

? The second law of thermodynamics tells us that heat naturally flows from a hot object (such as molten lava, shown here flowing into the ocean in Hawaii) to a cold one (such as ocean water, which is heated by the lava to make steam). Is it *ever* possible for heat to flow from a cold object to a hot one? (i) Yes, no matter what the temperature difference; (ii) yes, but for only certain temperature differences; (iii) no; (iv) answer depends on the compositions of the two objects.



20 The Second Law of Thermodynamics

LEARNING OUTCOMES

In this chapter, you'll learn...

- 20.1 The difference between reversible and irreversible processes.
- 20.2 What a heat engine is, and how to calculate its efficiency.
- 20.3 The physics of internal-combustion engines.
- 20.4 How refrigerators and heat engines are related, and how to analyze the performance of a refrigerator.
- 20.5 How the second law of thermodynamics sets limits on the efficiency of engines and the performance of refrigerators.
- 20.6 How to do calculations involving the idealized Carnot cycle for engines and refrigerators.
- 20.7 What is meant by entropy, and how to use this concept to analyze thermodynamic processes.
- 20.8 How to use the concept of microscopic states to understand entropy.

You'll need to review...

- 17.3 The Kelvin scale.
- 18.3 The Boltzmann constant.
- 19.1–19.8 Thermodynamic processes; first law of thermodynamics; free expansion of a gas.

Many thermodynamic processes proceed naturally in one direction but not the opposite. For example, heat by itself always flows from a hot object to a cooler object, never the reverse. Heat flow from a cool object to a hot object would not violate the first law of thermodynamics; energy would be conserved. But it doesn't happen in nature. Why not? As another example, note that it is easy to convert mechanical energy completely into heat; this happens every time we use a car's brakes to stop it. In the reverse direction, there are plenty of devices that convert heat *partially* into mechanical energy. (An automobile engine is an example.) But no one has ever managed to build a machine that converts heat *completely* into mechanical energy. Again, why not?

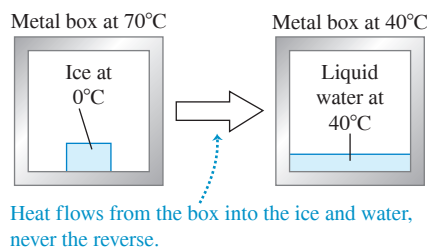
The answer to both of these questions has to do with the *directions* of thermodynamic processes and is called the *second law of thermodynamics*. This law places fundamental limitations on the efficiency of an engine or a power plant. It also places limitations on the minimum energy input needed to operate a refrigerator. So the second law is directly relevant for many important practical problems.

We can also state the second law in terms of the concept of *entropy*, a quantitative measure of the degree of randomness of a system. The idea of entropy helps explain why ink mixed with water never spontaneously unmixes and why we never observe a host of other seemingly possible processes.

20.1 DIRECTIONS OF THERMODYNAMIC PROCESSES

Thermodynamic processes that occur in nature are all **irreversible processes**. These are processes that proceed spontaneously in one direction but not the other (**Fig. 20.1a**). The flow of heat from a hot object to a cooler object is irreversible, as is the free expansion of a gas discussed in Sections 19.3 and 19.6. Sliding a book across a table converts mechanical energy into heat by friction; this process is irreversible, for no one has ever observed the reverse process (in which a book initially at rest on the table would spontaneously start moving and the table and book would cool down). Our main topic for this

(a) A block of ice melts *irreversibly* when we place it in a hot (70°C) metal box.



(b) A block of ice at 0°C can be melted *reversibly* if we put it in a 0°C metal box.

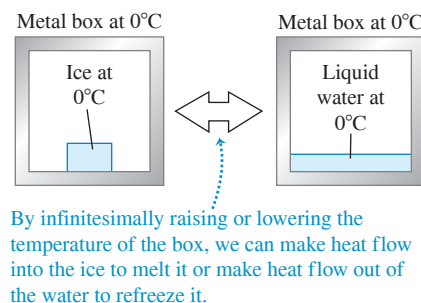


Figure 20.1 Reversible and irreversible processes.

chapter is the *second law of thermodynamics*, which determines the preferred direction for such processes.

Despite this preferred direction for every natural process, we can think of a class of idealized processes that *would* be reversible. A system that undergoes such an idealized **reversible process** is always very close to being in thermodynamic equilibrium within itself and with its surroundings. Any change of state that takes place can then be reversed by making only an infinitesimal change in the conditions of the system. For example, we can reverse heat flow between two objects whose temperatures differ only infinitesimally by making only a very small change in one temperature or the other (Fig. 20.1b).

Reversible processes are thus **equilibrium processes**, with the system always in thermodynamic equilibrium. Of course, if a system were *truly* in thermodynamic equilibrium, no change of state would take place. Heat would not flow into or out of a system with truly uniform temperature throughout, and a system that is truly in mechanical equilibrium would not expand and do work against its surroundings. A reversible process is an idealization that can never be precisely attained in the real world. But by making the temperature gradients and the pressure differences in the substance very small, we can keep the system very close to equilibrium states and make the process nearly reversible.

By contrast, heat flow with finite temperature difference, free expansion of a gas, and conversion of work to heat by friction are all *irreversible* processes; no small change in conditions could make any of them go the other way. They are also all *nonequilibrium* processes, in that the system is not in thermodynamic equilibrium at any point until the end of the process.

Disorder and Thermodynamic Processes

There is a relationship between the direction of a process and the *disorder* or *randomness* of the resulting state. For example, imagine a thousand names written on file cards and arranged in alphabetical order. Throw the alphabetized stack of cards into the air, and they will likely come down in a random, disordered state. In the free expansion of a gas discussed in Sections 19.3 and 19.6, the air is more disordered after it has expanded into the entire box than when it was confined in one side, just as your clothes are more disordered when scattered all over your floor than when confined to your closet.

Similarly, macroscopic kinetic energy is energy associated with organized, coordinated motions of many molecules, but heat transfer involves changes in energy of random, disordered molecular motion. Therefore conversion of mechanical energy into heat involves an increase of randomness or disorder.

In the following sections we'll introduce the second law of thermodynamics by considering two broad classes of devices: *heat engines*, which are partly successful in converting heat into work, and *refrigerators*, which are partly successful in transporting heat from cooler to hotter objects.

TEST YOUR UNDERSTANDING OF SECTION 20.1 Your left and right hands are normally at the same temperature, just like the metal box and ice in Fig. 20.1b. Is rubbing your hands together to warm them (i) a reversible process or (ii) an irreversible process?

ANSWER

(ii) Like sliding a book across a table, rubbing your hands together uses friction to convert mechanical energy into heat. The (impossible) reverse process would involve your hands spontaneously getting colder, with the released energy forcing your hands to move rhythmically back and forth!

20.2 HEAT ENGINES

The essence of our technological society is the ability to use sources of energy other than muscle power. Sometimes, mechanical energy is directly available; water power and wind power are examples. But most of our energy comes from the burning of fossil fuels (coal, oil, and gas) and from nuclear reactions. They supply energy that is transferred as *heat*. This is directly useful for heating buildings, for cooking, and for chemical processing, but to operate a machine or propel a vehicle, we need *mechanical energy*.

Thus it's important to know how to take heat from a source and convert as much of it as possible into mechanical energy or work. This is what happens in gasoline engines in automobiles, jet engines in airplanes, steam turbines in electric power plants, and many other systems. Closely related processes occur in the animal kingdom; food energy is “burned” (that is, carbohydrates combine with oxygen to yield water, carbon dioxide, and energy) and partly converted to mechanical energy as an animal’s muscles do work on its surroundings.

Any device that transforms heat partly into work or mechanical energy is called a **heat engine** (Fig. 20.2). Usually, a quantity of matter inside the engine undergoes inflow and outflow of heat, expansion and compression, and sometimes change of phase. We call this matter the **working substance** of the engine. In internal-combustion engines, such as those used in automobiles, the working substance is a mixture of air and fuel; in a steam turbine it is water.

The simplest kind of engine to analyze is one in which the working substance undergoes a **cyclic process**, a sequence of processes that eventually leaves the substance in the same state in which it started. In a steam turbine the water is recycled and used over and over. Internal-combustion engines do not use the same air over and over, but we can still analyze them in terms of cyclic processes that approximate their actual operation.

Hot and Cold Reservoirs

All heat engines *absorb* heat from a source at a relatively high temperature, perform some mechanical work, and *discard* or *reject* some heat at a lower temperature. As far as the engine is concerned, the discarded heat is wasted. In internal-combustion engines the waste heat is that discarded in the hot exhaust gases and the cooling system; in a steam turbine it is the heat that must flow out of the used steam to condense and recycle the water.

When a system is carried through a cyclic process, its initial and final internal energies are equal, so the first law of thermodynamics requires that

$$U_2 - U_1 = 0 = Q - W \quad \text{so} \quad Q = W$$

That is, the net heat flowing into the engine in a cyclic process equals the net work done by the engine.

When we analyze heat engines, it helps to think of two objects with which the working substance of the engine can interact. One of these, called the *hot reservoir*, represents the heat source; it can give the working substance large amounts of heat at a constant temperature T_H without appreciably changing its own temperature. The other object, called the *cold reservoir*, can absorb large amounts of discarded heat from the engine at a constant lower temperature T_C . In a steam-turbine system the flames and hot gases in the boiler are the hot reservoir, and the cold water and air used to condense and cool the used steam are the cold reservoir.

Figure 20.2 All motorized vehicles other than purely electric vehicles use heat engines for propulsion. (Hybrid vehicles use their internal-combustion engine to help charge the batteries for the electric motor.)



We denote the quantities of heat transferred from the hot and cold reservoirs as Q_H and Q_C , respectively. A quantity of heat Q is positive when heat is transferred *into* the working substance and is negative when heat leaves the working substance. Thus in a heat engine, Q_H is positive but Q_C is negative, representing heat *leaving* the working substance. This sign convention is consistent with the rules we stated in Section 19.1; we'll continue to use those rules here. For clarity, we'll often state the relationships in terms of the absolute values of the Q 's and W 's because absolute values are always positive.

Energy-Flow Diagrams and Efficiency

We can represent the energy transformations in a heat engine by the *energy-flow diagram* of **Fig. 20.3**. The engine itself is represented by the circle. The amount of heat Q_H supplied to the engine by the hot reservoir is proportional to the width of the incoming “pipeline” at the top of the diagram. The width of the outgoing pipeline at the bottom is proportional to the magnitude $|Q_C|$ of the heat rejected in the exhaust. The branch line to the right represents the portion of the heat supplied that the engine converts to mechanical work, W .

When an engine repeats the same cycle over and over, Q_H and Q_C represent the quantities of heat absorbed and rejected by the engine *during one cycle*; Q_H is positive, and Q_C is negative. The *net* heat Q absorbed per cycle is

$$Q = Q_H + Q_C = |Q_H| - |Q_C| \quad (20.1)$$

The useful output of the engine is the net work W done by the working substance. From the first law,

$$W = Q = Q_H + Q_C = |Q_H| - |Q_C| \quad (20.2)$$

Ideally, we would like to convert *all* the heat Q_H into work; in that case we would have $Q_H = W$ and $Q_C = 0$. Experience shows that this is impossible; there is always some heat wasted, and Q_C is *never* zero. We define the **thermal efficiency** of an engine, denoted by e , as the quotient

$$e = \frac{W}{Q_H} \quad (20.3)$$

The thermal efficiency e represents the fraction of Q_H that *is* converted to work. To put it another way, e is what you get divided by what you pay for. This is always less than unity, an all-too-familiar experience! In terms of the flow diagram of Fig. 20.3, the most efficient engine is one for which the branch pipeline representing the work output is as wide as possible and the exhaust pipeline representing the heat thrown away is as narrow as possible.

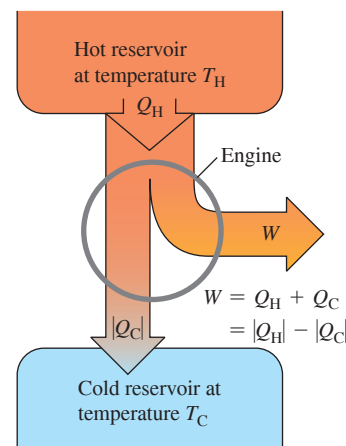
When we substitute the two expressions for W given by Eq. (20.2) into Eq. (20.3), we get the following equivalent expressions for e :

$$\text{Thermal efficiency of an engine } e = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 - \frac{|Q_C|}{|Q_H|} \quad (20.4)$$

Work done by engine Heat rejected by engine
Heat absorbed by engine

Note that e is a quotient of two energy quantities and thus is a pure number, without units. Of course, we must always express W , Q_H , and Q_C in the same units.

Figure 20.3 Schematic energy-flow diagram for a heat engine.



BIO APPLICATION Biological Efficiency

Although a biological organism is not a heat engine, the concept of efficiency still applies: Here e is the ratio of the work done to the energy that was used to do that work. To exercise on a stationary bike, your body must first convert the chemical-bond energy in glucose to chemical-bond energy in ATP (adenosine triphosphate), then convert energy from ATP into motion of your leg muscles, and finally convert muscular motion into motion of the pedals. The overall efficiency of this entire process is only about 25%. The remaining 75% of the energy liberated from glucose goes into heat.



PROBLEM-SOLVING STRATEGY 20.1 Heat Engines

Problems involving heat engines are, fundamentally, problems in the first law of thermodynamics. You should review Problem-Solving Strategy 19.1 (Section 19.4).

IDENTIFY *the relevant concepts:* A heat engine is any device that converts heat partially to work, as shown schematically in Fig. 20.3. We'll see in Section 20.4 that a refrigerator is essentially a heat engine running in reverse, so many of the same concepts apply.

SET UP *the problem* as suggested in Problem-Solving Strategy 19.1: Use Eq. (20.4) if the thermal efficiency of the engine is relevant. Sketch an energy-flow diagram like Fig. 20.3.

EXECUTE *the solution* as follows:

1. Be careful with the sign conventions for W and the various Q 's. W is positive when the system expands and does work; W is negative when the system is compressed and work is done on it.

Each Q is positive if it represents heat entering the system and is negative if it represents heat leaving the system. When you know that a quantity is negative, such as Q_C in the above discussion, it sometimes helps to write it as $Q_C = -|Q_C|$.

2. Power is work per unit time ($P = W/t$), and rate of heat transfer (heat current) H is heat transfer per unit time ($H = Q/t$). In problems involving these concepts it helps to ask, "What is W or Q in one second (or one hour)?"
3. Keeping steps 1 and 2 in mind, solve for the target variables.

EVALUATE *your answer:* Use the first law of thermodynamics to check your results. Pay particular attention to algebraic signs.

EXAMPLE 20.1 Analyzing a heat engine

WITH VARIATION PROBLEMS

A gasoline truck engine takes in 10,000 J of heat and delivers 2000 J of mechanical work per cycle. The heat is obtained by burning gasoline with heat of combustion $L_c = 5.0 \times 10^4$ J/g. (a) What is the thermal efficiency of this engine? (b) How much heat is discarded in each cycle? (c) If the engine goes through 25 cycles per second, what is its power output in watts? In horsepower? (d) How much gasoline is burned in each cycle? (e) How much gasoline is burned per second? Per hour?

IDENTIFY and SET UP This problem concerns a heat engine, so we can use the ideas of this section. **Figure 20.4** is our energy-flow diagram for one cycle. In each cycle the engine does $W = 2000$ J of work and takes in heat $Q_H = 10,000$ J. We use Eq. (20.4), in the form $e = W/Q_H$, to find the thermal efficiency. We use Eq. (20.2) to find the amount of heat Q_C rejected per cycle. The heat of combustion tells us how much gasoline must be burned per cycle and hence per unit time. The power output is the time rate at which the work W is done.

EXECUTE (a) From Eq. (20.4), the thermal efficiency is

$$e = \frac{W}{Q_H} = \frac{2000 \text{ J}}{10,000 \text{ J}} = 0.20 = 20\%$$

- (b) From Eq. (20.2), $W = Q_H + Q_C$, so

$$Q_C = W - Q_H = 2000 \text{ J} - 10,000 \text{ J} = -8000 \text{ J}$$

That is, 8000 J of heat leaves the engine during each cycle.

- (c) The power P equals the work per cycle multiplied by the number of cycles per second:

$$\begin{aligned} P &= (2000 \text{ J/cycle})(25 \text{ cycles/s}) = 50,000 \text{ W} = 50 \text{ kW} \\ &= (50,000 \text{ W}) \frac{1 \text{ hp}}{746 \text{ W}} = 67 \text{ hp} \end{aligned}$$

- (d) Let m be the mass of gasoline burned during each cycle. Then $Q_H = mL_c$ and

$$m = \frac{Q_H}{L_c} = \frac{10,000 \text{ J}}{5.0 \times 10^4 \text{ J/g}} = 0.20 \text{ g}$$

- (e) The mass of gasoline burned per second equals the mass per cycle multiplied by the number of cycles per second:

$$(0.20 \text{ g/cycle})(25 \text{ cycles/s}) = 5.0 \text{ g/s}$$

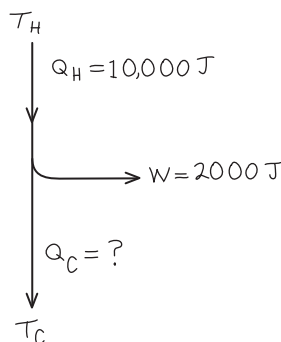
The mass burned per hour is

$$(5.0 \text{ g/s}) \frac{3600 \text{ s}}{1 \text{ h}} = 18,000 \text{ g/h} = 18 \text{ kg/h}$$

EVALUATE An efficiency of 20% is fairly typical for cars and trucks if W includes only the work delivered to the wheels. We can check the mass burned per hour by expressing it in miles per gallon ("mileage"). The density of gasoline is about 0.70 g/cm^3 , so this is about $25,700 \text{ cm}^3$, 25.7 L, or 6.8 gallons of gasoline per hour. If the truck is traveling at 55 mi/h (88 km/h), this represents fuel consumption of 8.1 miles/gallon (3.4 km/L). This is a fairly typical mileage for large trucks.

KEYCONCEPT A heat engine takes in energy in the form of heat from a hot reservoir, uses some of that energy to do work, and rejects the remaining energy as heat that goes into a cold reservoir. The fraction of the heat from the hot reservoir that is converted into work is called the thermal efficiency of the engine.

