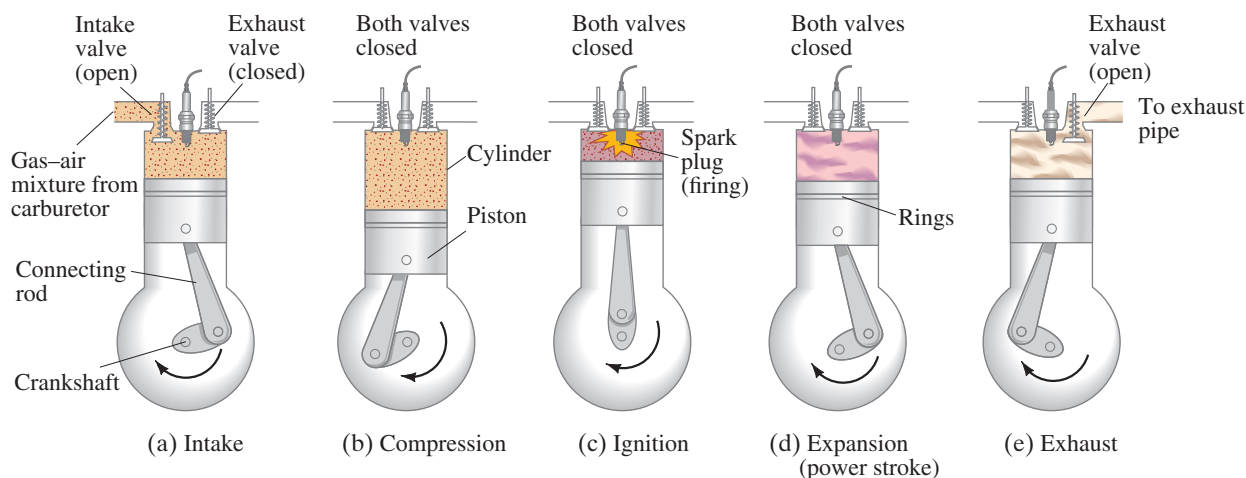

FIGURE 15–13 Four-stroke-cycle internal combustion engine: (a) the gasoline–air mixture flows into the cylinder as the piston moves down; (b) the piston moves upward and compresses the gas; (c) the brief instant when firing of the spark plug ignites the highly compressed gasoline–air mixture, raising it to a high temperature; (d) the gases, now at high temperature and pressure, expand against the piston in this, the power stroke; (e) the burned gases are pushed out to the exhaust pipe. When the piston reaches the top, the exhaust valve closes and the intake valve opens, and the whole cycle repeats. (a), (b), (d), and (e) are the four strokes of the cycle.

*Why a ΔT Is Needed to Drive a Heat Engine

To see why a *temperature difference* is required to run an engine, consider a steam engine. In the reciprocating engine, for example, suppose there were no condenser or pump (Fig. 15–12a), and that the steam was at the same temperature throughout the system. Then the pressure of the gas being exhausted would be the same as on intake. The work done by the gas *on* the piston when it expanded would equal the amount of work done *by* the piston to force the steam out the exhaust; hence, no net work would be done. In a real engine, the exhausted gas is cooled to a lower temperature and condensed so that the exhaust pressure is less than the intake pressure. Thus, the work the piston must do on the gas to expel it on the exhaust stroke is less than the work done by the gas on the piston during the intake. So a net amount of work can be obtained—but only if there is this difference of temperature. Similarly, in the gas turbine if the gas isn't cooled, the pressure on each side of the blades would be the same. By cooling the gas on the exhaust side, the pressure on the back side of the blade is less and hence the turbine turns.

[†]Even nuclear power plants utilize steam turbines; the nuclear fuel—uranium—serves as fuel to heat the steam.
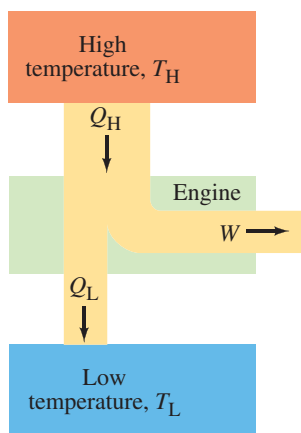
FIGURE 15–11 (Repeated.) Schematic diagram of energy transfers for a heat engine.

Efficiency

The **efficiency**, e, of any heat engine can be defined as the ratio of the work it does, W, to the heat input at the high temperature, Q_H (Fig. 15–11):

$$e = \frac{W}{Q_H}. \qquad \textbf{(15–4a)}$$

This is a sensible definition since W is the output (what you get from the engine), whereas Q_H is what you put in and pay for in burned fuel. Since energy is conserved, the heat input Q_H must equal the work done plus the heat that flows out at the low temperature (Q_L):

$$Q_H = W + Q_L.$$

Thus $W = Q_H - Q_L$, and the efficiency of an engine is

$$e = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H}$$

or

$$e = 1 - \frac{Q_L}{Q_H}. \qquad \textbf{(15–4b)}$$

To give the efficiency as a percent, we multiply Eq. 15–4 by 100. Note that e could be 1.0 (or 100%) only if Q_L were zero—that is, only if no heat were exhausted to the environment (which we will see shortly never happens).

EXAMPLE 15–8 | Car efficiency. An automobile engine has an efficiency of 20% and produces an average of 23,000 J of mechanical work per second during operation. (*a*) How much heat input is required, and (*b*) how much heat is discharged as waste heat from this engine, per second?

APPROACH We want to find the heat input Q_H as well as the heat output Q_L, given $W = 23,000$ J each second and an efficiency $e = 0.20$. We can use the definition of efficiency, Eq. 15–4 in its various forms, to find first Q_H and then Q_L.

SOLUTION (*a*) From Eq. 15–4a, $e = W/Q_H$, we solve for Q_H:

$$Q_H = \frac{W}{e} = \frac{23,000 \text{ J}}{0.20}$$
$$= 1.15 \times 10^5 \text{ J} = 115 \text{ kJ}.$$

The engine requires $115 \text{ kJ/s} = 115 \text{ kW}$ of heat input.

(*b*) Now we use Eq. 15–4b $(e = 1 - Q_L/Q_H)$ and solve for Q_L:

$$\frac{Q_L}{Q_H} = 1 - e$$

so

$$Q_L = (1 - e)Q_H = (0.80)115 \text{ kJ}$$
$$= 92 \text{ kJ}.$$

The engine discharges heat to the environment at a rate of $92 \text{ kJ/s} = 92 \text{ kW}$.

NOTE Of the 115 kJ that enters the engine per second, only 23 kJ (20%) does useful work whereas 92 kJ (80%) is wasted as heat output.

NOTE The problem was stated in terms of energy per unit time. We could just as well have stated it in terms of power, since $1 \text{ J/s} = 1$ watt.

Carnot Engine

To see how to increase efficiency, the French scientist Sadi Carnot (1796–1832) examined the characteristics of an ideal engine, now called a **Carnot engine**. No Carnot engine actually exists, but as a theoretical idea it played an important role in the development and understanding of the second law of thermodynamics.
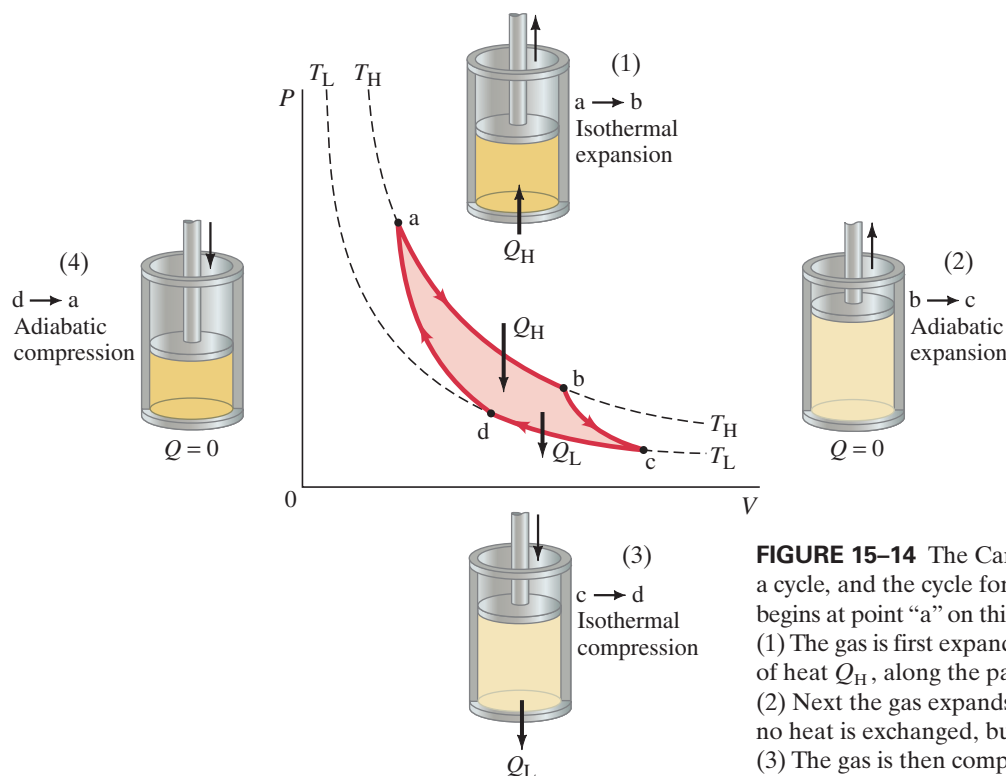
FIGURE 15–14 The Carnot cycle. Heat engines work in a cycle, and the cycle for the theoretical Carnot engine begins at point "a" on this *PV* diagram for an ideal gas. (1) The gas is first expanded isothermally, with the addition of heat Q_H, along the path "ab" at temperature T_H. (2) Next the gas expands adiabatically from "b" to "c"— no heat is exchanged, but the temperature drops to T_L. (3) The gas is then compressed at constant temperature T_L, path cd, and heat Q_L flows out. (4) Finally, the gas is compressed adiabatically, path da, back to its original state.

The idealized Carnot engine consisted of four processes done in a cycle, two of which are adiabatic ($Q = 0$) and two are isothermal ($\Delta T = 0$). This idealized cycle is shown in Fig. 15–14. Each of the processes was considered to be done **reversibly**. That is, each of the processes (say, during expansion of the gases against a piston) was done so slowly that the process could be considered a series of equilibrium states, and the whole process could be done in reverse with no change in the magnitude of work done or heat exchanged. A real process, on the other hand, would occur more quickly; there would be turbulence in the gas, friction would be present, and so on. Because of these factors, a real process cannot be done precisely in reverse—the turbulence would be different and the heat lost to friction would not reverse itself. Thus, real processes are **irreversible**.

The isothermal processes of a Carnot engine, where heats Q_H and Q_L are transferred, are assumed to be done at constant temperatures T_H and T_L. That is, the system is assumed to be in contact with idealized *heat reservoirs* (page 414) which are so large their temperatures don't change significantly when Q_H and Q_L are transferred.

Carnot showed that for an ideal reversible engine, the heats Q_H and Q_L are proportional to the operating temperatures T_H and T_L (in kelvins): $Q_H/Q_L = T_H/T_L$. So the efficiency can be written as

$$e_{\text{ideal}} = \frac{T_H - T_L}{T_H} = 1 - \frac{T_L}{T_H}. \qquad \left[\begin{array}{c} \text{Carnot (ideal)} \\ \text{efficiency} \end{array}\right] \quad \textbf{(15–5)}$$

Equation 15–5 expresses the fundamental upper limit to the efficiency of any heat engine. A higher efficiency would violate the second law of thermodynamics.[†] Real engines always have an efficiency lower than this because of losses due to friction and the like. Real engines that are well designed reach 60 to 80% of the Carnot efficiency.