Figure 20.4 Our sketch for this problem.



TEST YOUR UNDERSTANDING OF SECTION 20.2 Rank the following heat engines in order from highest to lowest thermal efficiency. (i) An engine that in one cycle absorbs 5000 J of heat and rejects 4500 J of heat; (ii) an engine that in one cycle absorbs 25,000 J of heat and does 2000 J of work; (iii) an engine that in one cycle does 400 J of work and rejects 2800 J of heat.

ANSWER

$$\begin{aligned} e &= 0.125. \\ W &= 400 \text{ J and } Q_C = -2800 \text{ J, so } Q_H = W - Q_C = 400 \text{ J} - (-2800 \text{ J}) = 3200 \text{ J and } e = 400 \text{ J} / (3200 \text{ J}) = 0.125. \\ Q_H &= 25,000 \text{ J and } W = 2000 \text{ J, so } e = 2000 \text{ J} / (25,000 \text{ J}) = 0.080. \text{ For engine (iii)} \\ W &= 5000 \text{ J and } Q_C = -4500 \text{ J, so } Q_H = 5000 \text{ J} + (-4500 \text{ J}) = 500 \text{ J and } e = 500 \text{ J} / (5000 \text{ J}) = 0.100. \text{ For engine (i)} \\ W &= Q_H + Q_C = |Q_H| - |Q_C|. \text{ For engine (i) } Q_H = 5000 \text{ J and } Q_C = -4500 \text{ J, so } W = 5000 \text{ J} - (-4500 \text{ J}) = 9500 \text{ J.} \\ \text{From Eq. (20.4) the efficiency is } e = W / Q_H, \text{ and from Eq. (20.2)} \end{aligned}$$

20.3 INTERNAL-COMBUSTION ENGINES

The gasoline engine, used in automobiles and many other types of machinery, is a familiar example of a heat engine. Let's look at its thermal efficiency. **Figure 20.5** shows the operation of one type of gasoline engine. First a mixture of air and gasoline vapor flows into a cylinder through an open intake valve while the piston descends, increasing the volume of the cylinder from a minimum of V (when the piston is all the way up) to a maximum of rV (when it is all the way down). The quantity r is called the **compression ratio**; for present-day automobile engines its value is typically 8 to 10. At the end of this *intake stroke*, the intake valve closes and the mixture is compressed, approximately adiabatically, to volume V during the *compression stroke*. The mixture is then ignited by the spark plug, and the heated gas expands, approximately adiabatically, back to volume rV , pushing on the piston and doing work; this is the *power stroke*. Finally, the exhaust valve opens, and the combustion products are pushed out (during the *exhaust stroke*), leaving the cylinder ready for the next intake stroke.

The Otto Cycle

Figure 20.6 (next page) is a pV -diagram for an idealized model of the thermodynamic processes in a gasoline engine. This model is called the **Otto cycle**. At point a the gasoline–air mixture has entered the cylinder. The mixture is compressed adiabatically to point b and is then ignited. Heat Q_H is added to the system by the burning gasoline along line bc , and the power stroke is the adiabatic expansion to d . The gas is cooled to the temperature of the outside air along line da ; during this process, heat $|Q_C|$ is rejected. This gas leaves the engine as exhaust and does not enter the engine again. But since an equivalent amount of gasoline and air enters, we may consider the process to be cyclic.

Figure 20.5 Cycle of a four-stroke internal-combustion engine.

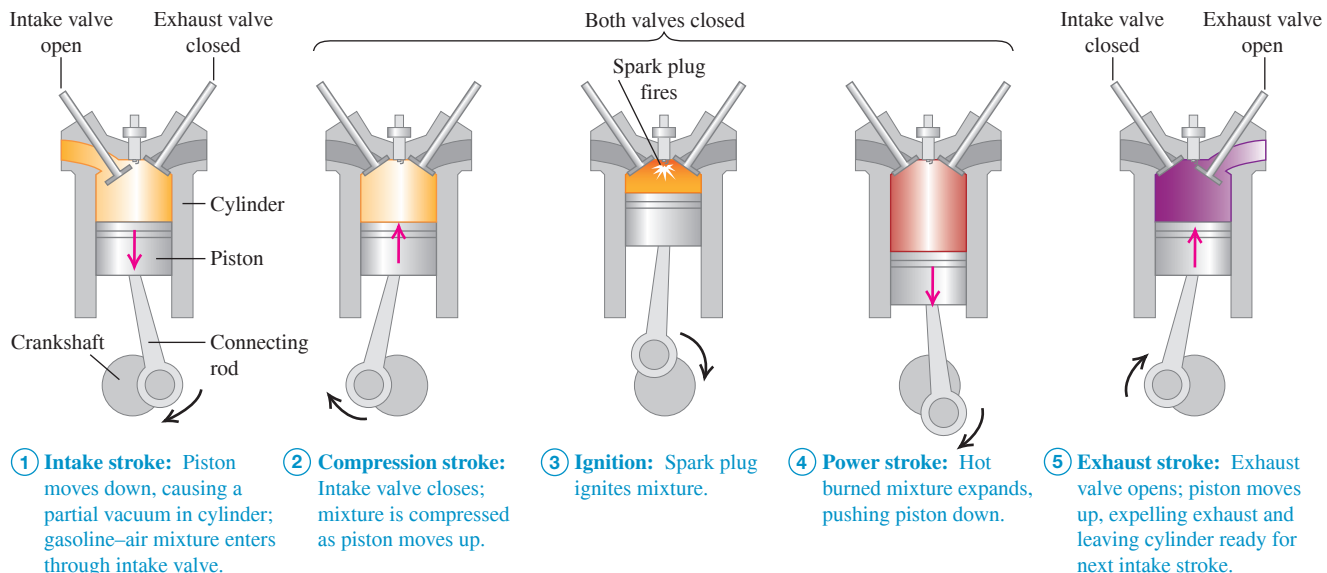
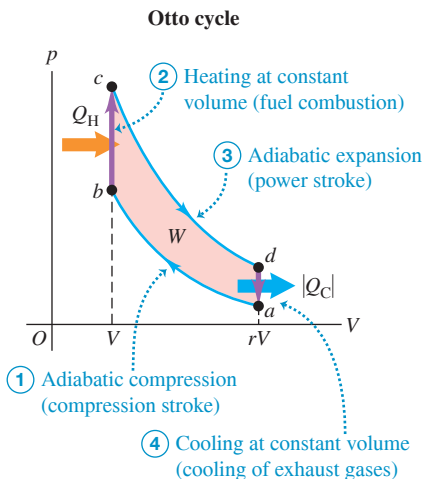


Figure 20.6 The pV -diagram for the Otto cycle, an idealized model of the thermodynamic processes in a gasoline engine.



We can calculate the efficiency of this idealized cycle. Processes bc and da are constant-volume, so the heats Q_H and Q_C are related simply to the temperatures at points a , b , c , and d :

$$Q_H = nC_V(T_c - T_b) > 0$$

$$Q_C = nC_V(T_a - T_d) < 0$$

The thermal efficiency is given by Eq. (20.4). Inserting the above expressions and canceling out the common factor nC_V , we find

$$e = \frac{Q_H + Q_C}{Q_H} = \frac{T_c - T_b + T_a - T_d}{T_c - T_b} \quad (20.5)$$

To simplify this further, we use the temperature–volume relationship for adiabatic processes for an ideal gas, Eq. (19.22). For the two adiabatic processes ab and cd ,

$$T_a(rV)^{\gamma-1} = T_b V^{\gamma-1} \quad \text{and} \quad T_d(rV)^{\gamma-1} = T_c V^{\gamma-1}$$

where γ is the ratio of heat capacities for the gas in the engine (see Section 19.7). We divide each of these equations by the common factor $V^{\gamma-1}$ and substitute the resulting expressions for T_b and T_c back into Eq. (20.5). The result is

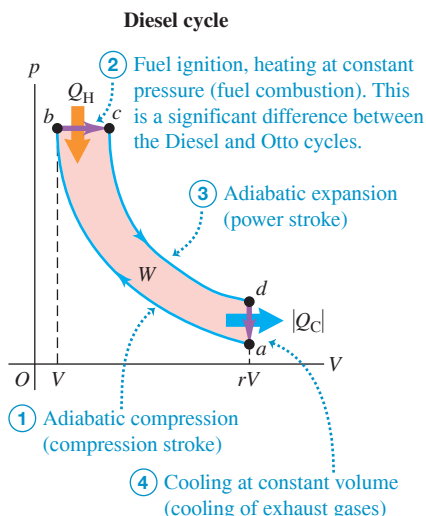
$$e = \frac{T_d r^{\gamma-1} - T_a r^{\gamma-1} + T_a - T_d}{T_d r^{\gamma-1} - T_a r^{\gamma-1}} = \frac{(T_d - T_a)(r^{\gamma-1} - 1)}{(T_d - T_a)r^{\gamma-1}}$$

Dividing out the common factor $(T_d - T_a)$, we get

$$\text{Thermal efficiency in Otto cycle} \quad e = 1 - \frac{1}{r^{\gamma-1}} \quad (20.6)$$

Compression ratio $\rightarrow r$ Ratio of heat capacities $\rightarrow \gamma$

Figure 20.7 The pV -diagram for the idealized Diesel cycle.



The thermal efficiency given by Eq. (20.6) is always less than unity, even for this idealized model. With $r = 8$ and $\gamma = 1.4$ (the value for air) the theoretical efficiency is $e = 0.56$, or 56%. The efficiency can be increased by increasing r . However, this also increases the temperature at the end of the adiabatic compression of the air–fuel mixture. If the temperature is too high, the mixture explodes spontaneously during compression instead of burning evenly after the spark plug ignites it. This is called *pre-ignition* or *detonation*; it causes a knocking sound and can damage the engine. The octane rating of a gasoline is a measure of its antiknock qualities. The maximum practical compression ratio for high-octane, or “premium,” gasoline is about 10 to 13.

The Otto cycle is a highly idealized model. It assumes that the mixture behaves as an ideal gas; it ignores friction, turbulence, loss of heat to cylinder walls, and many other effects that reduce the efficiency of an engine. Efficiencies of real gasoline engines are typically around 35%.

The Diesel Cycle

The Diesel engine is similar in operation to the gasoline engine. The most important difference is that there is no fuel in the cylinder at the beginning of the compression stroke. A little before the beginning of the power stroke, the injectors start to inject fuel directly into the cylinder, just fast enough to keep the pressure approximately constant during the first part of the power stroke. Because of the high temperature developed during the adiabatic compression, the fuel ignites spontaneously as it is injected; no spark plugs are needed.

Figure 20.7 shows the idealized **Diesel cycle**. Starting at point a , air is compressed adiabatically to point b , heated at constant pressure to point c , expanded adiabatically to point d , and cooled at constant volume to point a . Because there is no fuel in the cylinder during most of the compression stroke, pre-ignition cannot occur, and the compression ratio r can be much higher than for a gasoline engine. This improves efficiency

and ensures reliable ignition when the fuel is injected (because of the high temperature reached during the adiabatic compression). Values of r of 15 to 20 are typical; with these values and $\gamma = 1.4$, the theoretical efficiency of the idealized Diesel cycle is about 0.65 to 0.70. As with the Otto cycle, the efficiency of any actual engine is substantially less than this. While Diesel engines are very efficient, they must be built to much tighter tolerances than gasoline engines and the fuel-injection system requires careful maintenance.

TEST YOUR UNDERSTANDING OF SECTION 20.3 For an Otto-cycle engine with cylinders of a fixed size and a fixed compression ratio, which of the following aspects of the pV -diagram in Fig. 20.6 would change if you doubled the amount of fuel burned per cycle? (There may be more than one correct answer.) (i) The vertical distance between points b and c ; (ii) the vertical distance between points a and d ; (iii) the horizontal distance between points b and a .

ANSWER (i), (ii), (iii) Doubling the amount of fuel burned per cycle means that Q_H is doubled, so the resulting pressure increase from b to c in Fig. 20.6 is greater. The compression ratio and hence the efficiency remain the same, so $|Q_C|$ (the amount of heat rejected to the environment) must increase by the same factor as Q_H . Hence the pressure drop from d to a in Fig. 20.6 is also greater. The volume V and the compression ratio r don't change, so the horizontal dimensions of the pV -diagram don't change.

20.4 REFRIGERATORS

We can think of a **refrigerator** as a heat engine operating in reverse. A heat engine takes heat from a hot place and gives off heat to a colder place. A refrigerator does the opposite; it takes heat from a cold place (the inside of the refrigerator) and gives it off to a warmer place (usually the air in the room where the refrigerator is located). A heat engine has a net *output* of mechanical work; the refrigerator requires a net *input* of mechanical work. With the sign conventions from Section 20.2, for a refrigerator Q_C is positive but both W and Q_H are negative; hence $|W| = -W$ and $|Q_H| = -Q_H$.

Figure 20.8 shows an energy-flow diagram for a refrigerator. From the first law for a cyclic process,

$$Q_H + Q_C - W = 0 \quad \text{or} \quad -Q_H = Q_C - W$$

or, because both Q_H and W are negative,

$$|Q_H| = Q_C + |W| \quad (20.7)$$

Thus, as the diagram shows, the heat $|Q_H|$ leaving the working substance and given to the hot reservoir is always *greater* than the heat Q_C taken from the cold reservoir. Note that the absolute-value relationship

$$|Q_H| = |Q_C| + |W| \quad (20.8)$$

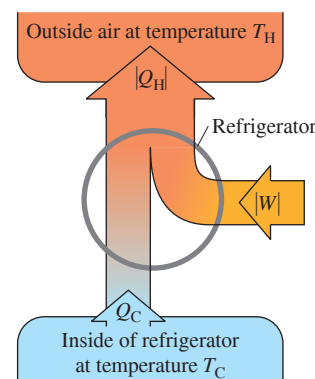
is valid for both heat engines and refrigerators.

From an economic point of view, the best refrigeration cycle is one that removes the greatest amount of heat $|Q_C|$ from the inside of the refrigerator for the least expenditure of mechanical work, $|W|$. The relevant ratio is therefore $|Q_C|/|W|$; the larger this ratio, the better the refrigerator. We call this ratio the **coefficient of performance**, K . From Eq. (20.8), $|W| = |Q_H| - |Q_C|$, so

$$K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|} \quad (20.9)$$

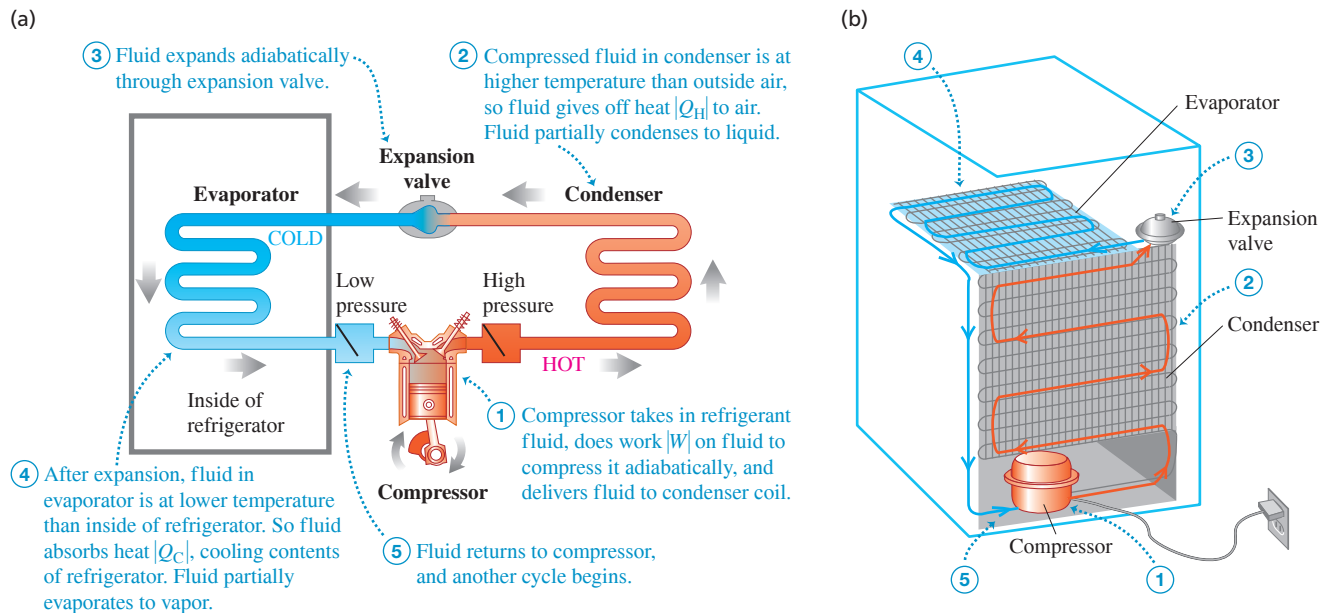
Coefficient of performance of a refrigerator Heat removed from inside of refrigerator
Work input of refrigerator Heat rejected to outside air

Figure 20.8 Schematic energy-flow diagram of a refrigerator.



As always, we measure Q_H , Q_C , and W all in the same energy units; K is then a dimensionless number.

Figure 20.9 (a) Principle of the mechanical refrigeration cycle. (b) How the key elements are arranged in a practical refrigerator.

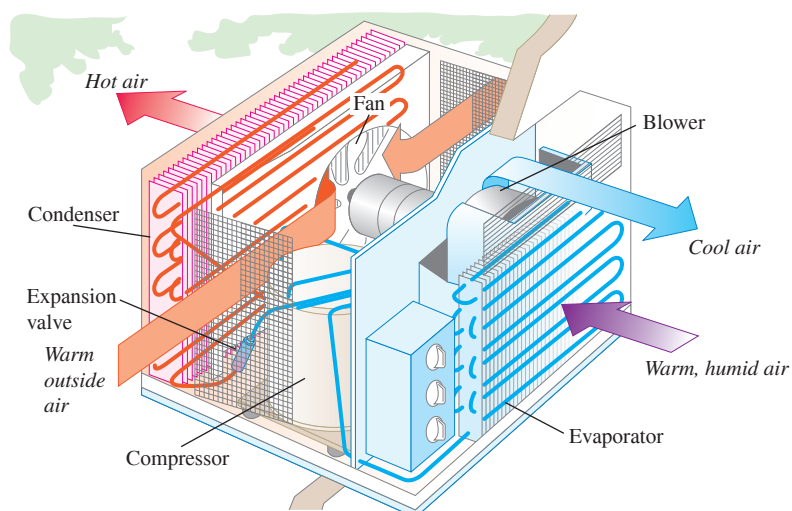


Practical Refrigerators

Figure 20.9a shows the principles of the cycle used in home refrigerators. The fluid “circuit” contains a refrigerant fluid (the working substance). The left side of the circuit (including the cooling coils inside the refrigerator) is at low temperature and low pressure; the right side (including the condenser coils outside the refrigerator) is at high temperature and high pressure. Ordinarily, both sides contain liquid and vapor in phase equilibrium. In each cycle the fluid absorbs heat $|Q_C|$ from the inside of the refrigerator on the left side and gives off heat $|Q_H|$ to the surrounding air on the right side. The compressor, usually driven by an electric motor (Fig. 20.9b), does work $|W|$ on the fluid during each cycle. So the compressor requires energy input, which is why refrigerators have to be plugged in.