[†]If an engine had a higher efficiency than Eq. 15–5, it could be used in conjunction with a Carnot engine that is made to work in reverse as a refrigerator. If W was the same for both, the net result would be a flow of heat at a low temperature to a high temperature without work being done. That would violate the Clausius statement of the second law.

EXAMPLE 15–9 **Steam engine efficiency.** A steam engine operates between 500°C and 270°C. What is the maximum possible efficiency of this engine?

APPROACH The maximum possible efficiency is the idealized Carnot efficiency, Eq. 15–5. We must use kelvin temperatures.

SOLUTION We first change the temperature to kelvins by adding 273 to the given Celsius temperatures: $T_H = 773$ K and $T_L = 543$ K. Then

$$e_{\text{ideal}} = 1 - \frac{543}{773} = 0.30.$$

To get the efficiency in percent, we multiply by 100. Thus, the maximum (or Carnot) efficiency is 30%. Realistically, an engine might attain 0.70 of this value, or 21%.

NOTE In this Example the exhaust temperature is still rather high, 270°C. Steam engines are often arranged in series so that the exhaust of one engine is used as intake by a second or third engine.

EXAMPLE 15–10 **A phony claim?** An engine manufacturer makes the following claims: An engine's heat input per second is 9.0 kJ at 435 K. The heat output per second is 4.0 kJ at 285 K. Do you believe these claims?

APPROACH The engine's efficiency can be calculated from the definition, Eq. 15–4. It must be less than the maximum possible, Eq. 15–5.
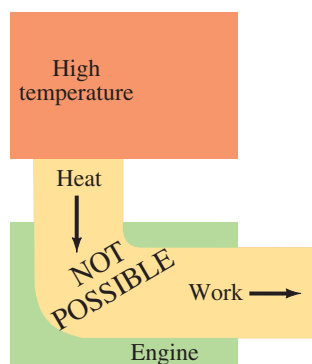
SOLUTION The claimed efficiency of the engine is (Eq. 15–4)

$$e = \frac{Q_H - Q_L}{Q_H}$$

$$= \frac{9.0\,\text{kJ} - 4.0\,\text{kJ}}{9.0\,\text{kJ}} = 0.56,$$

or 56%. The maximum possible efficiency is given by the Carnot efficiency, Eq. 15–5:

$$e_{\text{ideal}} = \frac{T_H - T_L}{T_H}$$

$$= \frac{435\,\text{K} - 285\,\text{K}}{435\,\text{K}} = 0.34,$$

or 34%. The manufacturer's claims violate the second law of thermodynamics and cannot be believed.

EXERCISE D A motor is running with an intake temperature $T_H = 400$ K and an exhaust temperature $T_L = 300$ K. Which of the following are *not* possible efficiencies for the engine? (*a*) 0.10; (*b*) 0.16; (*c*) 0.24; (*d*) 0.30; (*e*) 0.33.

We can see from Eq. 15–5 that at normal temperatures, a 100% efficient engine is not possible. Only if the exhaust temperature, T_L, were at absolute zero would 100% efficiency be reachable. But getting to absolute zero is a practical (as well as theoretical) impossibility. [Careful experimentation suggests that absolute zero is unattainable. This result is known as the **third law of thermodynamics**.] Because no engine can be 100% efficient, it can be stated that

> **no device is possible whose sole effect is to transform a given amount of heat completely into work.**

This is known as the **Kelvin-Planck statement of the second law of thermodynamics**. Figure 15–15 diagrams the ideal perfect heat engine, which can not exist.

FIGURE 15–15 Diagram of an impossible perfect heat engine in which all heat input is used to do work.

SECOND LAW OF THERMODYNAMICS
(Kelvin-Planck statement)

If the second law were not true, so that a perfect engine could be built, rather remarkable things could happen. For example, if the engine of a ship did not need a low-temperature reservoir to exhaust heat into, the ship could sail across the ocean using the vast resources of the internal energy of the ocean water. Indeed, we would have no fuel problems at all!

EXERCISE E Return to the Chapter-Opening Question, page 412, and answer it again now. Try to explain why you may have answered differently the first time.

15–6 Refrigerators, Air Conditioners, and Heat Pumps

The operating principle of refrigerators, air conditioners, and heat pumps is just the reverse of a heat engine. Each operates to transfer heat *out* of a cool environment into a warm environment. As diagrammed in Fig. 15–16, by doing work W, heat is taken from a low-temperature region, T_L (such as inside a refrigerator), and a greater amount of heat is exhausted at a high temperature, T_H (the room). Heat Q_L is removed from cooling coils *inside* the refrigerator and heat Q_H is given off by coils *outside* the rear of the refrigerator, Fig. 15–17. You can often feel this heated air coming out beneath the refrigerator. The work W is usually done by an electric motor which compresses a fluid, as illustrated in Fig. 15–17. (We assume Q_L, Q_H, and W are all positive, as in Section 15–5.)
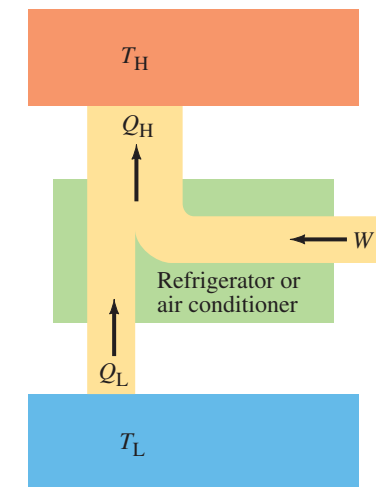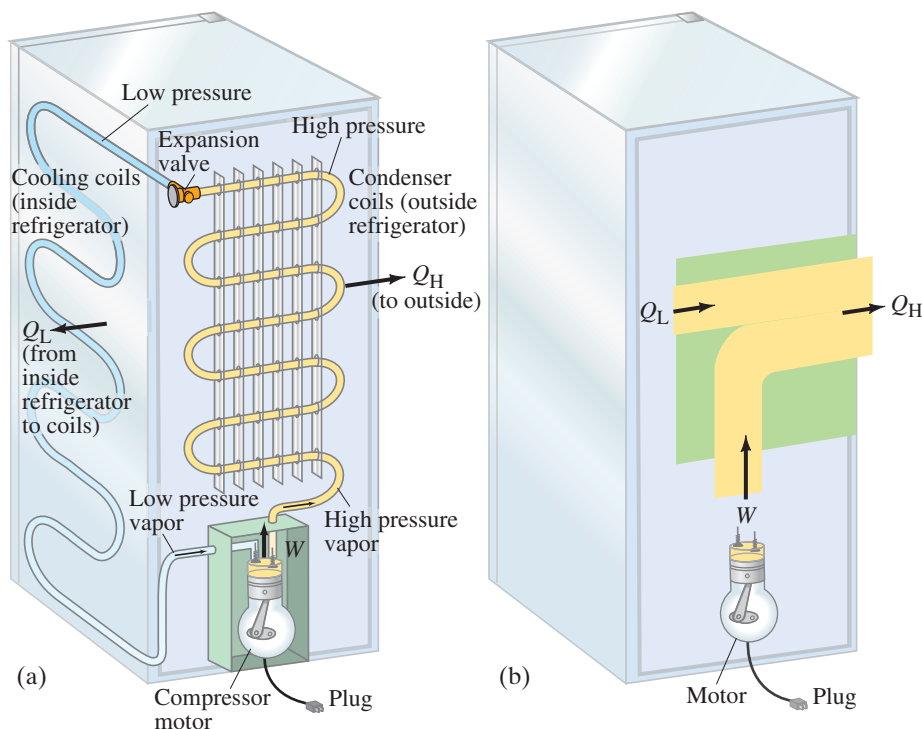
FIGURE 15–16 Schematic diagram of energy transfers for a refrigerator or air conditioner (AC).

(a)
Low pressure
Expansion valve
High pressure
Cooling coils (inside refrigerator)
Condenser coils (outside refrigerator)
Q_H (to outside)
Q_L (from inside refrigerator to coils)
Low pressure vapor
High pressure vapor
W
Compressor motor
Plug

(b)
Q_L
Q_H
W
Motor
Plug

FIGURE 15–17 (a) Typical refrigerator system. The electric compressor motor forces a gas at high pressure through a heat exchanger (condenser) on the rear *outside* wall of the refrigerator, where Q_H is given off and the gas cools to become liquid. The liquid passes from a high-pressure region, via a valve, to low-pressure tubes on the *inside* walls of the refrigerator; the liquid evaporates at this lower pressure and thus absorbs heat (Q_L) from the inside of the refrigerator. The fluid returns to the compressor, where the cycle begins again. (b) Schematic diagram, like Fig. 15–16.

A perfect **refrigerator**—one in which no work is required to take heat from the low-temperature region to the high-temperature region—is not possible. This is the **Clausius statement of the second law of thermodynamics**, already mentioned in Section 15–4: it can be stated formally as

> **no device is possible whose sole effect is to transfer heat from one system at a temperature T_L into a second system at a higher temperature T_H.**

To make heat flow from a low-temperature object (or system) to one at a higher temperature, work must be done. Thus, *there can be no perfect refrigerator*.

PHYSICS APPLIED
Refrigerator

SECOND LAW OF THERMODYNAMICS
(Clausius statement)
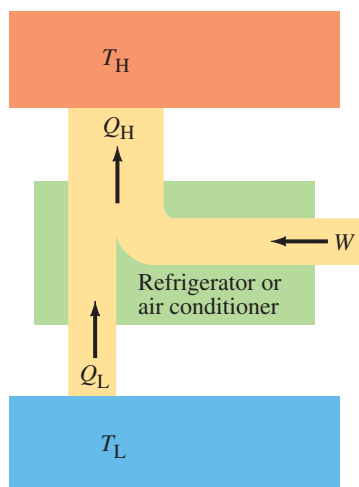
FIGURE 15–16 (Repeated.) Schematic diagram of energy transfers for a refrigerator or air conditioner (AC).

The **coefficient of performance** (COP) of a refrigerator is defined as the heat Q_L removed from the low-temperature area (inside a refrigerator) divided by the work W done to remove the heat (Fig. 15–16):

$$\text{COP} = \frac{Q_L}{W}. \qquad \left[\begin{array}{l}\text{refrigerator and}\\\text{air conditioner}\end{array}\right] \quad \textbf{(15–6a)}$$

We use Q_L because it is the heat removed from inside that matters from a practical point of view. This makes sense because the more heat Q_L that can be removed from inside the refrigerator for a given amount of work, the better (more efficient) the refrigerator is. Energy is conserved, so from the first law of thermodynamics we can write $Q_L + W = Q_H$, or $W = Q_H - Q_L$ (see Fig. 15–16). Then Eq. 15–6a becomes

$$\text{COP} = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L}. \qquad \left[\begin{array}{l}\text{refrigerator and}\\\text{air conditioner}\end{array}\right] \quad \textbf{(15–6b)}$$

For an ideal refrigerator (not a perfect one, which is impossible), the best we could do would be

$$\text{COP}_{\text{ideal}} = \frac{T_L}{T_H - T_L}, \qquad \left[\begin{array}{l}\text{refrigerator and}\\\text{air conditioner}\end{array}\right] \quad \textbf{(15–6c)}$$

analagous to an ideal (Carnot) engine (Eq. 15–5).