An air conditioner operates on exactly the same principle. In this case the refrigerator box becomes a room or an entire building. The evaporator coils are inside, the condenser is outside, and fans circulate air through these (Fig. 20.10). In large installations the condenser coils are often cooled by water. For air conditioners the quantities of greatest practical importance are the *rate* of heat removal (the heat current H from the region being

Figure 20.10 An air conditioner works on the same principle as a refrigerator.



cooled) and the *power* input $P = W/t$ to the compressor. If heat $|Q_C|$ is removed in time t , then $H = |Q_C|/t$. Then we can express the coefficient of performance as

$$K = \frac{|Q_C|}{|W|} = \frac{Ht}{Pt} = \frac{H}{P}$$

Typical room air conditioners have heat removal rates H of about 1500–3000 W and require electric power input of about 600 to 1200 W. Typical coefficients of performance are about 3; the actual values depend on the inside and outside temperatures.

A variation on this theme is the **heat pump**, used to heat buildings by cooling the outside air. It functions like a refrigerator turned inside out. The evaporator coils are outside, where they take heat from cold air, and the condenser coils are inside, where they give off heat to the warmer air. With proper design, the heat $|Q_H|$ delivered to the inside per cycle can be considerably greater than the work $|W|$ required to get it there.

Work is *always* needed to transfer heat from a colder to a hotter object. Heat flows spontaneously from hotter to colder, and to reverse this flow requires the addition of work from the outside. Experience shows that it is impossible to make a refrigerator that transports heat from a colder object to a hotter object without the addition of work. If no work were needed, the coefficient of performance would be infinite. We call such a device a *workless refrigerator*; it is a mythical beast, like the unicorn and the free lunch.

TEST YOUR UNDERSTANDING OF SECTION 20.4 Can you cool your house by leaving the refrigerator door open?

ANSWER

A refrigerator uses an input of work to transfer heat from one system (the refrigerator's interior) to another system (its exterior, which includes the house in which the refrigerator is installed). If the door is open, these two systems are really the *same* system and will eventually come to the same temperature. By the first law of thermodynamics, all of the work input to the refrigerator motor will be converted into heat and the temperature in your house will actually *increase*. To cool the house you need a system that will transfer heat from it to the outside world, such as an air conditioner or heat pump.

20.5 THE SECOND LAW OF THERMODYNAMICS

Experimental evidence suggests strongly that it is *impossible* to build a heat engine that converts heat completely to work—that is, an engine with 100% thermal efficiency. This impossibility is the basis of one statement of the **second law of thermodynamics**, as follows:

SECOND LAW OF THERMODYNAMICS (“engine” statement) It is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature and converts the heat completely into mechanical work, with the system ending in the same state in which it began.

This is also known to physicists as the *Kelvin–Planck statement* of the second law.

The basis of the second law of thermodynamics is the difference between the nature of internal energy and that of macroscopic mechanical energy. In a moving object the molecules have random motion, but superimposed on this is a coordinated motion of every molecule in the direction of the object's velocity. The kinetic energy associated with this *coordinated* macroscopic motion is what we call the kinetic energy of the moving object. The kinetic and potential energies associated with the *random* motion constitute the internal energy.

When an object sliding on a surface comes to rest as a result of friction, the organized motion of the object is converted to random motion of molecules in the object and in the surface. Since we cannot control the motions of individual molecules, we cannot convert this random motion completely back to organized motion. We can convert *part* of it, and this is what a heat engine does.

If the second law were *not* true, we could power an automobile or run a power plant by cooling the surrounding air. Neither of these impossibilities violates the *first* law of thermodynamics. The second law, therefore, is not a deduction from the first but stands by itself as a separate law of nature. The first law denies the possibility of creating or destroying energy; the second law limits the *availability* of energy and the ways in which it can be used and converted.

Restating the Second Law

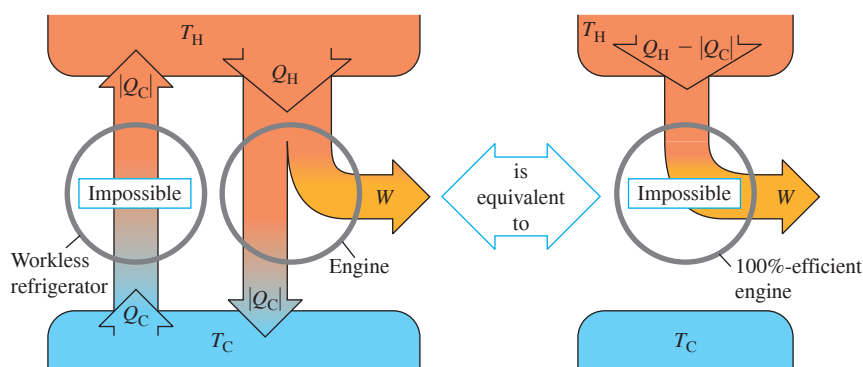
Our analysis of refrigerators in Section 20.4 forms the basis for an alternative statement of the second law of thermodynamics. Heat flows spontaneously from hotter to colder objects, never the reverse. A refrigerator does take heat from a colder to a hotter object, but its operation requires an input of mechanical energy or work. We can generalize this observation:

SECOND LAW OF THERMODYNAMICS (“refrigerator” statement) It is impossible for any process to have as its sole result the transfer of heat from a cooler to a hotter object.

This is also known as the *Clausius statement* of the second law. It may not seem to be very closely related to the “engine” statement. In fact, though, the two statements are completely equivalent. For example, if we could build a workless refrigerator, violating the second or “refrigerator” statement of the second law, we could use it in conjunction with a heat engine, pumping the heat rejected by the engine back to the hot reservoir to be reused. This composite machine (**Fig. 20.11a**) would violate the “engine” statement of the second

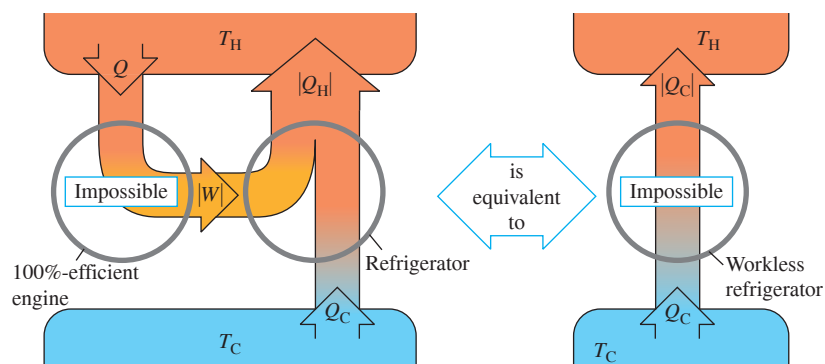
Figure 20.11 Energy-flow diagrams showing that the two forms of the second law are equivalent.

(a) The “engine” statement of the second law of thermodynamics



If a workless refrigerator were possible, it could be used in conjunction with an ordinary heat engine to form a 100%-efficient engine, converting heat $Q_H - |Q_C|$ completely to work.

(b) The “refrigerator” statement of the second law of thermodynamics



If a 100%-efficient engine were possible, it could be used in conjunction with an ordinary refrigerator to form a workless refrigerator, transferring heat Q_C from the cold to the hot reservoir with no input of work.

law because its net effect would be to take a net quantity of heat $Q_H - |Q_C|$ from the hot reservoir and convert it completely to work W .

Alternatively, if we could make an engine with 100% thermal efficiency, in violation of the first statement, we could run it using heat from the hot reservoir and use the work output to drive a refrigerator that pumps heat from the cold reservoir to the hot (Fig. 20.11b). This composite device would violate the “refrigerator” statement because its net effect would be to take heat Q_C from the cold reservoir and deliver it to the hot reservoir without requiring any input of work. Thus any device that violates one form of the second law can be used to make a device that violates the other form. If violations of the first form are impossible, so are violations of the second!

The conversion of work to heat and the heat flow from hot to cold across a finite temperature gradient are *irreversible* processes. The “engine” and “refrigerator” statements of the second law state that these processes can be only partially reversed. We could cite other examples. Gases naturally flow from a region of high pressure to a region of low pressure; gases and miscible liquids left by themselves always tend to mix, not to unmix. The second law of thermodynamics is an expression of the inherent one-way aspect of these and many other irreversible processes. Energy conversion is an essential aspect of all plant and animal life and of human technology, so the second law of thermodynamics is of fundamental importance.

TEST YOUR UNDERSTANDING OF SECTION 20.5 Would a 100%-efficient engine (Fig. 20.11a) violate the *first* law of thermodynamics? What about a workless refrigerator (Fig. 20.11b)?

ANSWER

no, no Both the 100%-efficient engine of Fig. 20.11a and the workless refrigerator of Fig. 20.11b return to the same state at the end of a cycle as at the beginning, so the net change in internal energy of each system is zero ($\Delta U = 0$). For the 100%-efficient engine, the net heat flow into the engine equals the net work done, so $Q = W$, and the first law ($\Delta U = 0$) is obeyed. For the workless refrigerator, no net work is done (so $W = 0$) and as much heat flows into it as out (so $Q = 0$), so again $Q = W = 0$ and $\Delta U = 0$ in accordance with the first law. It is the *second* law of thermodynamics that tells us that both the 100%-efficient engine and the workless refrigerator are impossible.

20.6 THE CARNOT CYCLE

According to the second law, no heat engine can have 100% efficiency. How great an efficiency *can* an engine have, given two heat reservoirs at temperatures T_H and T_C ? This question was answered in 1824 by the French engineer Sadi Carnot (1796–1832), who developed a hypothetical, idealized heat engine that has the maximum possible efficiency consistent with the second law. The cycle of this engine is called the **Carnot cycle**.

To understand the rationale of the Carnot cycle, we return to *reversibility* and its relationship to directions of thermodynamic processes. Conversion of work to heat is an irreversible process; the purpose of a heat engine is a *partial* reversal of this process, the conversion of heat to work with as great an efficiency as possible. For maximum heat-engine efficiency, therefore, *we must avoid all irreversible processes* (Fig. 20.12).

Heat flow through a finite temperature drop is an irreversible process. Therefore, during heat transfer in the Carnot cycle there must be *no* finite temperature difference. When the engine takes heat from the hot reservoir at temperature T_H , the working substance of the engine must also be at T_H ; otherwise, irreversible heat flow would occur. Similarly, when the engine discards heat to the cold reservoir at T_C , the engine itself must be at T_C . That is, every process that involves heat transfer must be *isothermal* at either T_H or T_C .

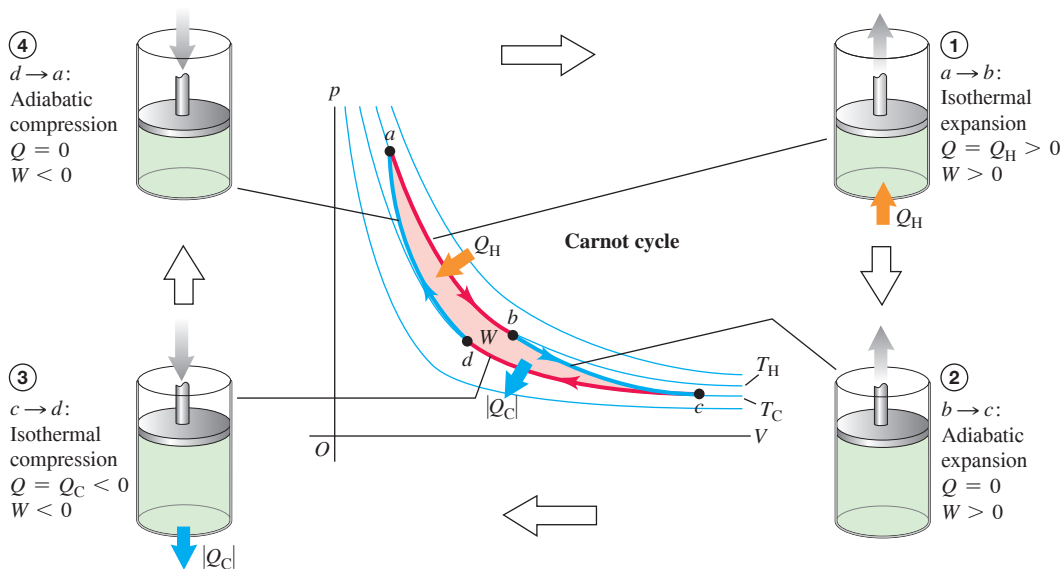
Conversely, in any process in which the temperature of the working substance of the engine is intermediate between T_H and T_C , there must be *no* heat transfer between the engine and either reservoir because such heat transfer could not be reversible. Therefore any process in which the temperature T of the working substance changes must be *adiabatic*.

The bottom line is that every process in our idealized cycle must be either isothermal or adiabatic. In addition, thermal and mechanical equilibrium must be maintained at all times so that each process is completely reversible.

Figure 20.12 The temperature of the firebox of a steam engine is much higher than the temperature of water in the boiler, so heat flows irreversibly from firebox to water. Carnot’s quest to understand the efficiency of steam engines led him to the idea that an ideal engine would involve only *reversible* processes.



Figure 20.13 The Carnot cycle for an ideal gas. The light blue lines in the pV -diagram are isotherms (curves of constant temperature) and the dark blue lines are adiabats (curves of zero heat flow).



Steps of the Carnot Cycle

The Carnot cycle consists of two reversible isothermal and two reversible adiabatic processes. **Figure 20.13** shows a Carnot cycle using as its working substance an ideal gas in a cylinder with a piston. It consists of the following steps:

1. The gas expands isothermally at temperature T_H , absorbing heat Q_H (ab).
2. It expands adiabatically until its temperature drops to T_C (bc).
3. It is compressed isothermally at T_C , rejecting heat $|Q_C|$ (cd).
4. It is compressed adiabatically back to its initial state at temperature T_H (da).

We can calculate the thermal efficiency e of a Carnot engine in the special case shown in Fig. 20.13 in which the working substance is an *ideal gas*. To do this, we'll first find the ratio Q_C/Q_H of the quantities of heat transferred in the two isothermal processes and then use Eq. (20.4) to find e .

For an ideal gas the internal energy U depends only on temperature and is thus constant in any isothermal process. For the isothermal expansion ab , $\Delta U_{ab} = 0$ and Q_H is equal to the work W_{ab} done by the gas during its isothermal expansion at temperature T_H . We calculated this work in Example 19.1 (Section 19.2); using that result, we have

$$Q_H = W_{ab} = nRT_H \ln \frac{V_b}{V_a} \quad (20.10)$$

Similarly,

$$Q_C = W_{cd} = nRT_C \ln \frac{V_d}{V_c} = -nRT_C \ln \frac{V_c}{V_d} \quad (20.11)$$

Because V_d is less than V_c , Q_C is negative ($Q_C = -|Q_C|$); heat flows out of the gas during the isothermal compression at temperature T_C .

The ratio of the two quantities of heat is thus

$$\frac{Q_C}{Q_H} = -\left(\frac{T_C}{T_H}\right) \frac{\ln(V_c/V_d)}{\ln(V_b/V_a)} \quad (20.12)$$

This can be simplified further by use of the temperature–volume relationship for an adiabatic process, Eq. (19.22). We find for the two adiabatic processes:

$$T_H V_b^{\gamma-1} = T_C V_c^{\gamma-1} \quad \text{and} \quad T_H V_a^{\gamma-1} = T_C V_d^{\gamma-1}$$

Dividing the first of these by the second, we find

$$\frac{V_b^{\gamma-1}}{V_a^{\gamma-1}} = \frac{V_c^{\gamma-1}}{V_d^{\gamma-1}} \quad \text{and} \quad \frac{V_b}{V_a} = \frac{V_c}{V_d}$$

Thus the two logarithms in Eq. (20.12) are equal, and that equation reduces to

$$\frac{Q_C}{Q_H} = -\frac{T_C}{T_H} \quad \text{or} \quad \frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H} \quad (\text{heat transfer in a Carnot engine}) \quad (20.13)$$

The ratio of the heat rejected at T_C to the heat absorbed at T_H is just equal to the ratio T_C/T_H . Then from Eq. (20.4) the efficiency of the Carnot engine is

$$\text{Efficiency of a Carnot engine } e_{\text{Carnot}} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H} \quad (20.14)$$

Temperature of hot reservoir Temperature of cold reservoir

This simple result says that the efficiency of a Carnot engine depends only on the temperatures of the two heat reservoirs. The efficiency is large when the temperature *difference* is large, and it is very small when the temperatures are nearly equal. The efficiency can never be exactly unity unless $T_C = 0$; we'll see later that this, too, is impossible.

CAUTION Use Kelvin temperature in all Carnot calculations In Carnot-cycle calculations, you must use *absolute* (Kelvin) temperatures only. That's because Eqs. (20.10) through (20.14) come from the ideal-gas equation $pV = nRT$, in which T is absolute temperature. ■

EXAMPLE 20.2 Analyzing a Carnot engine I

WITH VARIATION PROBLEMS

A Carnot engine takes 2000 J of heat from a reservoir at 500 K, does some work, and discards some heat to a reservoir at 350 K. How much work does it do, how much heat is discarded, and what is its efficiency?

IDENTIFY and SET UP This problem involves a Carnot engine, so we can use the ideas of this section and those of Section 20.2 (which apply to heat engines of all kinds). **Figure 20.14** shows the energy-flow diagram. We have $Q_H = 2000$ J, $T_H = 500$ K, and $T_C = 350$ K. We use Eq. (20.13) to find Q_C , and then use the first law of thermodynamics as given by Eq. (20.2) to find W . We find the efficiency e from T_C and T_H from Eq. (20.14).

EXECUTE From Eq. (20.13),

$$Q_C = -Q_H \frac{T_C}{T_H} = -(2000 \text{ J}) \frac{350 \text{ K}}{500 \text{ K}} = -1400 \text{ J}$$

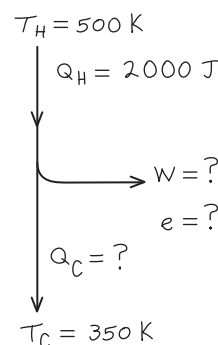
Then from Eq. (20.2), the work done is

$$W = Q_H + Q_C = 2000 \text{ J} + (-1400 \text{ J}) = 600 \text{ J}$$

From Eq. (20.14), the thermal efficiency is

$$e = 1 - \frac{T_C}{T_H} = 1 - \frac{350 \text{ K}}{500 \text{ K}} = 0.30 = 30\%$$

Figure 20.14 Our sketch for this problem.



EVALUATE The negative sign of Q_C is correct: It shows that 1400 J of heat flows *out* of the engine and into the cold reservoir. We can check our result for e by using the basic definition of thermal efficiency, Eq. (20.3):

$$e = \frac{W}{Q_H} = \frac{600 \text{ J}}{2000 \text{ J}} = 0.30 = 30\%$$

KEYCONCEPT An engine that utilizes the Carnot cycle, which consists of only reversible isothermal and reversible adiabatic processes, has the greatest efficiency possible consistent with the second law of thermodynamics. The smaller the ratio of the temperature of the cold reservoir to the temperature of the hot reservoir, the greater the Carnot efficiency.

EXAMPLE 20.3 Analyzing a Carnot engine II

WITH VARIATION PROBLEMS

Suppose 0.200 mol of an ideal diatomic gas ($\gamma = 1.40$) undergoes a Carnot cycle between 227°C and 27°C, starting at $p_a = 10.0 \times 10^5$ Pa at point a in the pV -diagram of Fig. 20.13. The volume doubles during the isothermal expansion step $a \rightarrow b$. (a) Find the pressure and volume at points a , b , c , and d . (b) Find Q , W , and ΔU for each step and for the entire cycle. (c) Find the efficiency directly from the results of part (b), and compare with the value calculated from Eq. (20.14).

IDENTIFY and SET UP This problem involves the properties of the Carnot cycle and those of an ideal gas. We are given the number of moles n and the pressure and temperature at point a (which is at the higher of the two reservoir temperatures); we can find the volume at a from the ideal-gas equation $pV = nRT$. We then find the pressure and volume at points b , c , and d from the known doubling of volume in step $a \rightarrow b$, from equations given in this section, and from $pV = nRT$. In each step we use Eqs. (20.10) and (20.11) to find the heat flow and work done and Eq. (19.13) to find the internal energy change.

EXECUTE (a) With $T_H = (227 + 273.15) \text{ K} = 500 \text{ K}$ and $T_C = (27 + 273.15) \text{ K} = 300 \text{ K}$, $pV = nRT$ yields

$$V_a = \frac{nRT_H}{p_a} = \frac{(0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(500 \text{ K})}{10.0 \times 10^5 \text{ Pa}} \\ = 8.31 \times 10^{-4} \text{ m}^3$$

The volume doubles during the isothermal expansion $a \rightarrow b$:

$$V_b = 2V_a = 2(8.31 \times 10^{-4} \text{ m}^3) = 16.6 \times 10^{-4} \text{ m}^3$$

Because the expansion $a \rightarrow b$ is isothermal, $p_a V_a = p_b V_b$, so

$$p_b = \frac{p_a V_a}{V_b} = 5.00 \times 10^5 \text{ Pa}$$

For the adiabatic expansion $b \rightarrow c$, we use the equation $T_H V_b^{\gamma-1} = T_C V_c^{\gamma-1}$ that follows Eq. (20.12) as well as the ideal-gas equation:

$$V_c = V_b \left(\frac{T_H}{T_C} \right)^{1/(\gamma-1)} = (16.6 \times 10^{-4} \text{ m}^3) \left(\frac{500 \text{ K}}{300 \text{ K}} \right)^{2.5} \\ = 59.6 \times 10^{-4} \text{ m}^3 \\ p_c = \frac{nRT_C}{V_c} = \frac{(0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{59.6 \times 10^{-4} \text{ m}^3} \\ = 0.837 \times 10^5 \text{ Pa}$$

For the adiabatic compression $d \rightarrow a$, we have $T_C V_d^{\gamma-1} = T_H V_a^{\gamma-1}$ and so

$$V_d = V_a \left(\frac{T_H}{T_C} \right)^{1/(\gamma-1)} = (8.31 \times 10^{-4} \text{ m}^3) \left(\frac{500 \text{ K}}{300 \text{ K}} \right)^{2.5} \\ = 29.8 \times 10^{-4} \text{ m}^3 \\ p_d = \frac{nRT_C}{V_d} = \frac{(0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{29.8 \times 10^{-4} \text{ m}^3} \\ = 1.67 \times 10^5 \text{ Pa}$$

(b) For the isothermal expansion $a \rightarrow b$, $\Delta U_{ab} = 0$. From Eq. (20.10),

$$W_{ab} = Q_H = nRT_H \ln \frac{V_b}{V_a} \\ = (0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(500 \text{ K})(\ln 2) = 576 \text{ J}$$

For the adiabatic expansion $b \rightarrow c$, $Q_{bc} = 0$. From the first law of thermodynamics, $\Delta U_{bc} = Q_{bc} - W_{bc} = -W_{bc}$; the work W_{bc} done by the gas in this adiabatic expansion equals the negative of the change in internal energy of the gas. From Eq. (19.13) we have $\Delta U = nC_V \Delta T$, where $\Delta T = T_C - T_H$. Using $C_V = 20.8 \text{ J/mol} \cdot \text{K}$ for an ideal diatomic gas, we find

$$W_{bc} = -\Delta U_{bc} = -nC_V(T_C - T_H) = nC_V(T_H - T_C) \\ = (0.200 \text{ mol})(20.8 \text{ J/mol} \cdot \text{K})(500 \text{ K} - 300 \text{ K}) = 832 \text{ J}$$

For the isothermal compression $c \rightarrow d$, $\Delta U_{cd} = 0$; Eq. (20.11) gives

$$W_{cd} = Q_C = nRT_C \ln \frac{V_d}{V_c} \\ = (0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K}) \left(\ln \frac{29.8 \times 10^{-4} \text{ m}^3}{59.6 \times 10^{-4} \text{ m}^3} \right) \\ = -346 \text{ J}$$

For the adiabatic compression $d \rightarrow a$, $Q_{da} = 0$ and

$$W_{da} = -\Delta U_{da} = -nC_V(T_H - T_C) = nC_V(T_C - T_H) \\ = (0.200 \text{ mol})(20.8 \text{ J/mol} \cdot \text{K})(300 \text{ K} - 500 \text{ K}) = -832 \text{ J}$$

We can tabulate these results as follows:

Process	Q	W	ΔU
$a \rightarrow b$	576 J	576 J	0
$b \rightarrow c$	0	832 J	-832 J
$c \rightarrow d$	-346 J	-346 J	0
$d \rightarrow a$	0	-832 J	832 J
Total	230 J	230 J	0

(c) From the above table, $Q_H = 576 \text{ J}$ and the total work is 230 J. Thus

$$e = \frac{W}{Q_H} = \frac{230 \text{ J}}{576 \text{ J}} = 0.40 = 40\%$$

We can compare this to the result from Eq. (20.14),

$$e = \frac{T_H - T_C}{T_H} = \frac{500 \text{ K} - 300 \text{ K}}{500 \text{ K}} = 0.40 = 40\%$$

EVALUATE The table in part (b) shows that for the entire cycle $Q = W$ and $\Delta U = 0$, just as we would expect: In a complete cycle, the *net* heat input is used to do work, and there is zero net change in the internal energy of the system. Note also that the quantities of work in the two adiabatic processes are negatives of each other. Can you show from the analysis leading to Eq. (20.13) that this must *always* be the case in a Carnot cycle?

KEYCONCEPT When analyzing any of the steps taken by a heat engine as it goes through a thermodynamic cycle, if you can calculate any two of the quantities ΔU , Q , and W , you can calculate the third using the first law of thermodynamics, $\Delta U = Q - W$. The efficiency of the engine equals the sum of the work done in all steps divided by the heat taken in from the hot reservoir.

The Carnot Refrigerator

Because each step in the Carnot cycle is reversible, the *entire cycle* may be reversed, converting the engine into a refrigerator. The coefficient of performance of the Carnot refrigerator is obtained by combining the general definition of K , Eq. (20.9), with Eq. (20.13) for the Carnot cycle. We first rewrite Eq. (20.9) as

$$K = \frac{|Q_C|}{|Q_H| - |Q_C|} \\ = \frac{|Q_C|/|Q_H|}{1 - |Q_C|/|Q_H|}$$

Then we substitute Eq. (20.13), $|Q_C|/|Q_H| = T_C/T_H$, into this expression:

$$\text{Coefficient of performance of a Carnot refrigerator} \quad K_{\text{Carnot}} = \frac{T_C}{T_H - T_C} \quad (20.15)$$

Temperature of cold reservoir Temperature of hot reservoir

When the temperature difference $T_H - T_C$ is small, K is much larger than unity; in this case a lot of heat can be “pumped” from the lower to the higher temperature with only a little expenditure of work. But the greater the temperature difference, the smaller the value of K and the more work is required to transfer a given quantity of heat.

EXAMPLE 20.4 Analyzing a Carnot refrigerator

WITH VARIATION PROBLEMS

If the cycle described in Example 20.3 is run backward as a refrigerator, what is its coefficient of performance?

IDENTIFY and SET UP This problem uses the ideas of Section 20.3 (for refrigerators in general) and the above discussion of Carnot refrigerators. Equation (20.9) gives the coefficient of performance K of *any* refrigerator in terms of the heat Q_C extracted from the cold reservoir per cycle and the work W that must be done per cycle.

EXECUTE In Example 20.3 we found that in one cycle the Carnot engine rejects heat $Q_C = -346$ J to the cold reservoir and does work $W = 230$ J. When run in reverse as a refrigerator, the system extracts heat $Q_C = +346$ J from the cold reservoir while requiring a work input of $W = -230$ J. From Eq. (20.9),

$$K = \frac{|Q_C|}{|W|} = \frac{346 \text{ J}}{230 \text{ J}} \\ = 1.50$$

Because this is a Carnot cycle, we can also use Eq. (20.15):

$$K = \frac{T_C}{T_H - T_C} = \frac{300 \text{ K}}{500 \text{ K} - 300 \text{ K}} \\ = 1.50$$

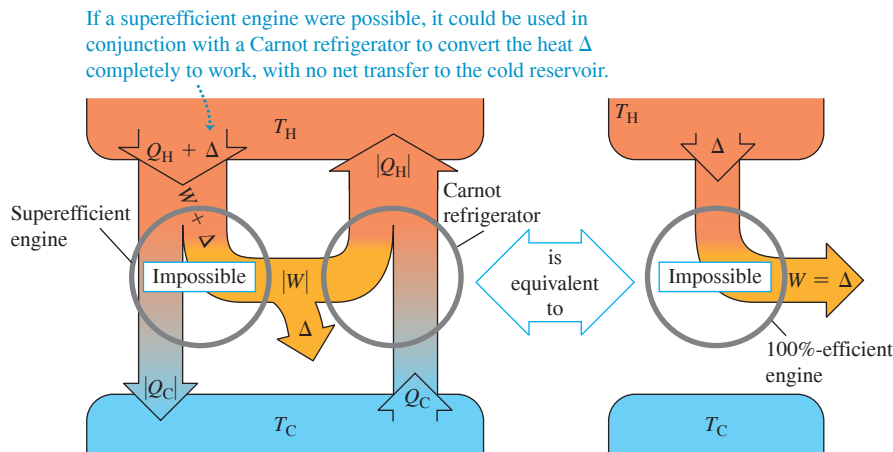
EVALUATE Equations (20.14) and (20.15) show that e and K for a Carnot cycle depend only on T_H and T_C , and we don’t need to calculate Q and W . For cycles containing irreversible processes, however, these two equations are not valid, and more detailed calculations are necessary.

KEYCONCEPT A refrigerator takes heat in from a cold reservoir and rejects heat to a hot reservoir. Work must be done on the refrigerator to make this happen. The coefficient of performance K of the refrigerator equals the amount of heat that is rejected to the hot reservoir divided by the amount of work that must be done on the refrigerator. The greater the value of K , the more heat can be removed from the cold reservoir for a given expenditure of work.

The Carnot Cycle and the Second Law

We can prove that **no engine can be more efficient than a Carnot engine operating between the same two temperatures**. The key to the proof is the above observation that since each step in the Carnot cycle is reversible, the *entire cycle* may be reversed. Run backward, the engine becomes a refrigerator. Suppose we have an engine that is more

Figure 20.15 Proving that the Carnot engine has the highest possible efficiency. A “superefficient” engine (more efficient than a Carnot engine) combined with a Carnot refrigerator could convert heat completely into work with no net heat transfer to the cold reservoir. This would violate the second law of thermodynamics.



efficient than a Carnot engine (Fig. 20.15). Let the Carnot engine, run backward as a refrigerator by negative work $-|W|$, take in heat Q_C from the cold reservoir and expel heat $|Q_H|$ to the hot reservoir. The superefficient engine expels heat $|Q_C|$, but to do this, it takes in a greater amount of heat $Q_H + \Delta$. Its work output is then $W + \Delta$, and the net effect of the two machines together is to take a quantity of heat Δ and convert it completely into work. This violates the “engine” statement of the second law. We could construct a similar argument that a superefficient engine could be used to violate the “refrigerator” statement of the second law. Note that we don’t have to assume that the superefficient engine is reversible. In a similar way we can show that *no refrigerator can have a greater coefficient of performance than a Carnot refrigerator operating between the same two temperatures*.

Thus the statement that no engine can be more efficient than a Carnot engine is yet another equivalent statement of the second law of thermodynamics. It also follows directly that **all Carnot engines operating between the same two temperatures have the same efficiency, irrespective of the nature of the working substance**. Although we derived Eq. (20.14) for a Carnot engine by using an ideal gas as its working substance, it is in fact valid for *any* Carnot engine, no matter what its working substance.

Equation (20.14), the expression for the efficiency of a Carnot engine, sets an upper limit to the efficiency of a real engine such as a steam turbine. To maximize this upper limit and the actual efficiency of the real engine, the designer must make the intake temperature T_H as high as possible and the exhaust temperature T_C as low as possible (Fig. 20.16).

The exhaust temperature cannot be lower than the lowest temperature available for cooling the exhaust. For a steam turbine at an electric power plant, T_C may be the temperature of river or lake water; then we want the boiler temperature T_H to be as high as possible. The vapor pressures of all liquids increase rapidly with temperature, so we are limited by the mechanical strength of the boiler. At 500°C the vapor pressure of water is about $240 \times 10^5 \text{ Pa}$ (235 atm); this is about the maximum practical pressure in large present-day steam boilers.

The Kelvin Temperature Scale

In Chapter 17 we expressed the need for a temperature scale that doesn’t depend on the properties of any particular material. We can now use the Carnot cycle to define such a scale. The thermal efficiency of a Carnot engine operating between two heat reservoirs at temperatures T_H and T_C is independent of the nature of the working substance and depends only on the temperatures. From Eq. (20.4), this thermal efficiency is

$$e = \frac{Q_H + Q_C}{Q_H} = 1 + \frac{Q_C}{Q_H}$$

Figure 20.16 To maximize efficiency, the temperatures inside a jet engine are made as high as possible. Exotic ceramic materials are used that can withstand temperatures in excess of 1000°C without melting or becoming soft.



Therefore the ratio Q_C/Q_H is the same for *all* Carnot engines operating between two given temperatures T_H and T_C .

Kelvin proposed that we *define* the ratio of the temperatures, T_C/T_H , to be equal to the magnitude of the ratio Q_C/Q_H of the quantities of heat absorbed and rejected:

$$\frac{T_C}{T_H} = \frac{|Q_C|}{|Q_H|} = -\frac{Q_C}{Q_H} \quad (\text{definition of Kelvin temperature}) \quad (20.16)$$

Equation (20.16) looks identical to Eq. (20.13), but there is a subtle and crucial difference. The temperatures in Eq. (20.13) are based on an ideal-gas thermometer, as defined in Section 17.3, while Eq. (20.16) *defines* a temperature scale based on the Carnot cycle and the second law of thermodynamics and is independent of the behavior of any particular substance. Thus the **Kelvin temperature scale** is truly *absolute*. To complete the definition of the Kelvin scale, we assign, as in Section 17.3, the arbitrary value of 273.16 K to the temperature of the triple point of water. When a substance is taken around a Carnot cycle, the ratio of the heats absorbed and rejected, $|Q_H|/|Q_C|$, is equal to the ratio of the temperatures of the reservoirs *as expressed on the gas-thermometer scale* defined in Section 17.3. Since the triple point of water is chosen to be 273.16 K in both scales, it follows that *the Kelvin and ideal-gas scales are identical*.

The zero point on the Kelvin scale is called **absolute zero**. At absolute zero a system has its *minimum* possible total internal energy (kinetic plus potential). Because of quantum effects, however, it is *not* true that at $T = 0$, all molecular motion ceases. There are theoretical reasons for believing that absolute zero cannot be attained experimentally, although temperatures below 10^{-8} K have been achieved. The more closely we approach absolute zero, the more difficult it is to get closer. One statement of the *third law of thermodynamics* is that it is impossible to reach absolute zero in a finite number of thermodynamic steps.

TEST YOUR UNDERSTANDING OF SECTION 20.6 An inventor looking for financial support comes to you with an idea for a gasoline engine that runs on a novel type of thermodynamic cycle. His design is made entirely of copper and is air-cooled. He claims that the engine will be 85% efficient. Should you invest in this marvelous new engine? (*Hint:* See Table 17.4.)