An **air conditioner** works very much like a refrigerator, although the actual construction details are different: an air conditioner takes heat Q_L from inside a room or building at a low temperature, and deposits heat Q_H outside to the environment at a higher temperature. Equations 15–6 also describe the coefficient of performance for an air conditioner.

EXAMPLE 15–11 Making ice. A freezer has a COP of 2.8 and uses 200 watts of power. How long would it take to freeze an ice-cube tray that contains 600 g of water at 0°C?

APPROACH In Eq. 15–6b, Q_L is the heat that must be transferred out of the water so it will become ice. To determine Q_L, we use the latent heat of fusion L of water and Eq. 14–4, $Q = mL$.

SOLUTION From Table 14–3, $L = 333$ kJ/kg for water. Hence

$$Q_L = mL = (0.600\text{ kg})(3.33 \times 10^5\text{ J/kg}) = 2.0 \times 10^5\text{ J}$$

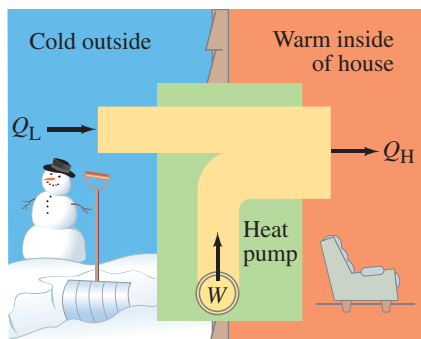is the total energy that needs to be removed from the water. The freezer does work at the rate of 200 watts = 200 J/s = W/t, which is the work W it can do in t seconds. We solve for t: $t = W/(200\text{ J/s})$. For W, we can also use Eq. 15–6a: $W = Q_L/\text{COP}$. Thus

$$t = \frac{W}{200\text{ J/s}} = \frac{Q_L/\text{COP}}{200\text{ J/s}}$$
$$= \frac{2.0 \times 10^5\text{ J}}{(2.8)(200\text{ J/s})} = 360\text{ s},$$

or about 6 min.

FIGURE 15–18 A heat pump uses an electric motor to "pump" heat from the cold outside to the warm inside of a house.

Heat naturally flows from high temperature to low temperature. Refrigerators and air conditioners do work to accomplish the opposite: to make heat flow from cold to hot. We might say they "pump" heat from cold areas to hotter areas, against the natural tendency of heat to flow from hot to cold, just as water can be pumped uphill, against the natural tendency to flow downhill. The term **heat pump** is usually reserved for a device that can heat a house in winter by using an electric motor that does work W to take heat Q_L from the outside at low temperature and delivers heat Q_H to the warmer inside of the house; see Fig. 15–18.

As in a refrigerator, there is an indoor and an outdoor heat exchanger (coils of the refrigerator) and an electric compressor motor. The operating principle is like that for a refrigerator or air conditioner; but the objective of a heat pump is to heat (deliver Q_H), rather than to cool (remove Q_L). Thus, the coefficient of performance of a heat pump is defined differently than for an air conditioner because it is the heat Q_H delivered to the inside of the house that is important now:

$$\text{COP} = \frac{Q_H}{W}. \qquad \text{[heat pump]} \quad \textbf{(15–7)}$$

The COP is necessarily greater than 1. Typical heat pumps today have COP $\approx$ 2.5 to 3. Most heat pumps can be "turned around" and used as air conditioners in the summer.

EXAMPLE 15–12 **Heat pump.** A heat pump has a coefficient of performance of 3.0 and is rated to do work at 1500 watts. (*a*) How much heat can it add to a room per second? (*b*) If the heat pump were turned around to act as an air conditioner in the summer, what would you expect its coefficient of performance to be, assuming all else stays the same?

APPROACH We use the definitions of coefficient of performance, which are different for the two devices in (*a*) and (*b*).

SOLUTION (*a*) We use Eq. 15–7 for the heat pump, and, since our device does 1500 J of work per second, it can pour heat into the room at a rate of

$$Q_H = \text{COP} \times W = 3.0 \times 1500 \text{ J} = 4500 \text{ J}$$

per second, or at a rate of 4500 W. [≈ 4 Btu/s.]

(*b*) If our device is turned around in summer, it can take heat Q_L from inside the house, doing 1500 J of work per second to then dump $Q_H = 4500$ J per second to the hot outside. Energy is conserved, so $Q_L + W = Q_H$ (see Fig. 15–18, but reverse the inside and outside of the house). Then

$$Q_L = Q_H - W = 4500 \text{ J} - 1500 \text{ J} = 3000 \text{ J}.$$

The coefficient of performance as an air conditioner would thus be (Eq. 15–6a)

$$\text{COP} = \frac{Q_L}{W} = \frac{3000 \text{ J}}{1500 \text{ J}} = 2.0.$$

NOTE The coefficients of performance are defined differently for heat pumps and air conditioners.

EXERCISE F The heat pump of Example 15–12 uses 1500 W of electric power to deliver 4500 W of heat. Does this sound like we're getting something for nothing? (*a*) Explain why we aren't. (*b*) Compare to the refrigerator of Example 15–11: the motor uses 200 W to extract how much heat?

A good heat pump can sometimes be a money saver and an energy saver, depending on the cost of the unit and installation, etc. Compare, for example, our heat pump in Example 15–12 to, say, a 1500-W electric heater. We plug the heater into the wall, it draws 1500 W of electricity, and it delivers 1500 W of heat to the room. Our heat pump when plugged into the wall also draws 1500 W of electricity (which is what we pay for), but it delivers 4500 W of heat!

*SEER Rating

Cooling devices such as refrigerators and air conditioners are often given a rating known as SEER (Seasonal Energy Efficiency Ratio), which is defined as

$$\text{SEER} = \frac{(\text{heat removed in Btu})}{(\text{electrical input in watt-hours})},$$

as measured by averaging over varying (seasonal) conditions. The definition of the SEER is basically the same as the COP except for the (unfortunate) mixed units. Given that 1 Btu = 1056 J (see Section 14–1 and Problem 5 in Chapter 14), then a SEER = 1 is a COP equal to $(1 \text{ Btu}/1 \text{ W·h}) = (1056 \text{ J})/(1 \text{ J/s} \times 3600 \text{ s}) = 0.29$. A COP = 1 is a SEER = 1/0.29 = 3.4.

15–7 Entropy and the Second Law of Thermodynamics

Thus far we have stated the second law of thermodynamics for specific situations. What we really need is a general statement of the second law of thermodynamics that will cover all situations, including processes discussed earlier in this Chapter that are not observed in nature even though they would not violate the first law of thermodynamics. It was not until the latter half of the nineteenth century that the second law of thermodynamics was finally stated in a general way—namely, in terms of a quantity called **entropy**, introduced by Clausius in the 1860s. Entropy, unlike heat, is a function of the state of a system. That is, a system in a given state has a temperature, a volume, a pressure, a mass, and also has a particular value of entropy. In the next Section, we will see that entropy can be interpreted as a measure of the order or disorder of a system.

When we deal with entropy—as with potential energy—it is the *change* in entropy during a process that is important, not the absolute amount. According to Clausius, the change in entropy S of a system, when an amount of heat Q is *added* to it by a reversible[†] process at constant temperature, is given by

$$\Delta S = \frac{Q}{T}, \tag{15–8}$$

where T is the kelvin temperature. (If heat is lost, Q is negative in this equation, as per our original sign conventions on page 413.)

EXAMPLE 15–13 **Entropy change in melting.** An ice cube of mass 56 g is taken from a storage compartment at 0°C and placed in a paper cup. After a few minutes, exactly half of the mass of the ice cube has melted, becoming water at 0°C. Find the change in entropy of the ice/water.

APPROACH We consider the 56 g of water, initially in the form of ice, as our system. To determine the entropy change, we first must find the heat needed to melt the ice, which we do using the latent heat of fusion of water, $L = 333\ \text{kJ/kg}$ (Section 14–5). The heat Q required comes from the surroundings.

SOLUTION The heat required to melt 28 g of ice (half of the 56-g ice cube) is
$$Q = mL = (0.028\ \text{kg})(333\ \text{kJ/kg}) = 9.3\ \text{kJ}.$$
The temperature remains constant in our process, so we can find the change in entropy from Eq. 15–8:
$$\Delta S = \frac{Q}{T} = \frac{9.3\ \text{kJ}}{273\ \text{K}} = 34\ \text{J/K}.$$

NOTE The change in entropy of the surroundings (cup, air) has not been computed.

The temperature in Example 15–13 was constant, so the calculation was short. If the temperature varies during a process, a summation of the heat flow over the changing temperature can often be calculated using calculus or a computer. However, if the temperature change is not too great, a reasonable approximation can be made using the average value of the temperature, as indicated in the next Example.

EXAMPLE 15–14 **ESTIMATE** **Entropy change when water samples are mixed.** A sample of 50.0 kg of water at 20.00°C is mixed with 50.0 kg of water at 24.00°C. Estimate the change in entropy.

APPROACH The final temperature of the mixture will be 22.00°C, since we started with equal amounts of water. We use the specific heat of water and the methods of calorimetry (Sections 14–3 and 14–4) to determine the heat transferred. Then we use the average temperature of each sample of water to estimate the entropy change $(\Delta Q/T)$.

[†]Real processes are irreversible. Because entropy is a state variable, the change in entropy ΔS for an irreversible process can be determined by calculating ΔS for a reversible process between the same two states.

SOLUTION A quantity of heat,

$$Q = mc\,\Delta T = (50.0\,\text{kg})(4186\,\text{J/kg}\cdot\text{C}°)(2.00\,\text{C}°) = 4.186 \times 10^5\,\text{J},$$

flows out of the hot water as it cools down from 24°C to 22°C, and this heat flows into the cold water as it warms from 20°C to 22°C. The total change in entropy, ΔS, will be the sum of the changes in entropy of the hot water, ΔS_H, and that of the cold water, ΔS_C:

$$\Delta S = \Delta S_\text{H} + \Delta S_\text{C}.$$

We estimate entropy changes by writing $\Delta S = Q/T_\text{av}$, where T_av is an "average" temperature for each process, which ought to give a reasonable estimate since the temperature change is small. For the hot water we use an average temperature of 23°C (296 K), and for the cold water an average temperature of 21°C (294 K). Thus

$$\Delta S_\text{H} \approx -\frac{4.186 \times 10^5\,\text{J}}{296\,\text{K}} = -1414\,\text{J/K}$$

which is negative because this heat flows out (sign conventions, page 413), whereas heat is added to the cold water:

$$\Delta S_\text{C} \approx \frac{4.186 \times 10^5\,\text{J}}{294\,\text{K}} = 1424\,\text{J/K}.$$

The entropy of the hot water (S_H) decreases because heat flows out of the hot water. But the entropy of the cold water (S_C) increases by a greater amount. The total change in entropy is

$$\Delta S = \Delta S_\text{H} + \Delta S_\text{C} \approx -1414\,\text{J/K} + 1424\,\text{J/K} \approx 10\,\text{J/K}.$$

In Example 15–14, we saw that although the entropy of one part of the system decreased, the entropy of the other part increased by a greater amount; the net change in entropy of the whole system was positive. This result, which we have calculated for a specific case in Example 15–14, has been found to hold in all other cases tested. That is, the total entropy of an isolated system is found to increase in all natural processes. The second law of thermodynamics can be stated in terms of entropy as follows: *The entropy of an isolated system never decreases. It can only stay the same or increase*. Entropy can remain the same only for an idealized (reversible) process. For any real process, the change in entropy ΔS is greater than zero:

$$\Delta S > 0. \qquad\qquad \text{[real process]} \quad \textbf{(15–9)}$$

If the system is not isolated, then the change in entropy of the system, ΔS_sys, plus the change in entropy of the environment, ΔS_env, must be greater than or equal to zero:

$$\Delta S = \Delta S_\text{sys} + \Delta S_\text{env} \geq 0. \qquad\qquad \textbf{(15–10)}$$

Only idealized processes can have $\Delta S = 0$. Real processes always have $\Delta S > 0$. This, then, is the *general statement of the second law of thermodynamics*:

the total entropy of any system plus that of its environment increases as a result of any natural process.