ANSWER 85% efficiency. You should invest your money elsewhere. The efficiency can be no better than that of a Carnot engine running between the same two temperature limits, $e_{\text{Carnot}} = 1 - (T_C/T_H)$ [Eq. (20.14)]. The temperature T_C of the cold reservoir for this air-cooled engine is about 300 K (ambient temperature), and the temperature T_H of the hot reservoir cannot exceed the melting point of copper, 1356 K (see Table 17.4). Hence the maximum possible Carnot efficiency is $e = 1 - (300 \text{ K})/(1356 \text{ K}) = 0.78$, or 78%. The temperature of any real engine would be less than this, so it would be impossible for the inventor's engine to attain 85% efficiency.

CAUTION Changes to the Kelvin scale

As we mentioned in Sections 17.3 and 18.3, in 2019 the Kelvin scale was redefined to be based not on the triple point of water but rather on the values of the joule ($1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$) and the Boltzmann constant. Despite this change in definition, the Kelvin and ideal-gas scales remain identical. ■

20.7 ENTROPY

The second law of thermodynamics, as we have stated it, is not an equation or a quantitative relationship but rather a statement of *impossibility*. However, the second law *can* be stated as a quantitative relationship with the concept of *entropy*, the subject of this section.

We have talked about several processes that proceed naturally in the direction of increasing randomness. Irreversible heat flow increases randomness: The molecules are initially sorted into hotter and cooler regions, but this sorting is lost when the system comes to thermal equilibrium. Adding heat to an object also increases average molecular speeds; therefore, molecular motion becomes more random. In the free expansion of a gas, the molecules have greater randomness of position after the expansion than before. **Figure 20.17** shows another process in which randomness increases.

Figure 20.17 When firecrackers explode, randomness increases: The neatly packaged chemicals within each firecracker are dispersed in all directions, and the stored chemical energy is converted to random kinetic energy of the fragments. ■



Entropy and Randomness

Entropy provides a *quantitative* measure of randomness. To introduce this concept, let's consider an infinitesimal isothermal expansion of an ideal gas. We add heat dQ and let the gas expand just enough to keep the temperature constant. Because the internal energy of an ideal gas depends on only its temperature, the internal energy is also constant; thus from the first law, the work dW done by the gas is equal to the heat dQ added. That is,

$$dQ = dW = p dV = \frac{nRT}{V} dV \quad \text{so} \quad \frac{dV}{V} = \frac{dQ}{nRT}$$

The gas is more disordered after the expansion than before: The molecules are moving in a larger volume and have more randomness of position. Thus the fractional volume change dV/V is a measure of the increase in randomness, and the above equation shows that it is proportional to the quantity dQ/T . We introduce the symbol S for the entropy of the system, and we define the infinitesimal entropy change dS during an infinitesimal reversible process at absolute temperature T as

$$dS = \frac{dQ}{T} \quad (\text{infinitesimal reversible process}) \quad (20.17)$$

If a total amount of heat Q is added during a reversible isothermal process at absolute temperature T , the total entropy change $\Delta S = S_2 - S_1$ is given by

$$\Delta S = S_2 - S_1 = \frac{Q}{T} \quad (\text{reversible isothermal process}) \quad (20.18)$$

Entropy has units of energy divided by temperature; the SI unit of entropy is 1 J/K.

We can see how the quotient Q/T is related to the increase in randomness. Higher temperature means greater randomness of motion. If the substance is initially cold, with little molecular motion, adding heat Q causes a substantial fractional increase in molecular motion and randomness. But if the substance is already hot, the same quantity of heat adds relatively little to the greater molecular motion already present. In the first case the quantity Q/T is large because T in the denominator is small; in the second case Q/T is small because T is large. So Q/T is an appropriate characterization of the increase in randomness when heat flows into a system.

CAUTION Be mindful of the signs of Q and ΔS When calculating the entropy change for a reversible process, remember that Q is positive if heat flows into a system and negative if heat flows out of a system. So the entropy of a system increases (ΔS is positive) when heat flows into it, and the entropy decreases (ΔS is negative) when heat flows out of it. ■

EXAMPLE 20.5 Entropy change in melting

What is the change of entropy of 1 kg of ice that is melted reversibly at 0°C and converted to water at 0°C ? The heat of fusion of water is $L_f = 3.34 \times 10^5 \text{ J/kg}$.

IDENTIFY and SET UP The melting occurs at a constant temperature $T = 0^\circ\text{C} = 273 \text{ K}$, so this is an *isothermal* reversible process. We can calculate the added heat Q required to melt the ice, then calculate the entropy change ΔS from Eq. (20.18).

EXECUTE The heat needed to melt the ice is $Q = mL_f = 3.34 \times 10^5 \text{ J}$. Then from Eq. (20.18),

$$\Delta S = S_2 - S_1 = \frac{Q}{T} = \frac{3.34 \times 10^5 \text{ J}}{273 \text{ K}} = 1.22 \times 10^3 \text{ J/K}$$

EVALUATE This entropy increase corresponds to the increase in disorder when the water molecules go from the state of a crystalline solid to the much more randomly arranged state of a liquid. In *any* isothermal reversible process, the entropy change equals the heat transferred divided by the absolute temperature. When we refreeze the water, Q has the opposite sign, and the entropy change is $\Delta S = -1.22 \times 10^3 \text{ J/K}$. The water molecules rearrange themselves into a crystal to form ice, so both randomness and entropy decrease.

KEYCONCEPT To find the entropy change of a system that goes through a reversible thermodynamic process at a constant temperature T , divide the heat Q that flows into the system during the process by T . If heat flows *in* (Q is positive), the entropy and disorder of the system *increase*; if heat flows *out* (Q is negative), the entropy and disorder of the system *decrease*.

Entropy in Reversible Processes

We can generalize the definition of entropy change to include *any* reversible process leading from one state to another, whether it is isothermal or not. We represent the process as a series of infinitesimal reversible steps. During a typical step, an infinitesimal quantity of heat dQ is added to the system at absolute temperature T . Then we sum (integrate) the quotients dQ/T for the entire process; that is,

$$\Delta S = \int_1^2 \frac{dQ}{T} \quad (20.19)$$

Entropy change in a reversible process ΔS Upper limit = final state
 Lower limit = initial state Infinitesimal heat flow into system
 Absolute temperature

Because entropy is a measure of the randomness of a system in any specific state, it must depend only on the current state of the system, not on its past history. (We'll verify this later.) When a system proceeds from an initial state with entropy S_1 to a final state with entropy S_2 , the change in entropy $\Delta S = S_2 - S_1$ defined by Eq. (20.19) does not depend on the path leading from the initial to the final state but is the same for *all possible* processes leading from state 1 to state 2. Thus the entropy of a system must also have a definite value for any given state of the system. *Internal energy*, introduced in Chapter 19, also has this property, although entropy and internal energy are very different quantities.

Since entropy is a function only of the state of a system, we can also compute entropy changes in *irreversible* (nonequilibrium) processes for which Eqs. (20.17) and (20.19) are not applicable. We simply invent a path connecting the given initial and final states that *does* consist entirely of reversible equilibrium processes and compute the total entropy change for that path. It is not the actual path, but the entropy change must be the same as for the actual path.

As with internal energy, the above discussion does not tell us how to calculate entropy itself, but only the change in entropy in any given process. Just as with internal energy, we may arbitrarily assign a value to the entropy of a system in a specified reference state and then calculate the entropy of any other state with reference to this.

EXAMPLE 20.6 Entropy change in a temperature change

WITH VARIATION PROBLEMS

One kilogram of water at 0°C is heated to 100°C . Compute its change in entropy. Assume that the specific heat of water is constant at $4190 \text{ J/kg} \cdot \text{K}$ over this temperature range.

IDENTIFY and SET UP The entropy change of the water depends only on the initial and final states of the system, no matter whether the process is reversible or irreversible. We can imagine a reversible process in which the water temperature is increased in a sequence of infinitesimal steps dT . We can use Eq. (20.19) to integrate over all these steps and calculate the entropy change for such a reversible process. (Heating the water on a stove whose cooking surface is maintained at 100°C would be an irreversible process. The entropy change would be the same, however.)

EXECUTE From Eq. (17.14) the heat required to carry out each infinitesimal step is $dQ = mc \, dT$. Substituting this into Eq. (20.19) and integrating, we find

$$\begin{aligned} \Delta S &= S_2 - S_1 = \int_1^2 \frac{dQ}{T} = \int_{T_1}^{T_2} mc \frac{dT}{T} = mc \ln \frac{T_2}{T_1} \\ &= (1.00 \text{ kg})(4190 \text{ J/kg} \cdot \text{K}) \left(\ln \frac{373 \text{ K}}{273 \text{ K}} \right) = 1.31 \times 10^3 \text{ J/K} \end{aligned}$$

EVALUATE The entropy change is positive, as it must be for a process in which the system absorbs heat. Our assumption about the specific heat is a pretty good one, since c for water varies by less than 1% between 0°C and 100°C (see Fig. 17.17).

CAUTION When $\Delta S = Q/T$ can (and cannot) be used In solving this problem you might be tempted to avoid doing an integral by using the simpler expression in Eq. (20.18), $\Delta S = Q/T$. This would be incorrect, however, because Eq. (20.18) is applicable only to *isothermal* processes, and the initial and final temperatures in our example are *not* the same. The *only* correct way to find the entropy change in a process with different initial and final temperatures is to use Eq. (20.19). I

KEYCONCEPT The entropy change ΔS of a thermodynamic system does not depend on the path taken between the initial and final states of the system. You can calculate ΔS for any initial and final states by analyzing a *reversible* process that takes the system between these states; in general this involves evaluating an integral.

CONCEPTUAL EXAMPLE 20.7 Entropy change in a reversible adiabatic process

WITH  VARIATION PROBLEMS

A gas expands adiabatically and reversibly. What is its change in entropy?

SOLUTION In an adiabatic process, no heat enters or leaves the system. Hence $dQ = 0$ and there is *no* change in entropy in this reversible process: $\Delta S = 0$. Every *reversible* adiabatic process is a constant-entropy process. (That's why such processes are also called *isentropic*

processes.) The increase in randomness resulting from the gas occupying a greater volume is exactly balanced by the decrease in randomness associated with the lowered temperature and reduced molecular speeds.

KEYCONCEPT In the special case where a system undergoes a reversible adiabatic process, the system undergoes *no* change in entropy.

EXAMPLE 20.8 Entropy change in a free expansion

WITH  VARIATION PROBLEMS

A partition divides a thermally insulated box into two compartments, each of volume V (Fig. 20.18). Initially, one compartment contains n moles of an ideal gas at temperature T , and the other compartment is evacuated. We break the partition and the gas expands, filling both compartments. What is the entropy change in this free-expansion process?

IDENTIFY and SET UP For this process, $Q = 0$, $W = 0$, $\Delta U = 0$, and therefore (because the system is an ideal gas) $\Delta T = 0$. We might think that the entropy change is zero because there is no heat exchange. But Eq. (20.19) can be used to calculate entropy changes for *reversible* processes only; this free expansion is *not* reversible, and there *is* an entropy change. As we mentioned at the beginning of this section, entropy increases in a free expansion because the positions of the molecules are more random than before the expansion. To calculate ΔS , we recall

that the entropy change depends only on the initial and final states. We can devise a *reversible* process having the same endpoints as this free expansion, and in general we can then use Eq. (20.19) to calculate its entropy change, which will be the same as for the free expansion. An appropriate reversible process is an *isothermal* expansion from V to $2V$ at temperature T , which allows us to use the simpler Eq. (20.18) to calculate ΔS . The gas does work W during this expansion, so an equal amount of heat Q must be supplied to keep the internal energy constant.

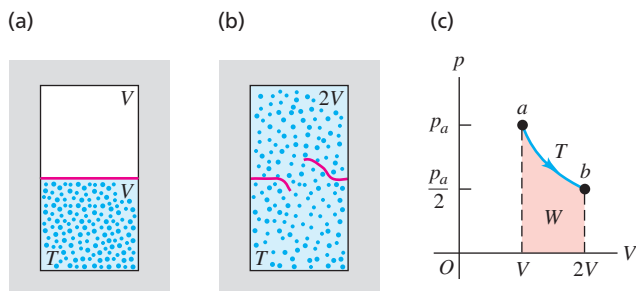
EXECUTE We saw in Example 19.1 that the work done by n moles of ideal gas in an isothermal expansion from V_1 to V_2 is $W = nRT \ln(V_2/V_1)$. With $V_1 = V$ and $V_2 = 2V$, we have

$$Q = W = nRT \ln \frac{2V}{V} = nRT \ln 2$$

From Eq. (20.18), the entropy change is

$$\Delta S = \frac{Q}{T} = nR \ln 2$$

Figure 20.18 (a, b) Free expansion of an insulated ideal gas. (c) The free-expansion process doesn't pass through equilibrium states from a to b . However, the entropy change $S_b - S_a$ can be calculated by using the isothermal path shown or *any* reversible path from a to b .



EVALUATE For 1 mole, $\Delta S = (1 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(\ln 2) = 5.76 \text{ J/K}$. The entropy change is positive, as we predicted. The factor $(\ln 2)$ in our answer is a result of the volume having increased by a factor of 2, from V to $2V$. Can you show that if the volume increases in a free expansion from V to xV , where x is an arbitrary number, the entropy change is $\Delta S = nR \ln x$?

KEYCONCEPT To calculate the entropy change of a system in an *irreversible* process such as a free expansion, you must consider a *reversible* process that takes the system from the same initial state to the same final state.

EXAMPLE 20.9 Entropy and the Carnot cycle

WITH  VARIATION PROBLEMS

For the Carnot engine in Example 20.2 (Section 20.6), what is the total entropy change during one cycle?

IDENTIFY and SET UP All four steps in the Carnot cycle (see Fig. 20.13) are reversible, so we can use our expressions for the entropy change ΔS in a reversible process. We find ΔS for each step and add them to get ΔS for the complete cycle.

EXECUTE There is no entropy change during the adiabatic expansion $b \rightarrow c$ or the adiabatic compression $d \rightarrow a$. During the isothermal expansion $a \rightarrow b$ at $T_H = 500 \text{ K}$, the engine takes in 2000 J of heat, and from Eq. (20.18),

$$\Delta S_H = \frac{Q_H}{T_H} = \frac{2000 \text{ J}}{500 \text{ K}} = 4.0 \text{ J/K}$$

During the isothermal compression $c \rightarrow d$ at $T_C = 350 \text{ K}$, the engine gives off 1400 J of heat, and

$$\begin{aligned} \Delta S_C &= \frac{Q_C}{T_C} = \frac{-1400 \text{ J}}{350 \text{ K}} \\ &= -4.0 \text{ J/K} \end{aligned}$$

The total entropy change in the engine during one cycle is $\Delta S_{\text{tot}} = \Delta S_H + \Delta S_C = 4.0 \text{ J/K} + (-4.0 \text{ J/K}) = 0$.

EVALUATE The result $\Delta S_{\text{total}} = 0$ tells us that when the Carnot engine completes a cycle, it has the same entropy as it did at the beginning of the cycle. We'll explore this result in the next subsection.

What is the total entropy change of the engine's *environment* during this cycle? During the reversible isothermal expansion $a \rightarrow b$, the hot (500 K) reservoir gives off 2000 J of heat, so its entropy change is $(-2000 \text{ J})/(500 \text{ K}) = -4.0 \text{ J/K}$. During the reversible isothermal compression $c \rightarrow d$, the cold (350 K) reservoir absorbs 1400 J of heat, so its entropy change is $(+1400 \text{ J})/(350 \text{ K}) = +4.0 \text{ J/K}$. Thus the hot and cold reservoirs each have an entropy change, but the sum of these changes—that is, the total entropy change of the system's environment—is zero.

These results apply to the special case of the Carnot cycle, for which *all* of the processes are reversible. In this case the total entropy

change of the system and the environment together is zero. We'll see that if the cycle includes irreversible processes (as is the case for the Otto and Diesel cycles of Section 20.3), the total entropy change of the system and the environment *cannot* be zero, but rather must be positive.

KEYCONCEPT For the special case of a heat engine that uses the Carnot cycle, the net entropy change of the engine and its environment (the hot and cold reservoirs) in a complete cycle is zero. This is not the case for other, less ideal cycles.

Entropy in Cyclic Processes

Example 20.9 showed that the total entropy change for a cycle of a particular Carnot engine, which uses an ideal gas as its working substance, is zero. This result follows directly from Eq. (20.13), which we can rewrite as

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0 \quad (20.20)$$

The quotient Q_H/T_H equals ΔS_H , the entropy change of the engine that occurs at $T = T_H$. Likewise, Q_C/T_C equals ΔS_C , the (negative) entropy change of the engine that occurs at $T = T_C$. Hence Eq. (20.20) says that $\Delta S_H + \Delta S_C = 0$; that is, there is zero net entropy change in one cycle.

What about Carnot engines that use a different working substance? According to the second law, *any* Carnot engine operating between given temperatures T_H and T_C has the same efficiency $e = 1 - T_C/T_H$ [Eq. (20.14)]. Combining this expression for e with Eq. (20.4), $e = 1 + Q_C/Q_H$, just reproduces Eq. (20.20). So Eq. (20.20) is valid for any Carnot engine working between these temperatures, whether its working substance is an ideal gas or not. We conclude that *the total entropy change in one cycle of any Carnot engine is zero*.

This result can be generalized to show that the total entropy change during *any* reversible cyclic process is zero. A reversible cyclic process appears on a pV -diagram as a closed path (**Fig. 20.19a**). We can approximate such a path as closely as we like by a sequence of isothermal and adiabatic processes forming parts of many long, thin Carnot cycles (Fig. 20.19b). The total entropy change for the full cycle is the sum of the entropy changes for each small Carnot cycle, each of which is zero. So **the total entropy change during any reversible cycle is zero**:

$$\int \frac{dQ}{T} = 0 \quad (\text{reversible cyclic process}) \quad (20.21)$$

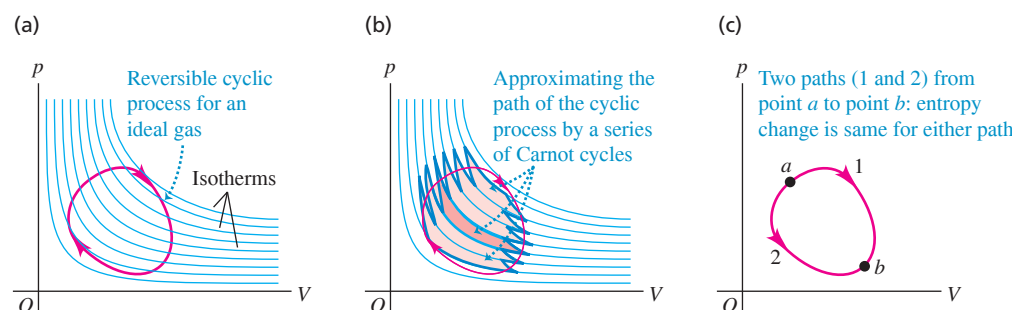


Figure 20.19 (a) A reversible cyclic process for an ideal gas is shown as a red closed path on a pV -diagram. Several ideal-gas isotherms are shown in blue. (b) We can approximate the path in (a) by a series of long, thin Carnot cycles; one of these is highlighted in color. The total entropy change is zero for each Carnot cycle and for the actual cyclic process. (c) The entropy change between points a and b is independent of the path.

BIO APPLICATION Entropy Changes in a Living Organism

When a puppy or other growing animal eats, it takes organized chemical energy from the food and uses it to make new cells that are even more highly organized. This process alone lowers entropy. But most of the energy in the food is either excreted in the animal's feces or used to generate heat, processes that lead to a large increase in entropy. So while the entropy of the animal alone decreases, the *total* entropy of animal plus food *increases*.



It follows that when a system undergoes a reversible process leading from any state *a* to any other state *b*, the *entropy change of the system is independent of the path* (Fig. 20.19c). If the entropy change for path 1 were different from the change for path 2, the system could be taken along path 1 and then backward along path 2 to the starting point, with a nonzero net change in entropy. This would violate the conclusion that the total entropy change in such a cyclic process must be zero. Because the entropy change in such processes is independent of path, we conclude that in any given state, the system has a definite value of entropy that depends only on the state, not on the processes that led to that state.

Entropy in Irreversible Processes

In an idealized, reversible process involving only equilibrium states, the total entropy change of the system and its surroundings is zero. But all *irreversible* processes involve an increase in entropy. Unlike energy, *entropy is not a conserved quantity*. The entropy of an isolated system *can* change, but as we shall see, it can never decrease. The free expansion of a gas (Example 20.8) is an irreversible process in an isolated system in which there is an entropy increase.

EXAMPLE 20.10 Entropy change in an irreversible process**WITH VARIATION PROBLEMS**

Suppose 1.00 kg of water at 100°C is placed in thermal contact with 1.00 kg of water at 0°C. What is the total change in entropy? Assume that the specific heat of water is constant at 4190 J/kg · K over this temperature range.

IDENTIFY and SET UP This process involves irreversible heat flow because of the temperature differences. There are equal masses of 0°C water and 100°C water, so the final temperature is the average of these two temperatures: 50°C = 323 K. Although the processes are irreversible, we can calculate the entropy changes for the (initially) hot water and the (initially) cold water by assuming that the process occurs reversibly. As in Example 20.6, we must use Eq. (20.19) to calculate ΔS for each substance because the temperatures are not constant.

EXECUTE The entropy changes of the hot water (subscript H) and the cold water (subscript C) are

$$\begin{aligned}\Delta S_H &= mc \int_{T_1}^{T_2} \frac{dT}{T} = (1.00 \text{ kg})(4190 \text{ J/kg} \cdot \text{K}) \int_{373 \text{ K}}^{323 \text{ K}} \frac{dT}{T} \\ &= (4190 \text{ J/K}) \left(\ln \frac{323 \text{ K}}{373 \text{ K}} \right) = -603 \text{ J/K} \\ \Delta S_C &= (4190 \text{ J/K}) \left(\ln \frac{323 \text{ K}}{273 \text{ K}} \right) = +705 \text{ J/K}\end{aligned}$$

The *total* entropy change of the system is

$$\Delta S_{\text{tot}} = \Delta S_H + \Delta S_C = (-603 \text{ J/K}) + 705 \text{ J/K} = +102 \text{ J/K}$$

EVALUATE An irreversible heat flow in an isolated system is accompanied by an increase in entropy. We could reach the same end state by mixing the hot and cold water, which is also an irreversible process; the total entropy change, which depends only on the initial and final states of the system, would again be 102 J/K.

Note that the entropy of the system increases *continuously* as the two quantities of water come to equilibrium. For example, the first 4190 J of heat transferred cools the hot water to 99°C and warms the cold water to 1°C. The net change in entropy for this step is approximately

$$\Delta S = \frac{-4190 \text{ J}}{373 \text{ K}} + \frac{4190 \text{ J}}{273 \text{ K}} = +4.1 \text{ J/K}$$

Can you show in a similar way that the net entropy change is positive for *any* one-degree temperature change leading to the equilibrium condition?

KEYCONCEPT When heat flows irreversibly from an object at higher temperature to one at lower temperature, the entropy of the high-temperature object decreases and the entropy of the low-temperature object increases. The *net* entropy of the two objects together always increases.

Entropy and the Second Law

The results of Example 20.10 about the flow of heat from a higher to a lower temperature are characteristic of *all* natural (that is, irreversible) processes. When we include the entropy changes of all the systems taking part in the process, the increases in entropy are always greater than the decreases. In the special case of a *reversible* process, the increases



Figure 20.20 The mixing of colored ink and water starts from a state of low entropy in which each fluid is separate and distinct from the other. In the final state, both the ink and water molecules are spread randomly throughout the volume of liquid, so the entropy is greater. Spontaneous unmixing of the ink and water, a process in which there would be a net decrease in entropy, is never observed.

and decreases are equal. Hence we can state the general principle: **When all systems taking part in a process are included, the entropy either remains constant or increases.** This gives us a third, alternative way of stating the second law of thermodynamics:

SECOND LAW OF THERMODYNAMICS (“entropy” statement) No process is possible in which the total entropy decreases, when all systems that take part in the process are included.

This is equivalent to the “engine” and “refrigerator” statements that we discussed in Section 20.5. **Figure 20.20** shows a specific example of this general principle.

The increase of entropy in every natural, irreversible process measures the increase of randomness in the universe associated with that process. Consider again the example of mixing hot and cold water (Example 20.10). We *might* have used the hot and cold water as the high- and low-temperature reservoirs of a heat engine. While removing heat from the hot water and giving heat to the cold water, we could have obtained some mechanical work. But once the hot and cold water have been mixed and have come to a uniform temperature, this opportunity to convert heat to mechanical work is lost irretrievably. The lukewarm water will never *unmix* itself and separate into hotter and colder portions. No decrease in *energy* occurs when the hot and cold water are mixed. What has been lost is the *opportunity* to convert part of the heat from the hot water into mechanical work. Hence when entropy increases, energy becomes less *available*, and the universe becomes more random or “run down.”

TEST YOUR UNDERSTANDING OF SECTION 20.7 Suppose 2.00 kg of water at 50°C spontaneously changes temperature, so that half of the water cools to 0°C while the other half spontaneously warms to 100°C. (All of the water remains liquid, so it doesn’t freeze or boil.) What would be the entropy change of the water? Is this process possible? (*Hint:* See Example 20.10.)






ANSWER

The result violates the second law of thermodynamics, which states that the entropy of an isolated system cannot decrease. **–102 J/K, no** The process described is exactly the opposite of the process used in Example 20.10.

20.8 MICROSCOPIC INTERPRETATION OF ENTROPY

We described in Section 19.4 how the internal energy of a system could be calculated, at least in principle, by adding up all the kinetic energies of its constituent particles and all the potential energies of interaction among the particles. This is called a *microscopic* calculation of the internal energy. We can also make a microscopic calculation of the entropy S of a system. Unlike energy, however, entropy is not something

Figure 20.21 All possible microscopic states of four coins. There can be several possible microscopic states for each macroscopic state.

Macroscopic state	Corresponding microscopic states
Four heads	
Three heads, one tails	
Two heads, two tails	
One heads, three tails	
Four tails	

that belongs to each individual particle or pair of particles in the system. Rather, entropy is a measure of the randomness of the system as a whole. To see how to calculate entropy microscopically, we first have to introduce the idea of *macroscopic* and *microscopic states*.

Suppose you toss N identical coins on the floor, and half of them show heads and half show tails. This is a description of the large-scale or **macroscopic state** of the system of N coins. A description of the **microscopic state** of the system includes information about each individual coin: Coin 1 was heads, coin 2 was tails, coin 3 was tails, and so on. There can be many microscopic states that correspond to the same macroscopic description. For instance, with $N = 4$ coins there are six possible states in which half are heads and half are tails (**Fig. 20.21**). The number of microscopic states grows rapidly with increasing N ; for $N = 100$ there are $2^{100} = 1.27 \times 10^{30}$ microscopic states, of which 1.01×10^{29} are half heads and half tails.

The least probable outcomes of the coin toss are the states that are either all heads or all tails. It is certainly possible that you could throw 100 heads in a row, but don't bet on it; the probability of doing this is only 1 in 1.27×10^{30} . The most probable outcome of tossing N coins is that half are heads and half are tails. The reason is that this *macroscopic* state has the greatest number of corresponding *microscopic* states, as **Fig. 20.21** shows.

To make the connection to the concept of entropy, note that the macroscopic description “all heads” completely specifies the state of each one of the N coins. The same is true if the coins are all tails. But the macroscopic description “half heads, half tails” by itself tells you very little about the state (heads or tails) of each individual coin. Compared to the state “all heads” or “all tails,” the state “half heads, half tails” has much greater *randomness* because the system could be in any of a much greater number of possible microscopic states. Hence the “half heads, half tails” state has much greater entropy (which is a quantitative measure of randomness).

Now instead of N coins, consider a mole of an ideal gas containing Avogadro's number of molecules. The macroscopic state of this gas is given by its pressure p , volume V , and temperature T ; a description of the microscopic state involves stating the position and velocity for each molecule in the gas. At a given pressure, volume, and temperature, the gas may be in any one of an astronomically large number of microscopic states, depending on the positions and velocities of its 6.02×10^{23} molecules. If the gas undergoes a free expansion into a greater volume, the range of possible positions increases, as does the number of possible microscopic states. The system becomes more random, and the entropy increases as calculated in Example 20.8 (Section 20.7).

We can draw the following general conclusion: **For any thermodynamic system, the most probable macroscopic state is the one with the greatest number of corresponding microscopic states, which is also the macroscopic state with the greatest randomness and the greatest entropy.**

Calculating Entropy: Microscopic States

Let w represent the number of possible microscopic states for a given macroscopic state. (For the four coins shown in **Fig. 20.21** the state of four heads has $w = 1$, the state of three heads and one tails has $w = 4$, and so on.) Then the entropy S of a macroscopic state can be shown to be given by

$$S = k \ln w \quad (20.22)$$

Expression for entropy in microscopic terms
 Boltzmann constant (gas constant per molecule)
 Number of microscopic states for the given macroscopic state

(We introduced the Boltzmann constant in Section 18.3.) As **Eq. (20.22)** shows, increasing the number of possible microscopic states w increases the entropy S .

What matters in a thermodynamic process is not the absolute entropy S but the *difference* in entropy between the initial and final states. Hence an equally valid and useful definition would be $S = k \ln w + C$, where C is a constant, since C cancels in any calculation of an entropy difference between two states. But it's convenient to set this constant equal to zero and use Eq. (20.22). With this choice, since the smallest possible value of w is unity, the smallest possible value of S for any system is $k \ln 1 = 0$. Entropy can *never* be negative.

In practice, calculating w is a difficult task, so Eq. (20.22) is typically used only to calculate the absolute entropy S of certain special systems. But we can use this relationship to calculate *differences* in entropy between one state and another. Consider a system that undergoes a thermodynamic process that takes it from macroscopic state 1, for which there are w_1 possible microscopic states, to macroscopic state 2, with w_2 associated microscopic states. The change in entropy in this process is

$$\Delta S = S_2 - S_1 = k \ln w_2 - k \ln w_1 = k \ln \frac{w_2}{w_1} \quad (20.23)$$

The *difference* in entropy between the two macroscopic states depends on the *ratio* of the numbers of possible microscopic states.

As the following example shows, using Eq. (20.23) to calculate a change in entropy from one macroscopic state to another gives the same results as considering a reversible process connecting those two states and using Eq. (20.19).

EXAMPLE 20.11 A microscopic calculation of entropy change

Use Eq. (20.23) to calculate the entropy change in the free expansion of n moles of gas at temperature T described in Example 20.8 (Fig. 20.22).

IDENTIFY and SET UP We are asked to calculate the entropy change by using the number of microscopic states in the initial and final macroscopic states (Figs. 20.22a and b). When the partition is broken, no work is done, so the velocities of the molecules are unaffected. But each molecule now has twice as much volume in which it can move and hence has twice the number of possible positions. This is all we need to calculate the entropy change using Eq. (20.23).

EXECUTE Let w_1 be the number of microscopic states of the system as a whole when the gas occupies volume V (Fig. 20.22a). The number of molecules is $N = nN_A$, and each of these N molecules has twice as many possible states after the partition is broken. Hence the number w_2 of microscopic states when the gas occupies volume $2V$ (Fig. 20.22b) is greater by a factor of 2^N ; that is, $w_2 = 2^N w_1$. The change in entropy in this process is

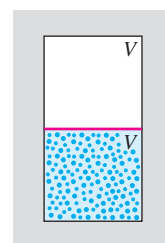
$$\begin{aligned} \Delta S &= k \ln \frac{w_2}{w_1} = k \ln \frac{2^N w_1}{w_1} \\ &= k \ln 2^N = Nk \ln 2 \end{aligned}$$

Since $N = nN_A$ and $k = R/N_A$, this becomes

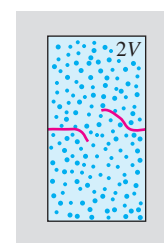
$$\begin{aligned} \Delta S &= (nN_A)(R/N_A) \ln 2 \\ &= nR \ln 2 \end{aligned}$$

Figure 20.22 In a free expansion of N molecules in which the volume doubles, the number of possible microscopic states increases by a factor of 2^N .

(a) Gas occupies volume V ; number of microscopic states $= w_1$.



(b) Gas occupies volume $2V$; number of microscopic states $= w_2 = 2^N w_1$.



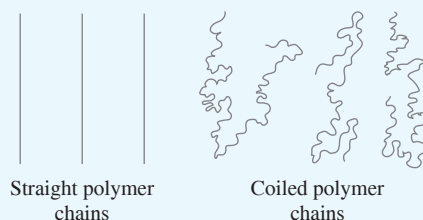
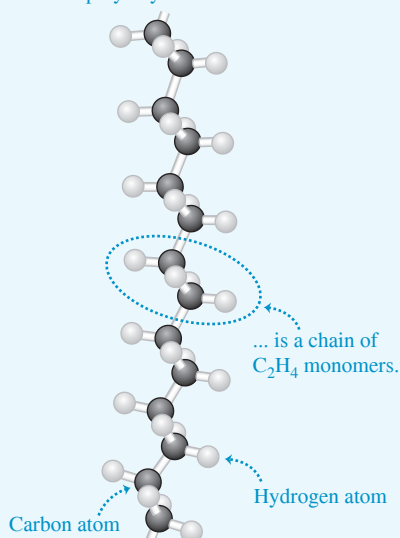
EVALUATE We found the same result as in Example 20.8, but without any reference to the thermodynamic path taken.

KEYCONCEPT An alternative way to calculate entropy changes is in terms of the number of microscopic states available to the system. If there are w possible microscopic states of the system for a given macroscopic state, the entropy for the macroscopic state equals the Boltzmann constant k multiplied by the natural logarithm of w .

APPLICATION Polymers Coil in

Solution A molecule of polyethylene, the most common plastic, is a polymer—a long chain of monomer units (C_2H_4). In solution these molecules coil on themselves, and the entropy concept explains why. The polymer can coil in many ways (microscopic states), but there is only one microscopic state in which the polymer is fully stretched out. Thus the entropy of the coiled polymer is much greater than that of a stretched-out polymer. The second law of thermodynamics says that isolated systems always move toward greater entropy, so we expect a polymer chain in solution to be in a coiled state.

A polyethylene molecule ...

**Microscopic States and the Second Law**

The relationship between entropy and the number of microscopic states gives us new insight into the entropy statement of the second law of thermodynamics: that the entropy of a closed system can never decrease. From Eq. (20.22) this means that a closed system can never spontaneously undergo a process that decreases the number of possible microscopic states.

An example of such a forbidden process would be if all of the air in your room spontaneously moved to one half of the room, leaving a vacuum in the other half. Such a “free compression” would be the reverse of the free expansion of Examples 20.8 and 20.11. This would decrease the number of possible microscopic states by a factor of 2^N . Strictly speaking, this process is not impossible! The probability of finding a given molecule in one half of the room is $\frac{1}{2}$, so the probability of finding all of the molecules in one half of the room at once is $(\frac{1}{2})^N$. (This is exactly the same as the probability of having a tossed coin come up heads N times in a row.) This probability is *not* zero. But lest you worry about suddenly finding yourself gasping for breath in the evacuated half of your room, consider that a typical room might hold 1000 moles of air, and so $N = 1000N_A = 6.02 \times 10^{26}$ molecules. The probability of all the molecules being in the same half of the room is therefore $(\frac{1}{2})^{6.02 \times 10^{26}}$. Expressed as a decimal, this number has more than 10^{26} zeros to the right of the decimal point!

Because the probability of such a “free compression” taking place is so vanishingly small, it has almost certainly never occurred anywhere in the universe since the beginning of time. We conclude that for all practical purposes the second law of thermodynamics is never violated.

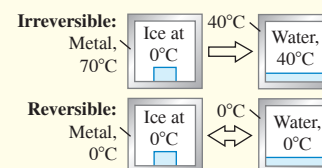
TEST YOUR UNDERSTANDING OF SECTION 20.8 A quantity of N molecules of an ideal gas initially occupies volume V . The gas then expands to volume $2V$. The number of microscopic states of the gas increases in this expansion. Under which of the following circumstances will this number increase the most? (i) If the expansion is reversible and isothermal; (ii) if the expansion is reversible and adiabatic; (iii) the number will change by the same amount for both circumstances.