SECOND LAW OF THERMODYNAMICS (general statement)

Although the entropy of one part of the universe may decrease in any natural process (see Example 15–14), the entropy of some other part of the universe always increases by a greater amount, so the total entropy always increases.

Now that we finally have a quantitative general statement of the second law of thermodynamics, we can see that it is an unusual law. It differs considerably from other laws of physics, which are typically equalities (such as $F = ma$) or conservation laws (such as for energy and momentum). The second law of thermodynamics introduces a new quantity, the entropy S, but does not tell us it is conserved. Quite the opposite. Entropy is *not* conserved in natural processes. Entropy always increases in time for real processes.

15–8 Order to Disorder

The concept of entropy, as we have discussed it so far, may seem rather abstract. But we can relate it to the more ordinary concepts of *order* and *disorder*. In fact, the entropy of a system can be considered a *measure of the disorder of the system*. Then the second law of thermodynamics can be stated simply as:

natural processes tend to move toward a state of greater disorder.

SECOND LAW OF THERMODYNAMICS
(general statement)

Exactly what we mean by **disorder** may not always be clear, so we now consider a few examples. Some of these will show us how this very general statement of the second law applies beyond what we usually consider as thermodynamics.

Let us look at the simple processes mentioned in Section 15–4. First, a jar containing separate layers of salt and pepper is more orderly than a jar in which the salt and pepper are all mixed up. Shaking a jar containing separate layers results in a mixture, and no amount of shaking brings the orderly layers back again. The natural process is from a state of relative order (layers) to one of relative disorder (a mixture), not the reverse. That is, disorder increases. Second, a solid coffee cup is a more "orderly" and useful object than the pieces of a broken cup. Cups break when they fall, but they do not spontaneously mend themselves (as faked in Fig. 15–10). Again, the normal course of events is an increase of disorder.

Let us consider some processes for which we have actually calculated the entropy change, and see that an increase in entropy results in an increase in disorder (or vice versa). When ice melts to water at $0°C$, the entropy of the water increases (Example 15–13). Intuitively, we can think of solid water, ice, as being more ordered than the less orderly fluid state which can flow all over the place. This change from order to disorder can be seen more clearly from the molecular point of view: the orderly arrangement of water molecules in an ice crystal has changed to the disorderly and somewhat random motion of the molecules in the fluid state.

When a hot substance is put in contact with a cold substance, heat flows from the high temperature to the low until the two substances reach the same intermediate temperature. Entropy increases, as we saw in Example 15–14. At the beginning of the process we can distinguish two classes of molecules: those with a high average kinetic energy (the hot object), and those with a low average kinetic energy (the cooler object). After the process in which heat flows, all the molecules are in one class with the same average kinetic energy; we no longer have the more orderly arrangement of molecules in two classes. Order has gone to disorder. Furthermore, the separate hot and cold objects could serve as the hot- and cold-temperature regions of a heat engine, and thus could be used to obtain useful work. But once the two objects are put in contact and reach the same temperature, no work can be obtained. Disorder has increased, because a system that has the ability to perform work must surely be considered to have a higher order than a system no longer able to do work.

When a stone falls to the ground, its macroscopic kinetic energy is transformed to thermal energy. (We noted earlier that the reverse never happens: a stone never absorbs thermal energy and rises into the air of its own accord.) This is another example of order changing to disorder. Thermal energy is associated with the disorderly random motion of molecules, but the molecules in the falling stone all have the same velocity downward in addition to their own random velocities. Thus, the more orderly kinetic energy of the stone as a whole (which could do useful work) is changed to disordered thermal energy when the stone strikes the ground. Disorder increases in this process, as it does in all processes that occur in nature.

Biological Development

PHYSICS APPLIED
Biological development

An interesting example of the increase in entropy relates to the biological development and growth of organisms. Clearly, a human being is a highly ordered organism. The development of an individual from a single cell to a grown person is a process of increasing order. Evolution too might be seen as an increase in order.

Do these processes violate the second law of thermodynamics? No, they do not. In the processes of growth and evolution, and even during the mature life of an individual, waste products are eliminated. These small molecules that remain as a result of metabolism are simple molecules without much order. Thus they represent relatively higher disorder or entropy. Indeed, the total entropy of the molecules cast aside by organisms during the processes of development and growth is greater than the decrease in entropy associated with the order of the growing individual or evolving species.

"Time's Arrow"

Another aspect of the second law of thermodynamics is that it tells us in which *direction* processes go. If you were to see a film being run backward, you would undoubtedly be able to tell that it *was* run backward. For you would see odd occurrences, such as a broken coffee cup rising from the floor and reassembling on a table, or a torn balloon suddenly becoming whole again and filled with air. We know these things don't happen in real life; they are processes in which order increases—or entropy decreases. They violate the second law of thermodynamics. When watching a movie (or imagining that time could go backward), we are tipped off to a reversal of time by observing whether entropy (and disorder) is increasing or decreasing. Hence, entropy has been called **time's arrow**, because it can tell us in which direction time is going.

15–9 Unavailability of Energy; Heat Death

In the process of heat conduction from a hot object to a cold one, we have seen that entropy increases and that order goes to disorder. The separate hot and cold objects could serve as the high- and low-temperature regions for a heat engine and thus could be used to obtain useful work. But after the two objects are put in contact with each other and reach the same uniform temperature, no work can be obtained from them. With regard to being able to do useful work, order has gone to disorder in this process.

The same can be said about a falling rock that comes to rest upon striking the ground. Before hitting the ground, all the kinetic energy of the rock could have been used to do useful work. But once the rock's mechanical kinetic energy becomes thermal energy, doing useful work is no longer possible.

Both these examples illustrate another important aspect of the second law of thermodynamics:

in any natural process, some energy becomes unavailable to do useful work.

In any process, no energy is ever lost (it is always conserved). Rather, energy becomes less useful—it can do less useful work. As time goes on, **energy is degraded**, in a sense. It goes from more orderly forms (such as mechanical) eventually to the least orderly form: internal, or thermal, energy. Entropy is a factor here because the amount of energy that becomes unavailable to do work is proportional to the change in entropy during any process.

A natural outcome of the degradation of energy is the prediction that as time goes on, the universe should approach a state of maximum disorder. Matter would become a uniform mixture, and heat would have flowed from high-temperature regions to low-temperature regions until the whole universe is at one temperature. No work could then be done. All the energy of the universe would have degraded to thermal energy. This prediction, called the **heat death** of the universe, has been much discussed, but it would lie *very* far in the future. It is a complicated subject, and some scientists question whether thermodynamics, as we now understand it, actually applies to the universe as a whole, which is at a much larger scale.[†]

[†]When a star, like our Sun, loses energy by radiation, it becomes *hotter* (not cooler). By losing energy, gravity is able to compress the gas of which the Sun is made—becoming smaller and denser means the Sun gets hotter. For astronomical objects, when heat flows from a hot object to a cooler object, the hot object gets hotter and the cool one cooler. That is, the temperature difference *increases*.

*15–10 Statistical Interpretation of Entropy and the Second Law

The ideas of entropy and disorder are made clearer with the use of a statistical or probabilistic analysis of the molecular state of a system. This statistical approach, which was first applied toward the end of the nineteenth century by Ludwig Boltzmann (1844–1906), makes a clear distinction between the "macrostate" and the "microstate" of a system. The **microstate** of a system would be specified by giving the position and velocity of every particle (or molecule). The **macrostate** of a system is specified by giving the far fewer macroscopic properties of the system—the temperature, pressure, number of moles, and so on. In reality, we can know only the macrostate of a system. There are generally far too many molecules in a system to be able to know the velocity and position of every one at a given moment. Nonetheless, we can hypothesize a great many different microstates that can correspond to the *same* macrostate.

Let us take a very simple example. Suppose you repeatedly shake four coins in your hand and drop them on a table. Specifying the *number* of heads and the number of tails that appear on a given throw is the *macrostate* of this system. Specifying *each coin* as being a head or a tail is the *microstate* of the system. In the following Table we see how many microstates correspond to each macrostate:

Macrostate	Possible Microstates (H = heads, T = tails)	Number of Microstates
4 heads	H H H H	1
3 heads, 1 tail	H H H T, H H T H, H T H H, T H H H	4
2 heads, 2 tails	H H T T, H T H T, T H H T, H T T H, T H T H, T T H H	6
1 head, 3 tails	T T T H, T T H T, T H T T, H T T T	4
4 tails	T T T T	1

⚠️ **CAUTION**

Careful use of probability

A basic assumption behind the statistical approach is that *each microstate is equally probable*. Thus the number of microstates that give the same macrostate corresponds to the relative probability of that macrostate occurring. The macrostate of two heads and two tails is the most probable one in our case of tossing four coins; out of the total of 16 possible microstates, six correspond to two heads and two tails, so the probability of throwing two heads and two tails is 6 out of 16, or 38%. The probability of throwing one head and three tails is 4 out of 16, or 25%. The probability of four heads is only 1 in 16, or 6%. If you threw the coins 16 times, you might not find that two heads and two tails appear exactly 6 times, or four tails exactly once. These are only probabilities or averages. But if you made 1600 throws, very nearly 38% of them would be two heads and two tails. The greater the number of tries, the closer the percentages are to the calculated probabilities.

EXERCISE G In the Table above, what is the probability that there will be at least two heads? (a) $\frac{1}{2}$; (b) $\frac{1}{16}$; (c) $\frac{1}{8}$; (d) $\frac{3}{8}$; (e) $\frac{11}{16}$.

If we toss more coins—say, 100 all at the same time—the relative probability of throwing all heads (or all tails) is greatly reduced. There is only one microstate corresponding to all heads. For 99 heads and 1 tail, there are 100 microstates because each of the coins could be the one tail. The relative probabilities for other macrostates are given in Table 15–3 (top of next page). About 1.3×10^{30} microstates are possible.[†] Thus the relative probability of finding all heads is about 1 in 10^{30}, an incredibly unlikely event! The probability of obtaining 50 heads and 50 tails (see Table 15–3) is $(1.0 \times 10^{29})/(1.3 \times 10^{30}) = 0.08$ or 8%. The probability of obtaining anything between 45 and 55 heads is about 70%.

[†]Each coin has two possibilities, heads or tails. Then the possible number of microstates is $2 \times 2 \times 2 \times \cdots = 2^{100} = 1.3 \times 10^{30}$ (using a calculator or logarithms).

TABLE 15–3 Probabilities of Various Macrostates for 100 Coin Tosses

Macrostate		Number of Microstates	Probability
Heads	Tails		
100	0	1	7.9×10^{-31}
99	1	1.0×10^2	7.9×10^{-29}
90	10	1.7×10^{13}	1.4×10^{-17}
80	20	5.4×10^{20}	4.2×10^{-10}
60	40	1.4×10^{28}	0.011
55	45	6.1×10^{28}	0.047
50	50	1.0×10^{29}	0.077
45	55	6.1×10^{28}	0.047
40	60	1.4×10^{28}	0.011
20	80	5.4×10^{20}	4.2×10^{-10}
10	90	1.7×10^{13}	1.4×10^{-17}
1	99	1.0×10^2	7.9×10^{-29}
0	100	1	7.9×10^{-31}

Thus we see that as the number of coins increases, the probability of obtaining the most orderly arrangement (all heads or all tails) becomes extremely unlikely. The least orderly arrangement (half heads, half tails) is the most probable, and the probability of being within, say, 5% of the most probable arrangement greatly increases as the number of coins increases. These same ideas can be applied to the molecules of a system. For example, the most probable state of a gas (say, the air in a room) is one in which the molecules take up the whole space and move about randomly; this corresponds to the Maxwellian distribution, Fig. 15–19a (and see Section 13–10). On the other hand, the very orderly arrangement of all the molecules located in one corner of the room and all moving with the same velocity (Fig. 15–19b) is extremely unlikely.

From these examples, we can see that probability is directly related to disorder and hence to entropy. That is, the most probable state is the one with greatest entropy, or greatest disorder and randomness. The processes we actually observe are those where the entropy increase is greatest.

In terms of probability, the second law of thermodynamics—which tells us that entropy increases in any process—reduces to the statement that **those processes occur which are most probable**.

There is an additional element, however. The second law in terms of probability does not *forbid* a decrease in entropy. Rather, it says the probability is extremely low. It is not impossible that salt and pepper could separate spontaneously into layers, or that a broken cup could mend itself (Fig. 15–10). It is even possible that a lake could freeze over on a hot summer day (that is, for heat to flow out of the cold lake into the warmer surroundings). But the probability for such events occurring is almost always miniscule. In our coin examples, we saw that increasing the number of coins from 4 to 100 drastically reduced the probability of large deviations from the average, or most probable, arrangement. In ordinary systems we are not dealing with only 100 molecules, but with extremely large numbers of molecules: in 1 mole alone there are 6×10^{23} molecules. Hence the probability of deviation far from the average is incredibly tiny. For example, it has been calculated that the probability that a stone resting on the ground could transform 1 cal of thermal energy into mechanical energy and rise up into the air is much less likely than the probability that a group of monkeys typing randomly would by chance produce the complete works of Shakespeare. Put another way, the probability is less than once in the entire age of the universe; this could be what "never" means.
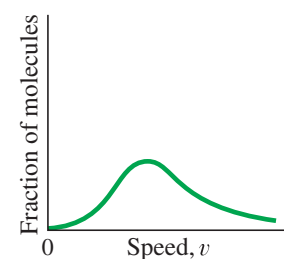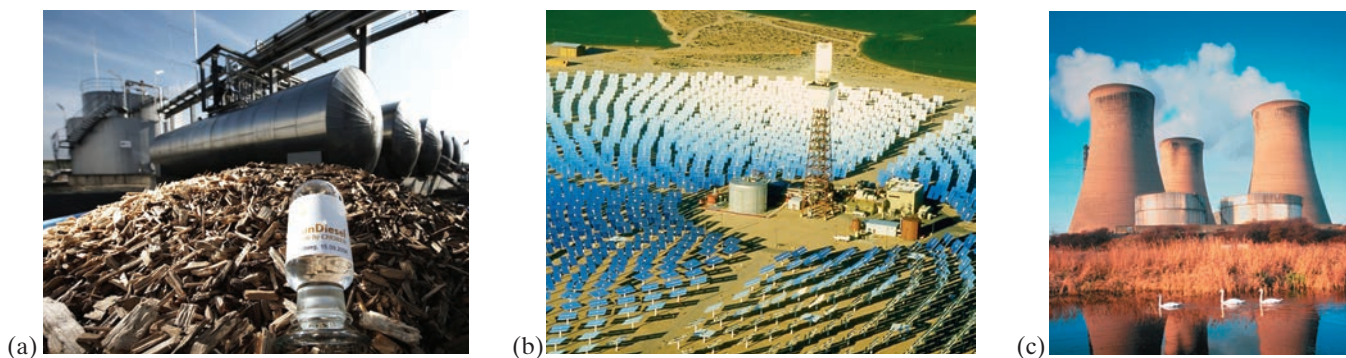

(a)
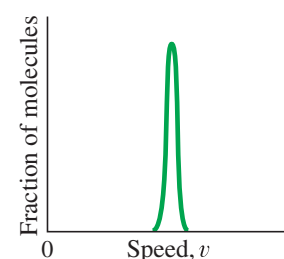
(b)

FIGURE 15–19 (a) Most probable distribution of molecular speeds in a gas (Maxwellian, or random). (b) Orderly, but highly unlikely, distribution of speeds in which all molecules have nearly the same speed.

FIGURE 15–20 (a) A fossil-fuel steam plant (this one uses forest waste products = biomass).
(b) An array of mirrors focuses sunlight on a boiler to produce steam at a solar energy installation.
(c) Large cooling towers at an electric generating plant.

FIGURE 15–21 Mechanical energy is transformed to electric energy with a turbine and generator.

Source of energy:
water, steam, wind

Electric generator

Turbine
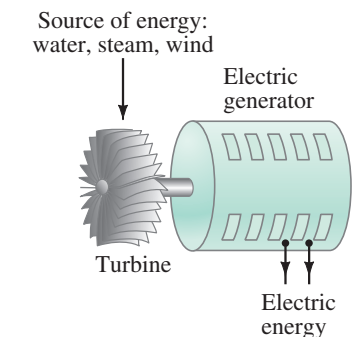
Electric energy

🏃 **PHYSICS APPLIED**
Heat engines and thermal pollution

*15–11 Thermal Pollution, Global Warming, and Energy Resources

Much of the energy we use in everyday life—from motor vehicles to most of the electricity produced by power plants—uses a heat engine. More than $\frac{2}{3}$ of the electric energy produced in the U.S. is generated at fossil-fuel steam plants (coal, oil, or gas—see Fig. 15–20a), and they make use of a heat engine (steam engines). In electric power plants, the steam drives the turbines and generators (Fig. 15–21) whose output is electric energy. The various means to turn the turbine are shown in Table 15–4, along with some of the advantages and disadvantages of each. Even nuclear power plants use a steam engine, run on nuclear fuel. Electricity produced by falling water at dams, by windmills, or by solar cells (Fig. 15–20b) does not involve a heat engine.

The heat output Q_L from every heat engine, from power plants to cars, is referred to as **thermal pollution** because this heat (Q_L) must be absorbed by the environment—such as by water from rivers or lakes, or by the air using large cooling towers (Fig. 15–20c). When water is the coolant, this heat raises the temperature of the water before returning it to its source, altering the natural ecology of aquatic life (largely because warmer water holds less oxygen). In the case of air cooling towers, the output heat Q_L raises the temperature of the atmosphere, which affects weather.

Air pollution—by which we mean the chemicals released in the burning of fossil fuels in cars, power plants, and industrial furnaces—gives rise to smog and other problems. Another issue is the buildup of CO_2 in the Earth's atmosphere due to the burning of fossil fuels; the carbon in them combines with O_2 of the air, forming CO_2. This CO_2 absorbs some of the infrared radiation that the Earth naturally emits (Section 14–8), and thus contributes to **global warming**. The **carbon footprint** of any activity (home appliances, steel production, manufacture of goods, transportation) refers to the negative impact on the environment due to the burning of fossil fuels which release CO_2 (and other noxious products) into the atmosphere, contributing to climate change. A carbon footprint can be expressed in kg or tons of carbon (in the CO_2). Limiting the burning of fossil fuels can help reduce these problems.

Thermal pollution, however, is unavoidable. Engineers can try to design and build engines that are more efficient, but they cannot surpass the Carnot efficiency and must live with T_L being at best the ambient temperature of water or air. The second law of thermodynamics tells us the limit imposed by nature. Even alternative energy sources like wind and solar cells can contribute to global warming (windmills slow down cooling winds, solar cells are "dark" and absorb more of the incident energy). What we can do, in light of the second law of thermodynamics, is use less energy and conserve our fuel resources. There is no other solution.

TABLE 15–4 Electric Energy Resources

Form of Electric Energy Production	% of Production (approx.)		Advantages	Disadvantages
	U.S.	World		
Fossil-fuel steam plants: burn coal, oil, or natural gas to boil water, producing high-pressure steam that turns a turbine of a generator (Figs. 15–12b, 15–21); uses heat engine.	72	66	We know how to build them; for now relatively inexpensive.	Air pollution; thermal pollution; limited efficiency; land devastation from extraction of raw materials (mining); global warming; accidents such as oil spills at sea; limited fuel supply (estimates range from a couple of decades to a few centuries).
Nuclear energy:				
Fission: nuclei of uranium or plutonium atoms split ("fission") with release of energy (Chapter 31) that heats steam; uses heat engine.	20	17	Normally almost no air pollution; less contribution to global warming; relatively inexpensive.	Thermal pollution; accidents can release damaging radioactivity; difficult disposal of radioactive by-products; possible diversion of nuclear material by terrorists; limited fuel supply.
Fusion: energy released when isotopes of hydrogen (or other small nuclei) combine or "fuse" (Chapter 31).	0	0	Relatively "clean"; vast fuel supply (hydrogen in water molecules in oceans); less contribution to global warming.	Not yet workable.
Hydroelectric: falling water turns turbines at the base of a dam.	7	16	No heat engine needed; no air, water, or thermal pollution; relatively inexpensive; high efficiency; dams can control flooding.	Reservoirs behind dams inundate scenic or inhabited land; dams block upstream migration of salmon and other fish for reproduction; few locations remain for new dams; drought.
Geothermal: natural steam from inside the Earth comes to the surface (hot springs, geysers, steam vents); or cold water passed down into contact with hot, dry rock is heated to steam.	<1	<1	No heat engine needed; little air pollution; good efficiency; relatively inexpensive and "clean."	Few appropriate sites; small production; mineral content of spent hot water can pollute.
Wind power: 3-kW to 5-MW windmills (vanes up to 50 m long) turn a generator.	≈1	<1	No heat engine; no air, water, or thermal pollution; relatively inexpensive.	Large array of big windmills might affect weather and be eyesores; slows down cooling winds; hazardous to migratory birds; winds not always strong.
Solar energy:	<1	<1		
Active solar heating: rooftop solar panels absorb the Sun's rays, which heat water in tubes for space heating and hot water supply.			No heat engine needed; no air or thermal pollution; unlimited fuel supply.	Space limitations; may require back-up; relatively expensive; less effective when cloudy.
Passive solar heating: architectural devices—windows along southern exposure, sunshade over windows to keep Sun's rays out in summer.			No heat engine needed; no air or thermal pollution; relatively inexpensive.	Almost none, but other methods needed too.
Solar cells (photovoltaic cells): convert sunlight directly into electricity without use of heat engine.			No heat engine; thermal, air, and water pollution very low; good efficiency (>30% and improving).	Expensive; chemical pollution at manufacture; much land needed as Sun's energy not concentrated; absorption (dark color) without reemission = global warming.

*SECTION 15–11 Thermal Pollution, Global Warming, and Energy Resources **435**
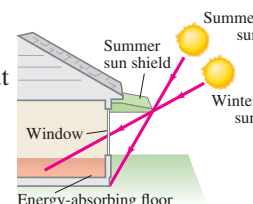
Thermodynamics

1. Define the **system** you are dealing with; distinguish the system under study from its surroundings.

2. When applying the first law of thermodynamics, be careful of **signs** associated with **work** and **heat**. In the first law, work done *by* the system is positive; work done *on* the system is negative. Heat *added* to the system is positive, but heat *removed* from it is negative. With heat engines, we usually consider the heat intake, the heat exhausted, and the work done as positive.