ANSWER

(i) For case (i), we saw in Example 20.8 (Section 20.7) that for an ideal gas, the entropy change in a free expansion is the same as in an isothermal expansion. From Eq. (20.23), this implies that the ratio of the number of microscopic states after and before the expansion, w_2/w_1 , is also the same for these two cases. From Example 20.11, $w_2/w_1 = 2^N$, so the number of microscopic states increases by a factor 2^N . For case (ii), in a reversible expansion the entropy change is $\Delta S = \int dQ/T = 0$; if the expansion is adiabatic there is no heat flow, so $\Delta S = 0$. From Eq. (20.23), $w_2/w_1 = 1$ and there is *no* change in the number of microscopic states. The difference is that in an adiabatic expansion the temperature drops and the molecules move more slowly, so they have fewer microscopic states available to them than in an isothermal expansion.

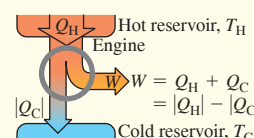
CHAPTER 20 SUMMARY

Reversible and irreversible processes: A reversible process is one whose direction can be reversed by an infinitesimal change in the conditions of the process, and in which the system is always in or very close to thermal equilibrium. All other thermodynamic processes are irreversible.



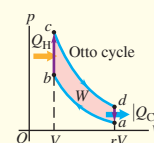
Heat engines: A heat engine takes heat Q_H from a source, converts part of it to work W , and discards the remainder $|Q_C|$ at a lower temperature. The thermal efficiency e of a heat engine measures how much of the absorbed heat is converted to work. (See Example 20.1.)

$$e = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 - \left| \frac{Q_C}{Q_H} \right| \quad (20.4)$$



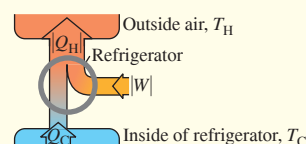
The Otto cycle: A gasoline engine operating on the Otto cycle has a theoretical maximum thermal efficiency e that depends on the compression ratio r and the ratio of heat capacities γ of the working substance.

$$e = 1 - \frac{1}{r^{\gamma-1}} \quad (20.6)$$

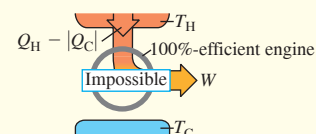


Refrigerators: A refrigerator takes heat Q_C from a colder place, has a work input $|W|$, and discards heat $|Q_H|$ at a warmer place. The effectiveness of the refrigerator is given by its coefficient of performance K .

$$K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|} \quad (20.9)$$

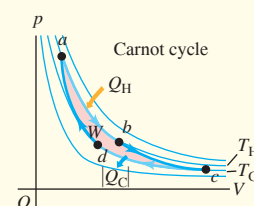


The second law of thermodynamics: The second law of thermodynamics describes the directionality of natural thermodynamic processes. It can be stated in two equivalent forms. The *engine* statement is that no cyclic process can convert heat completely into work. The *refrigerator* statement is that no cyclic process can transfer heat from a colder place to a hotter place with no input of mechanical work.



The Carnot cycle: The Carnot cycle operates between two heat reservoirs at temperatures T_H and T_C and uses only reversible processes. Its thermal efficiency depends only on T_H and T_C . An additional equivalent statement of the second law is that no engine operating between the same two temperatures can be more efficient than a Carnot engine. (See Examples 20.2 and 20.3.)

$$e_{\text{Carnot}} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H} \quad (20.14)$$



A Carnot engine run backward is a Carnot refrigerator. Its coefficient of performance depends on only T_H and T_C . Another form of the second law states that no refrigerator operating between the same two temperatures can have a larger coefficient of performance than a Carnot refrigerator. (See Example 20.4.)

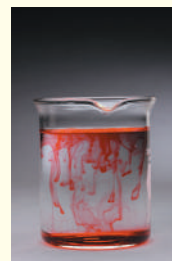
$$K_{\text{Carnot}} = \frac{T_C}{T_H - T_C} \quad (20.15)$$

Entropy: Entropy is a quantitative measure of the randomness of a system. The entropy change in any reversible process depends on the amount of heat flow and the absolute temperature T . Entropy depends only on the state of the system, and the change in entropy between given initial and final states is the same for all processes leading from one state to the other. This fact can be used to find the entropy change in an irreversible process. (See Examples 20.5–20.10.)

An important statement of the second law of thermodynamics is that the entropy of an isolated system may increase but can never decrease. When a system interacts with its surroundings, the total entropy change of system and surroundings can never decrease. When the interaction involves only reversible processes, the total entropy is constant and $\Delta S = 0$; when there is any irreversible process, the total entropy increases and $\Delta S > 0$.

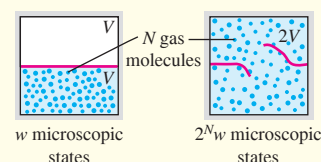
$$\Delta S = \int_1^2 \frac{dQ}{T} \quad (20.19)$$

(reversible process)



Entropy and microscopic states: When a system is in a particular macroscopic state, the particles that make up the system may be in any of w possible microscopic states. The greater the number w , the greater the entropy. (See Example 20.11.)

$$S = k \ln w \quad (20.22)$$



Chapter 20 Media Assets



GUIDED PRACTICE

For assigned homework and other learning materials, go to Mastering Physics.

KEY EXAMPLE VARIATION PROBLEMS

Be sure to review **EXAMPLE 20.1** (Section 20.2) before attempting these problems.

VP20.1.1 A diesel engine has efficiency 0.180. (a) In order for this engine to do 1.24×10^4 J of work, how many joules of heat must it take in? (b) How many joules of this heat is discarded?

VP20.1.2 In one cycle a heat engine absorbs 3.82×10^4 J of heat from the hot reservoir and rejects 3.16×10^4 J of heat to the cold reservoir. What is the efficiency of this engine?

VP20.1.3 Measurements of a gasoline engine show that it has an efficiency of 0.196 and that it exhausts 4.96×10^8 J of heat during 20 minutes of operation. During that time, (a) how much heat does the engine take in and (b) how much work does the engine do?

VP20.1.4 An aircraft piston engine that burns gasoline (heat of combustion 5.0×10^7 J/kg) has a power output of 1.10×10^5 W. (a) How much work does this engine do in 1.00 h? (b) This engine burns 34 kg of gasoline per hour. How much heat does the engine take in per hour? (c) What is the efficiency of the engine?

Be sure to review **EXAMPLES 20.2, 20.3 and 20.4** (Section 20.6) before attempting these problems.

VP20.4.1 In one cycle a Carnot engine takes in 8.00×10^4 J of heat and does 1.68×10^4 J of work. The temperature of the engine's cold reservoir is 25.0°C . (a) What is the efficiency of this engine? (b) How much heat does this engine exhaust per cycle? (c) What is the temperature (in $^\circ\text{C}$) of the hot reservoir?

VP20.4.2 For the Carnot cycle described in Example 20.3, you change the temperature of the cold reservoir from 27°C to -73°C . The initial pressure and volume at point a are unchanged, the volume still doubles

during the isothermal expansion $a \rightarrow b$, and the volume still decreases by one-half during the isothermal compression $c \rightarrow d$. For this modified cycle, calculate (a) the new efficiency of the cycle and (b) the amount of work done in each of the four steps of the cycle.

VP20.4.3 A Carnot refrigerator has a cold reservoir at -10.0°C and a hot reservoir at 25.0°C . (a) What is its coefficient of performance? (b) How much work input does this refrigerator require to remove 4.00×10^6 J of heat from the cold reservoir?

VP20.4.4 A Carnot engine uses the expansion and compression of n moles of argon gas, for which $C_V = \frac{3}{2}R$. This engine operates between temperatures T_C and T_H . During the isothermal expansion $a \rightarrow b$, the volume of the gas increases from V_a to $V_b = 2V_a$. (a) Calculate the work W_{ab} done during the isothermal expansion $a \rightarrow b$. Give your answer in terms of n , R , and T_H . (b) Calculate the work W_{bc} done during the adiabatic expansion $b \rightarrow c$. Give your answer in terms of n , R , T_C and T_H . (c) For this engine, $W_{ab} = W_{bc}$. Find the ratio T_C/T_H and the efficiency of the engine.

Be sure to review **EXAMPLES 20.6, 20.7, 20.8, 20.9, and 20.10** (Section 20.7) before attempting these problems.

VP20.10.1 Ethanol melts at 159 K (heat of fusion 1.042×10^5 J/kg) and boils at 351 K (heat of vaporization 8.54×10^5 J/kg). Liquid ethanol has a specific heat of 2428 J/kg \cdot K (which we assume does not depend on temperature). If you have 1.00 kg of ethanol originally in the solid state at 159 K, calculate the change in entropy of the ethanol when it (a) melts at 159 K, (b) increases in temperature as a liquid from 159 K to 351 K, and (c) boils at 351 K.

VP20.10.2 Initially 5.00 mol of helium (which we can treat as an ideal gas) occupies volume 0.120 m³ and is at temperature 20.0°C . You allow

the helium to expand so that its final volume is 0.360 m^3 and its final temperature is also 20.0°C . Calculate the net change in entropy of the helium if (a) you make the helium expand isothermally from 0.120 m^3 to 0.360 m^3 and (b) you first increase the temperature of the helium so that it expands at constant pressure from 0.120 m^3 to 0.360 m^3 , then cool the helium at constant volume to 20.0°C .

VP20.10.3 In one cycle of operation, an engine that does *not* use the Carnot cycle takes in $8.00 \times 10^4 \text{ J}$ of heat from a reservoir at 260°C , does $1.60 \times 10^4 \text{ J}$ of work, and rejects $6.40 \times 10^4 \text{ J}$ of heat to a reservoir at 20°C . At the end of the cycle, the engine is in the same state as at the beginning of the cycle. Calculate the change in entropy in one cycle

for (a) the engine, (b) the reservoir at 260°C , (c) the reservoir at 20°C , and (d) the system of engine and two reservoirs. Does the net entropy of the system increase, decrease, or stay the same?

VP20.10.4 You combine 1.00 kg of ice (heat of fusion $3.34 \times 10^5 \text{ J/K}$) at 0.0°C and 0.839 kg of liquid water (specific heat $4.19 \times 10^3 \text{ J/K}$) at 95.0°C . When the system comes to equilibrium, all of the ice has melted and the temperature of the mixture is 0.0°C . Calculate the change in entropy for (a) the ice as it melts, (b) the water that was initially at 95.0°C , and (c) the combination of the two. Does the net entropy of the system increase, decrease, or stay the same?

BRIDGING PROBLEM Entropy Changes: Cold Ice in Hot Water

An insulated container of negligible mass holds 0.600 kg of water at 45.0°C . You put a 0.0500 kg ice cube at -15.0°C in the water (**Fig. 20.23**). (a) Calculate the final temperature of the water once the ice has melted. (b) Calculate the change in entropy of the system.

SOLUTION GUIDE

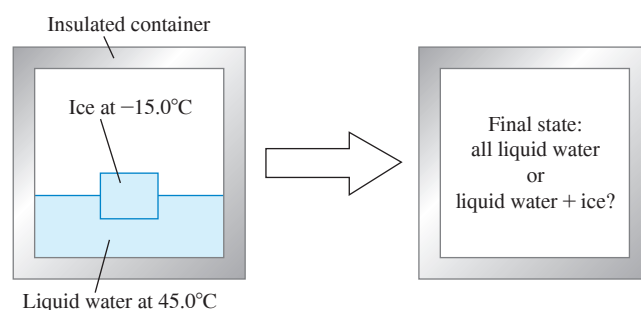
IDENTIFY and SET UP

1. Make a list of the known and unknown quantities, and identify the target variables.
2. How will you find the final temperature of the ice–water mixture? How will you decide whether or not all the ice melts?
3. Once you find the final temperature of the mixture, how will you determine the changes in entropy of (i) the ice initially at -15.0°C and (ii) the water initially at 45.0°C ?

EXECUTE

4. Use the methods of Chapter 17 to calculate the final temperature T . (*Hint*: First assume that all of the ice melts, then write an equation which says that the heat that flows into the ice equals the heat that flows out of the water. If your assumption is correct, the final temperature that you calculate will be greater than 0°C . If your assumption is incorrect, the final temperature will be 0°C or less, which means that some ice remains. You'll then need to redo the calculation to account for this.)

Figure 20.23 What becomes of this ice–water mixture?



5. Use your result from step 4 to calculate the entropy changes of the ice and the water. (*Hint*: You must include the heat flow associated with temperature changes, as in Example 20.6, as well as the heat flow associated with the change of phase.)
6. Find the total change in entropy of the system.

EVALUATE

7. Do the signs of the entropy changes make sense? Why or why not?

PROBLEMS

•, ••, •••: Difficulty levels. **CP**: Cumulative problems incorporating material from earlier chapters. **CALC**: Problems requiring calculus. **DATA**: Problems involving real data, scientific evidence, experimental design, and/or statistical reasoning. **BIO**: Biosciences problems.

DISCUSSION QUESTIONS

Q20.1 A pot is half-filled with water, and a lid is placed on it, forming a tight seal so that no water vapor can escape. The pot is heated on a stove, forming water vapor inside the pot. The heat is then turned off and the water vapor condenses back to liquid. Is this cycle reversible or irreversible? Why?

Q20.2 Give two examples of reversible processes and two examples of irreversible processes in purely mechanical systems, such as blocks sliding on planes, springs, pulleys, and strings. Explain what makes each process reversible or irreversible.

Q20.3 Household refrigerators have arrays or coils of tubing on the outside, usually at the back or bottom. When the refrigerator is running, the tubing becomes quite hot. Where does the heat come from?

Q20.4 Suppose you try to cool the kitchen of your house by leaving the refrigerator door open. What happens? Why? Would the result be the same if you left open a picnic cooler full of ice? Explain the reason for any differences.

Q20.5 Why must a room air conditioner be placed in a window rather than just set on the floor and plugged in? Why can a refrigerator be set on the floor and plugged in?

Q20.6 Is it a violation of the second law of thermodynamics to convert mechanical energy completely into heat? To convert heat completely into work? Explain your answers.

Q20.7 Imagine a special air filter placed in a window of a house. The tiny holes in the filter allow only air molecules moving faster than a certain speed to exit the house, and allow only air molecules moving slower than that speed to enter the house from outside. Explain why such an air filter would cool the house, and why the second law of thermodynamics makes building such a filter an impossible task.

Q20.8 An electric motor has its shaft coupled to that of an electric generator. The motor drives the generator, and some current from the generator is used to run the motor. The excess current is used to light a home. What is wrong with this scheme?

Q20.9 When a wet cloth is hung up in a hot wind in the desert, it is cooled by evaporation to a temperature that may be 20°C or so below that of the air. Discuss this process in light of the second law of thermodynamics.

Q20.10 Compare the pV -diagram for the Otto cycle in Fig. 20.6 with the diagram for the Carnot heat engine in Fig. 20.13. Explain some of the important differences between the two cycles.

Q20.11 The efficiency of heat engines is high when the temperature difference between the hot and cold reservoirs is large. Refrigerators, on the other hand, work better when the temperature difference is small. Thinking of the mechanical refrigeration cycle shown in Fig. 20.9, explain in physical terms why it takes less work to remove heat from the working substance if the two reservoirs (the inside of the refrigerator and the outside air) are at nearly the same temperature, than if the outside air is much warmer than the interior of the refrigerator.

Q20.12 What would be the efficiency of a Carnot engine operating with $T_H = T_C$? What would be the efficiency if $T_C = 0\text{ K}$ and T_H were any temperature above 0 K ? Interpret your answers.

Q20.13 Real heat engines, like the gasoline engine in a car, always have some friction between their moving parts, although lubricants keep the friction to a minimum. Would a heat engine with completely frictionless parts be 100% efficient? Why or why not? Does the answer depend on whether or not the engine runs on the Carnot cycle? Again, why or why not?

Q20.14 Does a refrigerator full of food consume more power if the room temperature is 20°C than if it is 15°C ? Or is the power consumption the same? Explain your reasoning.

Q20.15 In Example 20.4, a Carnot refrigerator requires a work input of only 230 J to extract 346 J of heat from the cold reservoir. Doesn't this discrepancy imply a violation of the law of conservation of energy? Explain why or why not.

Q20.16 How can the thermal conduction of heat from a hot object to a cold object increase entropy when the same amount of heat that flows out of the hot object flows into the cold one?

Q20.17 Explain why each of the following processes is an example of increasing randomness: mixing hot and cold water; free expansion of a gas; irreversible heat flow; developing heat by mechanical friction. Are entropy increases involved in all of these? Why or why not?

Q20.18 The free expansion of an ideal gas is an adiabatic process and so no heat is transferred. No work is done, so the internal energy does not change. Thus, $Q/T = 0$, yet the randomness of the system and thus its entropy have increased after the expansion. Why does Eq. (20.19) not apply to this situation?

Q20.19 Are the earth and sun in thermal equilibrium? Are there entropy changes associated with the transmission of energy from the sun to the earth? Does radiation differ from other modes of heat transfer with respect to entropy changes? Explain your reasoning.

Q20.20 Suppose that you put a hot object in thermal contact with a cold object and observe (much to your surprise) that heat flows from the cold object to the hot object, making the cold one colder and the hot one hotter. Does this process necessarily violate the first law of thermodynamics? The second law of thermodynamics? Explain.

Q20.21 If you run a movie film backward, it is as if the direction of time were reversed. In the time-reversed movie, would you see processes that violate conservation of energy? Conservation of linear momentum? Would you see processes that violate the second law of thermodynamics? In each case, if law-breaking processes could occur, give some examples.

Q20.22 BIO Some critics of biological evolution claim that it violates the second law of thermodynamics, since evolution involves simple life forms developing into more complex and more highly ordered organisms. Explain why this is not a valid argument against evolution.

Q20.23 BIO A growing plant creates a highly complex and organized structure out of simple materials such as air, water, and trace minerals. Does this violate the second law of thermodynamics? Why or why not? What is the plant's ultimate source of energy? Explain.

EXERCISES

Section 20.2 Heat Engines

20.1 • A diesel engine performs 2200 J of mechanical work and discards 4300 J of heat each cycle. (a) How much heat must be supplied to the engine in each cycle? (b) What is the thermal efficiency of the engine?

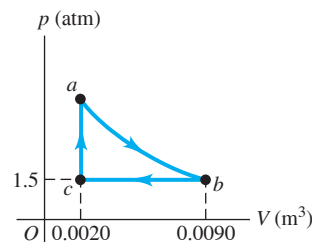
20.2 • An aircraft engine takes in 9000 J of heat and discards 6400 J each cycle. (a) What is the mechanical work output of the engine during one cycle? (b) What is the thermal efficiency of the engine?