3. Watch the **units** used for work and heat; work is most often expressed in joules, and heat can be in calories, kilocalories, or joules. Be consistent: choose only one unit for use throughout a given problem.

4. **Temperatures** must generally be expressed in kelvins; temperature *differences* may be expressed in C° or K.

5. **Efficiency** (or coefficient of performance) is a ratio of two energy transfers: useful output divided by required input. Efficiency (but *not* coefficient of performance) is always less than 1 in value, and hence is often stated as a percentage.

6. The **entropy** of a system increases when heat is added to the system, and decreases when heat is removed. If heat is transferred from system A to system B, the change in entropy of A is negative and the change in entropy of B is positive.

Summary

The **first law of thermodynamics** states that the change in internal energy ΔU of a system is equal to the heat *added* to the system, Q, minus the work done *by* the system, W:

$$\Delta U = Q - W. \qquad (15\text{–}1)$$

This important law is a statement of the conservation of energy, and is found to hold for all processes.

An **isothermal** process is a process carried out at constant temperature.

In an **adiabatic** process, no heat is exchanged ($Q = 0$).

The work W done by a gas at constant pressure P is given by

$$W = P\,\Delta V, \qquad (15\text{–}3)$$

where ΔV is the change in volume of the gas.

A **heat engine** is a device for changing thermal energy, by means of heat flow, into useful work.

The **efficiency** e of a heat engine is defined as the ratio of the work W done by the engine to the high temperature heat input Q_H. Because of conservation of energy, the work output equals $Q_H - Q_L$, where Q_L is the heat exhausted at low temperature to the environment; hence

$$e = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}. \qquad (15\text{–}4)$$

Q_H, Q_L, and W, as defined for heat engines, are positive.

The *upper limit* on the efficiency (the *Carnot efficiency*) can be written in terms of the higher and lower operating temperatures (in kelvins) of the engine, T_H and T_L, as

$$e_{ideal} = 1 - \frac{T_L}{T_H}. \qquad (15\text{–}5)$$

Real (irreversible) engines always have an efficiency less than this.

The operation of **refrigerators** and **air conditioners** is the reverse of a heat engine: work is done to extract heat Q_L from a cool region and exhaust it to a region at a higher temperature. The coefficient of performance (COP) for either is

$$COP = \frac{Q_L}{W}, \qquad \begin{bmatrix} \text{refrigerator or} \\ \text{air conditioner} \end{bmatrix} \quad (15\text{–}6a)$$

where W is the work needed to remove heat Q_L from the area with the low temperature.

A **heat pump** uses work W to bring heat Q_L from the cold outside and deliver heat Q_H to warm the interior. The coefficient of performance of a heat pump is

$$COP = \frac{Q_H}{W}, \qquad \text{[heat pump]} \quad (15\text{–}7)$$

because it is the heat Q_H delivered inside the building that counts.

The **second law of thermodynamics** can be stated in several equivalent ways:

(a) heat flows spontaneously from a hot object to a cold one, but not the reverse;

(b) there can be no 100% efficient heat engine—that is, one that can change a given amount of heat completely into work;

(c) natural processes tend to move toward a state of greater disorder or greater **entropy**.

Statement (c) is the most general statement of the second law of thermodynamics, and can be restated as: the total entropy, S, of any system plus that of its environment increases as a result of any natural process:

$$\Delta S > 0. \qquad (15\text{–}9)$$

The change in entropy in a process that transfers heat Q at a constant temperature T is

$$\Delta S = \frac{Q}{T}. \qquad (15\text{–}8)$$

Entropy is a quantitative measure of the **disorder** of a system. The second law of thermodynamics also indicates that as time goes on, energy is **degraded** to less useful forms—that is, it is less available to do useful work.

The second law of thermodynamics tells us in which direction processes tend to proceed; hence entropy is called "time's arrow."

[*Entropy can be examined from a statistical point of view, considering **macrostates** (for example, P, V, T) and **microstates** (state of each molecule). The most probable processes are the ones we observe. They are the ones that increase entropy the most. Processes that violate the second law "could" occur, but only with *extremely* low probability.]

[*All heat engines give rise to **thermal pollution** because they exhaust heat to the environment.]

Questions

1. In an isothermal process, 3700 J of work is done by an ideal gas. Is this enough information to tell how much heat has been added to the system? If so, how much? If not, why not?

2. Can mechanical energy ever be transformed completely into heat or internal energy? Can the reverse happen? In each case, if your answer is no, explain why not; if yes, give one or two examples.

3. Can the temperature of a system remain constant even though heat flows into or out of it? If so, give examples.

4. Explain why the temperature of a gas increases when it is compressed adiabatically.

5. An ideal monatomic gas expands slowly to twice its volume (1) isothermally; (2) adiabatically; (3) isobarically. Plot each on a PV diagram. In which process is ΔU the greatest, and in which is ΔU the least? In which is W the greatest and the least? In which is Q the greatest and the least?

6. (a) What happens if you remove the lid of a bottle containing chlorine gas? (b) Does the reverse process ever happen? Why or why not? (c) Can you think of two other examples of irreversibility?

7. Would a definition of heat engine efficiency as $e = W/Q_L$ be useful? Explain.

8. What are the high-temperature and the low-temperature areas for (a) an internal combustion engine, and (b) a steam engine? Are they, strictly speaking, heat reservoirs?

9. The oceans contain a tremendous amount of thermal (internal) energy. Why, in general, is it not possible to put this energy to useful work?

10. Can you warm a kitchen in winter by leaving the oven door open? Can you cool the kitchen on a hot summer day by leaving the refrigerator door open? Explain.

11. The COPs are defined differently for heat pumps and air conditioners. Explain why.

12. You are asked to test a machine that the inventor calls an "in-room air conditioner": a big box, standing in the middle of the room, with a cable that plugs into a power outlet. When the machine is switched on, you feel a stream of cold air coming out of it. How do you know that this machine cannot cool the room?

13. Think up several processes (other than those already mentioned) that would obey the first law of thermodynamics, but, if they actually occurred, would violate the second law.

14. Suppose a lot of papers are strewn all over the floor; then you stack them neatly. Does this violate the second law of thermodynamics? Explain.

15. The first law of thermodynamics is sometimes whimsically stated as, "You can't get something for nothing," and the second law as, "You can't even break even." Explain how these statements could be equivalent to the formal statements.

16. A gas is allowed to expand (a) adiabatically and (b) isothermally. In each process, does the entropy increase, decrease, or stay the same? Explain.

17. Which do you think has the greater entropy, 1 kg of solid iron or 1 kg of liquid iron? Why?

18. Give three examples, other than those mentioned in this Chapter, of naturally occurring processes in which order goes to disorder. Discuss the observability of the reverse process.

19. Entropy is often called "time's arrow" because it tells us in which direction natural processes occur. If a movie were run backward, name some processes that you might see that would tell you that time was "running backward."

20. Living organisms, as they grow, convert relatively simple food molecules into a complex structure. Is this a violation of the second law of thermodynamics? Explain your answer.

MisConceptual Questions

1. In an isobaric compression of an ideal gas,
   (a) no heat flows into the gas.
   (b) the internal energy of the gas remains constant.
   (c) no work is done on the gas.
   (d) work is done on the gas.
   (e) work is done by the gas.

2. Which is possible: converting (i) 100 J of work entirely into 100 J of heat, (ii) 100 J of heat entirely into 100 J of work?
   (a) Only (i) is possible.
   (b) Only (ii) is possible.
   (c) Both (i) and (ii) are possible.
   (d) Neither (i) nor (ii) is possible.

3. An ideal gas undergoes an isobaric compression and then an isovolumetric process that brings it back to its initial temperature. Had the gas undergone *one isothermal* process instead,
   (a) the work done on the gas would be the same.
   (b) the work done on the gas would be less.
   (c) the work done on the gas would be greater.
   (d) Need to know the temperature of the isothermal process.

4. An ideal gas undergoes an isothermal expansion from state A to state B. In this process (use sign conventions, page 413),
   (a) $Q = 0, \ \Delta U = 0, \ W > 0.$
   (b) $Q > 0, \ \Delta U = 0, \ W < 0.$
   (c) $Q = 0, \ \Delta U > 0, \ W > 0.$
   (d) $Q > 0, \ \Delta U = 0, \ W > 0.$
   (e) $Q = 0, \ \Delta U < 0, \ W < 0.$

5. An ideal gas undergoes an isothermal process. Which of the following statements are true? (i) No heat is added to or removed from the gas. (ii) The internal energy of the gas does not change. (iii) The average kinetic energy of the molecules does not change.
   (a) (i) only.
   (b) (i) and (ii) only.
   (c) (i) and (iii) only.
   (d) (ii) and (iii) only.
   (e) (i), (ii), and (iii).
   (f) None of the above.

6. An ideal gas undergoes an adiabatic expansion, a process in which no heat flows into or out of the gas. As a result,
(*a*) the temperature of the gas remains constant and the pressure decreases.
(*b*) both the temperature and pressure of the gas decrease.
(*c*) the temperature of the gas decreases and the pressure increases.
(*d*) both the temperature and volume of the gas increase.
(*e*) both the temperature and pressure of the gas increase.

7. A heat engine operates between a high temperature of about 600°C and a low temperature of about 300°C. What is the maximum theoretical efficiency for this engine?
(*a*) = 100%.   (*b*) ≈ 66%.   (*c*) ≈ 50%.   (*d*) ≈ 34%.
(*e*) Cannot be determined from the given information.

8. On a very hot day, could you cool your kitchen by leaving the refrigerator door open?
(*a*) Yes, but it would be very expensive.
(*b*) Yes, but only if the humidity is below 50%.
(*c*) No, the refrigerator would exhaust the same amount of heat into the room as it takes out of the room.
(*d*) No, the heat exhausted by the refrigerator into the room is more than the heat the refrigerator takes out of the room.

9. Which of the following possibilities could increase the efficiency of a heat engine or an internal combustion engine?
(*a*) Increase the temperature of the hot part of the system and reduce the temperature of the exhaust.
(*b*) Increase the temperatures of both the hot part and the exhaust part of the system by the same amount.
(*c*) Decrease the temperatures of both the hot part and the exhaust part of the system by the same amount.
(*d*) Decrease the temperature of the hot part and increase the temperature of the exhaust part by the same amount.
(*e*) None of the above; only redesigning the engine or using better gas could improve the engine's efficiency.

10. About what percentage of the heat produced by burning gasoline is turned into useful work by a typical automobile?
(*a*) 20%. (*b*) 50%. (*c*) 80%. (*d*) 90%. (*e*) Nearly 100%.

11. Which statement is true regarding the entropy change of an ice cube that melts?
(*a*) Since melting occurs at the melting point temperature, there is no temperature change so there is no entropy change.
(*b*) Entropy increases.
(*c*) Entropy decreases.

For assigned homework and other learning materials, go to the MasteringPhysics website. **MP**

Problems

15–1 and 15–2 First Law of Thermodynamics

[Recall sign conventions, page 413.]

1. (I) An ideal gas expands isothermally, performing 4.30×10^3 J of work in the process. Calculate (*a*) the change in internal energy of the gas, and (*b*) the heat absorbed during this expansion.

2. (I) One liter of air is cooled at constant pressure until its volume is halved, and then it is allowed to expand isothermally back to its original volume. Draw the process on a *PV* diagram.

3. (II) Sketch a *PV* diagram of the following process: 2.5 L of ideal gas at atmospheric pressure is cooled at constant pressure to a volume of 1.0 L, and then expanded isothermally back to 2.5 L, whereupon the pressure is increased at constant volume until the original pressure is reached.

4. (II) A gas is enclosed in a cylinder fitted with a light frictionless piston and maintained at atmospheric pressure. When 254 kcal of heat is added to the gas, the volume is observed to increase slowly from $12.0 \, \text{m}^3$ to $16.2 \, \text{m}^3$. Calculate (*a*) the work done by the gas and (*b*) the change in internal energy of the gas.

5. (II) A 1.0-L volume of air initially at 3.5 atm of (gauge) pressure is allowed to expand isothermally until the pressure is 1.0 atm. It is then compressed at constant pressure to its initial volume, and lastly is brought back to its original pressure by heating at constant volume. Draw the process on a *PV* diagram, including numbers and labels for the axes.

6. (II) The pressure in an ideal gas is cut in half slowly, while being kept in a container with rigid walls. In the process, 465 kJ of heat left the gas. (*a*) How much work was done during this process? (*b*) What was the change in internal energy of the gas during this process?

7. (II) In an engine, an almost ideal gas is compressed adiabatically to half its volume. In doing so, 2630 J of work is done on the gas. (*a*) How much heat flows into or out of the gas? (*b*) What is the change in internal energy of the gas? (*c*) Does its temperature rise or fall?

8. (II) An ideal gas expands at a constant total pressure of 3.0 atm from 410 mL to 690 mL. Heat then flows out of the gas at constant volume, and the pressure and temperature are allowed to drop until the temperature reaches its original value. Calculate (*a*) the total work done by the gas in the process, and (*b*) the total heat flow into the gas.

9. (II) 8.5 moles of an ideal monatomic gas expand adiabatically, performing 8300 J of work in the process. What is the change in temperature of the gas during this expansion?

10. (II) Consider the following two-step process. Heat is allowed to flow out of an ideal gas at constant volume so that its pressure drops from 2.2 atm to 1.4 atm. Then the gas expands at constant pressure, from a volume of 5.9 L to 9.3 L, where the temperature reaches its original value. See Fig. 15–22. Calculate (*a*) the total work done by the gas in the process, (*b*) the change in internal energy of the gas in the process, and (*c*) the total heat flow into or out of the gas.
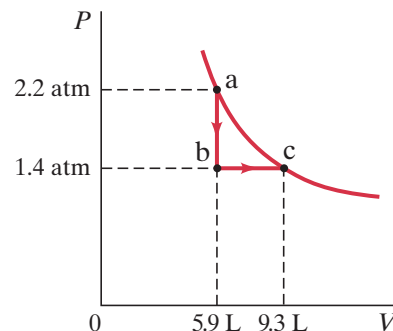

FIGURE 15–22
Problem 10.

11. (II) Use the conservation of energy to explain why the temperature of a well-insulated gas increases when it is compressed—say, by pushing down on a piston—whereas the temperature decreases when the gas expands. Show your reasoning.

12. (III) The PV diagram in Fig. 15–23 shows two possible states of a system containing 1.75 moles of a monatomic ideal gas. $(P_1 = P_2 = 425\ \text{N/m}^2,\ V_1 = 2.00\ \text{m}^3,\ V_2 = 8.00\ \text{m}^3.)$ (a) Draw the process which depicts an isobaric expansion from state 1 to state 2, and label this process A. (b) Find the work done by the gas and the change in internal energy of the gas in process A. (c) Draw the two-step process which depicts an isothermal expansion from state 1 to the volume V_2, followed by an isovolumetric increase in temperature to state 2, and label this process B. (d) Find the change in internal energy of the gas for the two-step process B.

FIGURE 15–23 Problem 12.
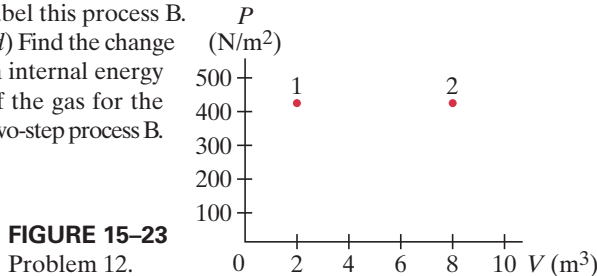
13. For the path ac, use the first law of thermodynamics to find the change in internal energy.

$$\Delta U_{ac} = Q_{ac} - W_{ac} = -175\ \text{J} - (-35\ \text{J}) = -140\ \text{J}$$

Since internal energy only depends on the initial and final temperatures, this ΔU applies to any path that starts at a and ends at c. And for any path that starts at c and ends at a, $\Delta U_{ac} = -\Delta U_{ac} = 140\ \text{J}$

(a) Use the first law of thermodynamics to find Q_{abc}.

$$\Delta U_{abc} = Q_{abc} - W_{abc} \longrightarrow Q_{abc} = \Delta U_{abc} + W_{abc}$$
$$= -140\ \text{J} + (-56\ \text{J}) = \boxed{-196\ \text{J}}$$

(b) Since the work along path bc is 0, $W_{abc} = W_{ab} = P_b\,\Delta V_{ab} = P_b(V_b - V_a)$. Also note that the work along path da is 0.

$$W_{cda} = W_{cd} = P_c\,\Delta V_{cd} = P_c(V_d - V_c)$$
$$= \tfrac{1}{2}P_b(V_a - V_b) = -\tfrac{1}{2}W_{abc}$$
$$= -\tfrac{1}{2}(-56\ \text{J}) = \boxed{28\ \text{J}}$$

(c) Use the first law of thermodynamics to find Q_{abc}.

$$\Delta U_{cda} = Q_{cda} - W_{cda} \longrightarrow Q_{cda} = \Delta U_{cda} + W_{cda}$$
$$= -140\ \text{J} + 28\ \text{J} = \boxed{168\ \text{J}}$$

(d) As found above, $U_c - U_a = \Delta U_{ca} = -\Delta U_{ac} = \boxed{140\ \text{J}}$
(e) Since $U_d - U_c = 42\ \text{J} \longrightarrow U_d = U_c + 42\ \text{J} \longrightarrow .$

$$\Delta U_{da} = U_a - U_d = U_a - U_c - 42\ \text{J} = \Delta U_{ca} - 42\ \text{J}$$
$$= 140\ \text{J} - 42\ \text{J} = 98\ \text{J}$$

Use the first law of thermodynamics to find Q_{da}.

$$\Delta U_{da} = Q_{da} - W_{da} \longrightarrow Q_{da} = \Delta U_{da} + W_{da}$$
$$= 98\ \text{J} + 0 = \boxed{98\ \text{J}}$$

*15–3 Human Metabolism

*14. (I) How much energy would the person of Example 15–7 transform if instead of working 11.0 h she took a noontime break and ran at 15 km/h for 1.0 h?

*15. (I) Calculate the average metabolic rate of a 65-kg person who sleeps 8.0 h, sits at a desk 6.0 h, engages in light activity 6.0 h, watches TV 2.0 h, plays tennis 1.5 h, and runs 0.50 h daily.

*16. (II) A 65-kg person decides to lose weight by sleeping one hour less per day, using the time for light activity. How much weight (or mass) can this person expect to lose in 1 year, assuming no change in food intake? Assume that 1 kg of fat stores about 40,000 kJ of energy.

*17. (II) (a) How much energy is transformed by a typical 65-kg person who runs at 15 km/h for 30 min/day in one week (Table 15–2)? (b) How many food calories would the person have to eat to make up for this energy loss?

15–5 Heat Engines

18. (I) A heat engine exhausts 8200 J of heat while performing 2600 J of useful work. What is the efficiency of this engine?

19. (I) What is the maximum efficiency of a heat engine whose operating temperatures are 560°C and 345°C?

20. (I) The exhaust temperature of a heat engine is 230°C. What is the high temperature if the Carnot efficiency is 34%?

21. (I) A heat engine does 9200 J of work per cycle while absorbing 25.0 kcal of heat from a high-temperature reservoir. What is the efficiency of this engine?

22. (I) A heat engine's high temperature T_H could be ambient temperature, because liquid nitrogen at 77 K could be T_L and is cheap. What would be the efficiency of a Carnot engine that made use of heat transferred from air at room temperature (293 K) to the liquid nitrogen "fuel" (Fig. 15–24)?

FIGURE 15–24 Problem 22.

23. (II) Which will improve the efficiency of a Carnot engine more: a 10 C° increase in the high-temperature reservoir, or a 10 C° decrease in the low-temperature reservoir? Give detailed results. Can you state a generalization?

24. (II) A certain power plant puts out 580 MW of electric power. Estimate the heat discharged per second, assuming that the plant has an efficiency of 32%.

25. (II) A nuclear power plant operates at 65% of its maximum theoretical (Carnot) efficiency between temperatures of 660°C and 330°C. If the plant produces electric energy at the rate of 1.4 GW, how much exhaust heat is discharged per hour?

26. (II) A heat engine exhausts its heat at 340°C and has a Carnot efficiency of 36%. What exhaust temperature would enable it to achieve a Carnot efficiency of 42%?

27. (II) A Carnot engine's operating temperatures are 210°C and 45°C. The engine's power output is 910 W. Calculate the rate of heat output.

28. (II) A heat engine uses a heat source at 580°C and has an ideal (Carnot) efficiency of 22%. To increase the ideal efficiency to 42%, what must be the temperature of the heat source?

29. (III) A typical compact car experiences a total drag force of about 350 N at 55 mi/h. If this car gets 32 miles per gallon of gasoline at this speed, and a liter of gasoline (1 gal = 3.8 L) releases about 3.2×10^7 J when burned, what is the car's efficiency?

15–6 Refrigerators, Air Conditioners, Heat Pumps

30. (I) If an ideal refrigerator keeps its contents at 2.5°C when the house temperature is 22°C, what is its COP?

31. (I) The low temperature of a freezer cooling coil is -8°C and the discharge temperature is 33°C. What is the maximum theoretical coefficient of performance?

32. (II) What is the temperature inside an ideal refrigerator-freezer that operates with a COP = 7.0 in a 22°C room?

33. (II) A heat pump is used to keep a house warm at 22°C. How much work is required of the pump to deliver 3100 J of heat into the house if the outdoor temperature is (a) 0°C, (b) -15°C? Assume a COP of 3.0. (c) Redo for both temperatures, assuming an ideal (Carnot) coefficient of performance $COP = T_H/(T_H - T_L)$.

34. (II) (a) What is the coefficient of performance of an ideal heat pump that extracts heat from 6°C air outside and deposits heat inside a house at 24°C? (b) If this heat pump operates on 1200 W of electrical power, what is the maximum heat it can deliver into the house each hour? See Problem 33.

35. (II) How much less per year would it cost a family to operate a heat pump that has a coefficient of performance of 2.9 than an electric heater that costs $2000 to heat their home for a year? If the conversion to the heat pump costs $15,000, how long would it take the family to break even on heating costs? How much would the family save in 20 years?

15–7 Entropy

36. (I) What is the change in entropy of 320 g of steam at 100°C when it is condensed to water at 100°C?

37. (I) 1.0 kg of water is heated from 0°C to 100°C. Estimate the change in entropy of the water.

38. (II) A 5.8-kg box having an initial speed of 4.0 m/s slides along a rough table and comes to rest. Estimate the total change in entropy of the universe. Assume all objects are at room temperature (293 K).

39. (II) If 1.00 m^3 of water at 0°C is frozen and cooled to -8.0°C by being in contact with a great deal of ice at -8.0°C, estimate the total change in entropy of the process.

40. (II) An aluminum rod conducts 8.40 cal/s from a heat source maintained at 225°C to a large body of water at 22°C. Calculate the rate at which entropy increases in this process.

41. (II) A falling rock has kinetic energy KE just before striking the ground and coming to rest. What is the total change in entropy of rock plus environment as a result of this collision?

42. (II) 1.0 kg of water at 35°C is mixed with 1.0 kg of water at 45°C in a well-insulated container. Estimate the net change in entropy of the system.

43. (III) A real heat engine working between heat reservoirs at 970 K and 650 K produces 550 J of work per cycle for a heat input of 2500 J. (a) Compare the efficiency of this real engine to that of an ideal (Carnot) engine. (b) Calculate the total entropy change of the universe per cycle of the real engine, and (c) also if the engine is ideal (Carnot).

*15–10 Statistical Interpretation

*44.** (II) Calculate the probabilities, when you throw two dice, of obtaining (a) a 4, and (b) a 10.

*45.** (II) Suppose that you repeatedly shake six coins in your hand and drop them on the floor. Construct a table showing the number of microstates that correspond to each macrostate. What is the probability of obtaining (a) three heads and three tails, and (b) six heads?

*46.** (III) A bowl contains many red, orange, and green jelly beans, in equal numbers. You are to make a line of 3 jelly beans by randomly taking 3 beans from the bowl. (a) Construct a table showing the number of microstates that correspond to each macrostate. Then determine the probability of (b) all 3 beans red, and (c) 2 greens, 1 orange.

*15–11 Energy Resources

*47.** (I) Solar cells (Fig. 15–25) can produce about 40 W of electricity per square meter of surface area if directly facing the Sun. How large an area is required to supply the needs of a house that requires 24 kWh/day? Would this fit on the roof of an average house? (Assume the Sun shines about 9 h/day.)

FIGURE 15–25
Problem 47.

*48.** (II) Energy may be stored by pumping water to a high reservoir when demand is low and then releasing it to drive turbines during peak demand. Suppose water is pumped to a lake 115 m above the turbines at a rate of 1.00×10^5 kg/s for 10.0 h at night. (a) How much energy (kWh) is needed to do this each night? (b) If all this energy is released during a 14-h day, at 75% efficiency, what is the average power output?

*49.** (II) Water is stored in an artificial lake created by a dam (Fig. 15–26). The water depth is 48 m at the dam, and a steady flow rate of 32 m^3/s is maintained through hydroelectric turbines installed near the base of the dam. How much electrical power can be produced?

FIGURE 15–26
Problem 49:
Flaming Gorge
Dam on the
Green River in
Utah.

General Problems

50. When 5.80×10^5 J of heat is added to a gas enclosed in a cylinder fitted with a light frictionless piston maintained at atmospheric pressure, the volume is observed to increase from 1.9 m^3 to 4.1 m^3. Calculate (a) the work done by the gas, and (b) the change in internal energy of the gas. (c) Graph this process on a PV diagram.

51. A restaurant refrigerator has a coefficient of performance of 4.6. If the temperature in the kitchen outside the refrigerator is 32°C, what is the lowest temperature that could be obtained inside the refrigerator if it were ideal?

52. A particular car does work at the rate of about 7.0 kJ/s when traveling at a steady 21.8 m/s along a level road. This is the work done against friction. The car can travel 17 km on 1.0 L of gasoline at this speed (about 40 mi/gal). What is the minimum value for T_H if T_L is 25°C? The energy available from 1.0 L of gas is 3.2×10^7 J.

53. A "Carnot" refrigerator (the reverse of a Carnot engine) absorbs heat from the freezer compartment at a temperature of −17°C and exhausts it into the room at 25°C. (a) How much work would the refrigerator do to change 0.65 kg of water at 25°C into ice at −17°C? (b) If the compressor output is 105 W and runs 25% of the time, how long will this take?

54. It has been suggested that a heat engine could be developed that made use of the temperature difference between water at the surface of the ocean and water several hundred meters deep. In the tropics, the temperatures may be 27°C and 4°C, respectively. (a) What is the maximum efficiency such an engine could have? (b) Why might such an engine be feasible in spite of the low efficiency? (c) Can you imagine any adverse environmental effects that might occur?

55. Refrigeration units can be rated in "tons." A 1-ton air conditioning system can remove sufficient energy to freeze 1 ton (2000 pounds = 909 kg) of 0°C water into 0°C ice in one 24-h day. If, on a 35°C day, the interior of a house is maintained at 22°C by the continuous operation of a 5-ton air conditioning system, how much does this cooling cost the homeowner per hour? Assume the work done by the refrigeration unit is powered by electricity that costs \$0.10 per kWh and that the unit's coefficient of performance is 18% that of an ideal refrigerator. 1 kWh = 3.60×10^6 J.

56. Two 1100-kg cars are traveling 85 km/h in opposite directions when they collide and are brought to rest. Estimate the change in entropy of the universe as a result of this collision. Assume $T = 20$°C.

57. A 110-g insulated aluminum cup at 35°C is filled with 150 g of water at 45°C. After a few minutes, equilibrium is reached. (a) Determine the final temperature, and (b) estimate the total change in entropy.

58. The burning of gasoline in a car releases about 3.0×10^4 kcal/gal. If a car averages 41 km/gal when driving 110 km/h, which requires 25 hp, what is the efficiency of the engine under those conditions?

59. A Carnot engine operates with $T_L = 20$°C and has an efficiency of 25%. By how many kelvins should the high operating temperature T_H be increased to achieve an efficiency of 35%?

60. Calculate the work done by an ideal gas in going from state A to state C in Fig. 15–27 for each of the following processes: (a) ADC, (b) ABC, and (c) AC directly.
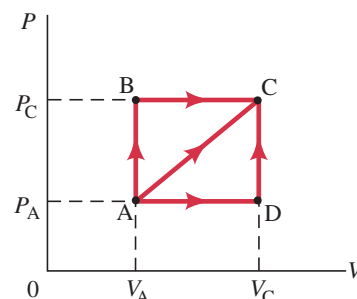
FIGURE 15–27
Problem 60.

61. A 38% efficient power plant puts out 850 MW of electrical power. Cooling towers take away the exhaust heat. (a) If the air temperature is allowed to rise 7.0 C°, estimate what volume of air (km^3) is heated per day. Will the local climate be heated significantly? (b) If the heated air were to form a layer 180 m thick, estimate how large an area it would cover for 24 h of operation. Assume the air has density 1.3 kg/m³ and has specific heat of about 1.0 kJ/kg·C° at constant pressure.

62. Suppose a power plant delivers energy at 880 MW using steam turbines. The steam goes into the turbines superheated at 625 K and deposits its unused heat in river water at 285 K. Assume that the turbine operates as an ideal Carnot engine. (a) If the river flow rate is 37 m³/s, estimate the average temperature increase of the river water immediately downstream from the power plant. (b) What is the entropy increase per kilogram of the downstream river water in J/kg·K?

63. An ideal monatomic gas is contained in a tall cylindrical jar of cross-sectional area 0.080 m^2 fitted with an airtight frictionless 0.15-kg movable piston. When the gas is heated (at constant pressure) from 25°C to 55°C, the piston rises 1.0 cm. How much heat was required for this process? Assume atmospheric pressure outside. [*Hint*: See Section 14–2.]

64. Metabolizing 1.0 kg of fat results in about 3.7×10^7 J of internal energy in the body. (a) In one day, how much fat does the body burn to maintain the body temperature of a person staying in bed and metabolizing at an average rate of 95 W? (b) How long would it take to burn 1.0 kg of fat this way assuming there is no food intake?

65. (*a*) At a steam power plant, steam engines work in pairs, the heat output of the first one being the approximate heat input of the second. The operating temperatures of the first are 750°C and 440°C, and of the second 415°C and 270°C. If the heat of combustion of coal is 2.8×10^7 J/kg, at what rate must coal be burned if the plant is to put out 950 MW of power? Assume the efficiency of the engines is 65% of the ideal (Carnot) efficiency. (*b*) Water is used to cool the power plant. If the water temperature is allowed to increase by no more than 4.5 C°, estimate how much water must pass through the plant per hour.

66. Suppose a heat pump has a stationary bicycle attachment that allows *you* to provide the work instead of using an electrical wall outlet. If your heat pump has a coefficient of performance of 2.0 and you can cycle at a racing pace (Table 15–2) for a half hour, how much heat can you provide?

67. An ideal air conditioner keeps the temperature inside a room at 21°C when the outside temperature is 32°C. If 4.8 kW of power enters a room through the windows in the form of direct radiation from the Sun, how much electrical power would be saved if the windows were shaded so only 500 W enters?

68. An ideal heat pump is used to maintain the inside temperature of a house at $T_{in} = 22$°C when the outside temperature is T_{out}. Assume that when it is operating, the heat pump does work at a rate of 1500 W. Also assume that the house loses heat via conduction through its walls and other surfaces at a rate given by $(650 \text{ W/C}°)(T_{in} - T_{out})$. (*a*) For what outside temperature would the heat pump have to operate all the time in order to maintain the house at an inside temperature of 22°C? (*b*) If the outside temperature is 8°C, what percentage of the time does the heat pump have to operate in order to maintain the house at an inside temperature of 22°C?

Search and Learn

1. What happens to the internal energy of water vapor in the air that condenses on the outside of a cold glass of water? Is work done or heat exchanged? Explain in detail.

2. Draw a *PV* diagram for an ideal gas which undergoes a three-step cyclic thermodynamic process in which the first step has $\Delta U = 0$ and $W > 0$, the second step has $W = 0$, and the third step has $Q = 0$ and $W < 0$.

3. A dehumidifier removes water vapor from air and has been referred to as a "refrigerator with an open door." The humid air is pulled in by a fan and passes over a cold coil, whose temperature is less than the dew point, and some of the air's water condenses. After this water is extracted, the air is warmed back to its original temperature and sent into the room. In a well-designed dehumidifier, the heat that is removed by the cooling coil mostly comes from the condensation of water vapor to liquid, and this heat is used to re-warm the air. Estimate how much water is removed in 1.0 h by an ideal dehumidifier, if the temperature of the room is 25°C, the water condenses at 8°C, and the dehumidifier does work at the rate of 600 W of electrical power. (See Sections 15–6, 13–12, and 14–5.)

4. A particular 1.5-m² photovoltaic panel operating in direct sunlight produces electricity at 20% efficiency. The resulting electricity is used to operate an electric stove that can be used to heat water. A second system uses a 1.5-m² curved mirror to concentrate the Sun's energy directly onto a container of water. Estimate how long it takes each system to heat 1.0 kg of water from 25°C to 95°C. (See also Chapter 14.)

***5. Trees offsetting CO₂.** Trees can help offset the buildup of CO_2 due to burning coal and other fossil fuels. CO_2 can be absorbed by tree foliage. Trees use the carbon to grow, and release O_2 into the atmosphere. Suppose a refrigerator uses 600 kWh of electricity per year (about 2×10^9 J) from a 33% efficient coal-fired power plant. Burning 1 kg of coal releases about 2×10^7 J of energy. Assume coal is all carbon, which when burned in air becomes CO_2. (*a*) How much coal is burned per year to run this refrigerator? (*b*) Assuming a forest can capture 1700 kg of carbon per hectare (= 10,000 m²) per year, estimate how many square meters of forest are needed to capture the carbon (in the form now of CO_2) emitted in (*a*).

ANSWERS TO EXERCISES

A: 700 J.
B: Less.
C: -6.8×10^3 J.
D: (*d*), (*e*).

E: (*c*).
F: (*a*) Heat Q_L comes from outside to conserve energy; (*b*) 560 W.
G: (*e*).