20.3 • A Gasoline Engine. A gasoline engine takes in $1.61 \times 10^4\text{ J}$ of heat and delivers 3700 J of work per cycle. The heat is obtained by burning gasoline with a heat of combustion of $4.60 \times 10^4\text{ J/g}$. (a) What is the thermal efficiency? (b) How much heat is discarded in each cycle? (c) What mass of fuel is burned in each cycle? (d) If the engine goes through 60.0 cycles per second, what is its power output in kilowatts? In horsepower?

20.4 • A gasoline engine has a power output of 180 kW (about 241 hp). Its thermal efficiency is 28.0%. (a) How much heat must be supplied to the engine per second? (b) How much heat is discarded by the engine per second?

20.5 •• The pV -diagram in Fig. E20.5 shows a cycle of a heat engine that uses 0.250 mol of an ideal gas with $\gamma = 1.40$. Process ab is adiabatic. (a) Find the pressure of the gas at point a . (b) How much heat enters this gas per cycle, and where does it happen? (c) How much heat leaves this gas in a cycle, and where does it occur? (d) How much work does this engine do in a cycle? (e) What is the thermal efficiency of the engine?

Figure E20.5



20.6 •• CP A heat engine uses a large insulated tank of ice water as its cold reservoir. In 100 cycles the engine takes in 8000 J of heat energy from the hot reservoir and the rejected heat melts 0.0180 kg of ice in the tank. During these 100 cycles, how much work is performed by the engine?

Section 20.3 Internal-Combustion Engines

20.7 • The theoretical efficiency of an Otto cycle is 63%. The ratio of the C_p and C_v heat capacities for the gas in the engine is $\frac{7}{5}$. (a) What is the compression ratio r ? (b) If the net work done per cycle is 12.6 kJ, how much heat is rejected and how much is absorbed by the engine during each cycle?

20.8 • (a) Calculate the theoretical efficiency for an Otto-cycle engine with $\gamma = 1.40$ and $r = 9.50$. (b) If this engine takes in 10,000 J of heat from burning its fuel, how much heat does it discard to the outside air?

20.9 •• The Otto-cycle engine in a Mercedes-Benz SLK230 has a compression ratio of 8.8. (a) What is the ideal efficiency of the engine? Use $\gamma = 1.40$. (b) The engine in a Dodge Viper GT2 has a slightly higher compression ratio of 9.6. How much increase in the ideal efficiency results from this increase in the compression ratio?

Section 20.4 Refrigerators

20.10 •• A freezer has a coefficient of performance of 2.40. The freezer is to convert 1.80 kg of water at 25.0°C to 1.80 kg of ice at -5.0°C in one hour. (a) What amount of heat must be removed from the water at 25.0°C to convert it to ice at -5.0°C? (b) How much electrical energy is consumed by the freezer during this hour? (c) How much wasted heat is delivered to the room in which the freezer sits?

20.11 •• A refrigerator has a coefficient of performance of 2.25, runs on an input of 135 W of electrical power, and keeps its inside compartment at 5°C. If you put a dozen 1.0 L plastic bottles of water at 31°C into this refrigerator, how long will it take for them to be cooled down to 5°C? (Ignore any heat that leaves the plastic.)

20.12 • A refrigerator has a coefficient of performance of 2.10. In each cycle it absorbs 3.10×10^4 J of heat from the cold reservoir. (a) How much mechanical energy is required each cycle to operate the refrigerator? (b) During each cycle, how much heat is discarded to the high-temperature reservoir?

Section 20.6 The Carnot Cycle

20.13 •• In a Carnot engine the hot reservoir is 72.0°C warmer than the cold reservoir. The engine's efficiency is 12.5%. What are the Kelvin temperatures of the two reservoirs?

20.14 • A Carnot engine is operated between two heat reservoirs at temperatures of 520 K and 300 K. (a) If the engine receives 6.45 kJ of heat energy from the reservoir at 520 K in each cycle, how many joules per cycle does it discard to the reservoir at 300 K? (b) How much mechanical work is performed by the engine during each cycle? (c) What is the thermal efficiency of the engine?

20.15 • A Carnot engine whose high-temperature reservoir is at 620 K takes in 550 J of heat at this temperature in each cycle and gives up 335 J to the low-temperature reservoir. (a) How much mechanical work does the engine perform during each cycle? What is (b) the temperature of the low-temperature reservoir; (c) the thermal efficiency of the cycle?

20.16 •• An ice-making machine operates in a Carnot cycle. It takes heat from water at 0.0°C and rejects heat to a room at 24.0°C. Suppose that 85.0 kg of water at 0.0°C are converted to ice at 0.0°C. (a) How much heat is discharged into the room? (b) How much energy must be supplied to the device?

20.17 • A Carnot engine performs 2.5×10^4 J of work in each cycle and has an efficiency of 66%. (a) How much heat does the engine extract from its heat source in each cycle? (b) If the engine exhausts heat at room temperature (20.0°C), what is the temperature of its heat source?

20.18 •• A certain brand of freezer is advertised to use 730 kW·h of energy per year. (a) Assuming the freezer operates for 5 hours each day, how much power does it require while operating? (b) If the freezer keeps its interior at -5.0°C in a 20.0°C room, what is its theoretical maximum performance coefficient? (c) What is the theoretical maximum amount of ice this freezer could make in an hour, starting with water at 20.0°C?

20.19 • A Carnot refrigerator is operated between two heat reservoirs at temperatures of 320 K and 270 K. (a) If in each cycle the refrigerator receives 415 J of heat energy from the reservoir at 270 K, how many joules of heat energy does it deliver to the reservoir at 320 K? (b) If the refrigerator completes 165 cycles each minute, what power input is required to operate it? (c) What is the coefficient of performance of the refrigerator?

20.20 •• A Carnot heat engine uses a hot reservoir consisting of a large amount of boiling water and a cold reservoir consisting of a large tub of ice and water. In 5 minutes of operation, the heat rejected by the engine melts 0.0400 kg of ice. During this time, how much work W is performed by the engine?

20.21 •• Carnot refrigerator A has a 16% higher coefficient of performance than Carnot refrigerator B . The temperature difference between the hot and cold reservoirs is 30% greater for B than for A . If the cold-reservoir temperature for refrigerator B is 180 K, what is the cold-reservoir temperature for refrigerator A ?

Section 20.7 Entropy

20.22 • **CALC** You decide to take a nice hot bath but discover that your thoughtless roommate has used up most of the hot water. You fill the tub with 195 kg of 30.0°C water and attempt to warm it further by pouring in 5.00 kg of boiling water from the stove. (a) Is this a reversible or an irreversible process? Use physical reasoning to explain. (b) Calculate the final temperature of the bath water. (c) Calculate the net change in entropy of the system (bath water + boiling water), assuming no heat exchange with the air or the tub itself.

20.23 • A sophomore with nothing better to do adds heat to 0.350 kg of ice at 0.0°C until it is all melted. (a) What is the change in entropy of the water? (b) The source of heat is a very massive object at 25.0°C. What is the change in entropy of this object? (c) What is the total change in entropy of the water and the heat source?

20.24 •• **CALC** You make tea with 0.250 kg of 85.0°C water and let it cool to room temperature (20.0°C). (a) Calculate the entropy change of the water while it cools. (b) The cooling process is essentially isothermal for the air in your kitchen. Calculate the change in entropy of the air while the tea cools, assuming that all of the heat lost by the water goes into the air. What is the total entropy change of the system tea + air?

20.25 • Three moles of an ideal gas undergo a reversible isothermal compression at 20.0°C. During this compression, 1850 J of work is done on the gas. What is the change of entropy of the gas?

20.26 •• What is the change in entropy of 0.130 kg of helium gas at the normal boiling point of helium when it all condenses isothermally to 1.00 L of liquid helium? (*Hint:* See Table 17.4 in Section 17.6.)

20.27 • (a) Calculate the change in entropy when 1.00 kg of water at 100°C is vaporized and converted to steam at 100°C (see Table 17.4). (b) Compare your answer to the change in entropy when 1.00 kg of ice is melted at 0°C, calculated in Example 20.5 (Section 20.7). Is the change in entropy greater for melting or for vaporization? Interpret your answer using the idea that entropy is a measure of the randomness of a system.

Section 20.8 Microscopic Interpretation of Entropy

20.28 • **CALC** Two moles of an ideal gas occupy a volume V . The gas expands isothermally and reversibly to a volume $3V$. (a) Is the velocity distribution changed by the isothermal expansion? Explain. (b) Use Eq. (20.23) to calculate the change in entropy of the gas. (c) Use Eq. (20.18) to calculate the change in entropy of the gas. Compare this result to that obtained in part (b).

20.29 • **CALC** A lonely party balloon with a volume of 2.40 L and containing 0.100 mol of air is left behind to drift in the temporarily uninhabited and depressurized International Space Station. Sunlight coming through a porthole heats and explodes the balloon, causing the air in it to undergo a free expansion into the empty station, whose total volume is 425 m³. Calculate the entropy change of the air during the expansion.

PROBLEMS

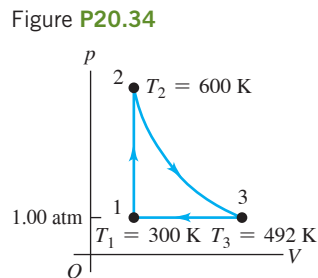
20.30 • CP As a budding mechanical engineer, you are called upon to design a Carnot engine that has 2.00 mol of a monatomic ideal gas as its working substance and operates from a high-temperature reservoir at 500°C. The engine is to lift a 15.0 kg weight 2.00 m per cycle, using 500 J of heat input. The gas in the engine chamber can have a minimum volume of 5.00 L during the cycle. (a) Draw a pV -diagram for this cycle. Show in your diagram where heat enters and leaves the gas. (b) What must be the temperature of the cold reservoir? (c) What is the thermal efficiency of the engine? (d) How much heat energy does this engine waste per cycle? (e) What is the maximum pressure that the gas chamber will have to withstand?

20.31 •• CP An ideal Carnot engine operates between 500°C and 100°C with a heat input of 250 J per cycle. (a) How much heat is delivered to the cold reservoir in each cycle? (b) What minimum number of cycles is necessary for the engine to lift a 500 kg rock through a height of 100 m?

20.32 •• BIO Entropy of Metabolism. An average sleeping person metabolizes at a rate of about 80 W by digesting food or burning fat. Typically, 20% of this energy goes into bodily functions, such as cell repair, pumping blood, and other uses of mechanical energy, while the rest goes to heat. Most people get rid of all this excess heat by transferring it (by conduction and the flow of blood) to the surface of the body, where it is radiated away. The normal internal temperature of the body (where the metabolism takes place) is 37°C, and the skin is typically 7°C cooler. By how much does the person's entropy change per second due to this heat transfer?

20.33 •• CP A certain heat engine operating on a Carnot cycle absorbs 410 J of heat per cycle at its hot reservoir at 135°C and has a thermal efficiency of 22.0%. (a) How much work does this engine do per cycle? (b) How much heat does the engine waste each cycle? (c) What is the temperature of the cold reservoir? (d) By how much does the engine change the entropy of the world each cycle? (e) What mass of water could this engine pump per cycle from a well 35.0 m deep?

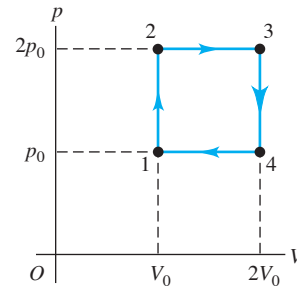
20.34 • A heat engine takes 0.350 mol of a diatomic ideal gas around the cycle shown in the pV -diagram of **Fig. P20.34**. Process 1→2 is at constant volume, process 2→3 is adiabatic, and process 3→1 is at a constant pressure of 1.00 atm. The value of γ for this gas is 1.40. (a) Find the pressure and volume at points 1, 2, and 3. (b) Calculate Q , W , and ΔU for each of the three processes. (c) Find the net work done by the gas in the cycle. (d) Find the net heat flow into the engine in one cycle. (e) What is the thermal efficiency of the engine? How does this compare to the efficiency of a Carnot-cycle engine operating between the same minimum and maximum temperatures T_1 and T_2 ?



20.35 •• BIO Entropy Change from Digesting Fat. Digesting fat produces 9.3 food calories per gram of fat, and typically 80% of this energy goes to heat when metabolized. (One food calorie is 1000 calories and therefore equals 4186 J.) The body then moves all this heat to the surface by a combination of thermal conductivity and motion of the blood. The internal temperature of the body (where digestion occurs) is normally 37°C, and the surface is usually about 30°C. By how much do the digestion and metabolism of a 2.50 g pat of butter change your body's entropy? Does it increase or decrease?

20.36 •• What is the thermal efficiency of an engine that takes n moles of diatomic ideal gas through the cycle 1→2→3→4→1 shown in **Fig. P20.36**?

Figure P20.36



20.37 •• CALC You build a heat engine that takes 1.00 mol of an ideal diatomic gas through the cycle shown in **Fig. P20.37**. (a) Show that process ab is an isothermal compression.

(b) During which process(es) of the cycle is heat absorbed by the gas? During which process(es) is heat rejected? How do you know? Calculate

(c) the temperature at points a , b , and c ; (d) the net heat exchanged with the surroundings and net work done by the engine in one cycle; (e) the thermal efficiency of the engine.

20.38 •• CALC One winter evening you fill a pint-sized plastic cup with ice and water to drink before going to bed. Estimate the volume of the ice and the volume of the water in the cup. Use the densities of ice and liquid water to find the mass of each. You set the cup on the kitchen counter, forget about it, and go to bed. The air in the kitchen is maintained at a constant 22.2°C by the central heating system of your apartment. When you wake up in the morning, the cup contains liquid water at 22.2°C. (a) What is the entropy change of the ice water during the process in which it went from 0°C to liquid water at 22.2°C as you slept? (b) What is the entropy change of the air in the room due to the heat that flows from it into the contents of the cup? (c) What is the total entropy change of the air-ice water system due to the heat exchange that changes the phase and temperature of the ice water? Is the total entropy change positive or negative?

20.39 • CALC A heat engine operates using the cycle shown in **Fig. P20.39**. The working substance is 2.00 mol of helium gas, which reaches a maximum temperature of 327°C. Assume the helium can be treated as an ideal gas. Process bc is isothermal. The pressure in states a and c is 1.00×10^5 Pa, and the pressure in state b is 3.00×10^5 Pa. (a) How much heat enters the gas and how much leaves the gas each cycle? (b)

How much work does the engine do each cycle, and what is its efficiency? (c) Compare this engine's efficiency with the maximum possible efficiency attainable with the hot and cold reservoirs used by this cycle.

Figure P20.37

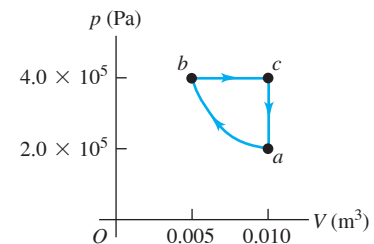
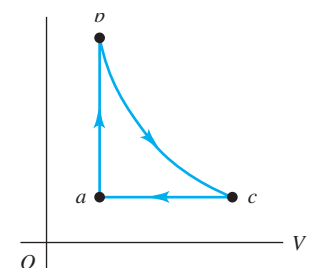


Figure P20.39

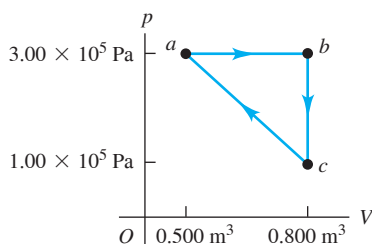


20.40 •• CP BIO A Human Engine. You decide to use your body as a Carnot heat engine. The operating gas is in a tube with one end in your mouth (where the temperature is 37.0°C) and the other end at the surface of your skin, at 30.0°C . (a) What is the maximum efficiency of such a heat engine? Would it be a very useful engine? (b) Suppose you want to use this human engine to lift a 2.50 kg box from the floor to a tabletop 1.20 m above the floor. How much must you increase the gravitational potential energy, and how much heat input is needed to accomplish this? (c) If your favorite candy bar has 350 food calories ($1\text{ food calorie} = 4186\text{ J}$) and 80% of the food energy goes into heat, how many of these candy bars must you eat to lift the box in this way?

20.41 ••• An experimental power plant at the Natural Energy Laboratory of Hawaii generates electricity from the temperature gradient of the ocean. The surface and deep-water temperatures are 27°C and 6°C , respectively. (a) What is the maximum theoretical efficiency of this power plant? (b) If the power plant is to produce 210 kW of power, at what rate must heat be extracted from the warm water? At what rate must heat be absorbed by the cold water? Assume the maximum theoretical efficiency. (c) The cold water that enters the plant leaves it at a temperature of 10°C . What must be the flow rate of cold water through the system? Give your answer in kg/h and in L/h .

20.42 • A monatomic ideal gas is taken around the cycle shown in **Fig. P20.42** in the direction shown in the figure. The path for process $c \rightarrow a$ is a straight line in the pV -diagram. (a) Calculate Q , W , and ΔU for each process $a \rightarrow b$, $b \rightarrow c$, and $c \rightarrow a$. (b) What are Q , W , and ΔU for one complete cycle? (c) What is the efficiency of the cycle?

Figure P20.42



20.43 • CALC A cylinder contains oxygen at a pressure of 2.00 atm . The volume is 4.00 L , and the temperature is 300 K . Assume that the oxygen may be treated as an ideal gas. The oxygen is carried through the following processes:

- Heated at constant pressure from the initial state (state 1) to state 2, which has $T = 450\text{ K}$.
- Cooled at constant volume to 250 K (state 3).
- Compressed at constant temperature to a volume of 4.00 L (state 4).
- Heated at constant volume to 300 K , which takes the system back to state 1.

(a) Show these four processes in a pV -diagram, giving the numerical values of p and V in each of the four states. (b) Calculate Q and W for each of the four processes. (c) Calculate the net work done by the oxygen in the complete cycle. (d) What is the efficiency of this device as a heat engine? How does this compare to the efficiency of a Carnot-cycle engine operating between the same minimum and maximum temperatures of 250 K and 450 K ?

20.44 ••• A typical coal-fired power plant generates 1000 MW of usable power at an overall thermal efficiency of 40% . (a) What is the rate of heat input to the plant? (b) The plant burns anthracite coal, which has a heat of combustion of $2.65 \times 10^7\text{ J/kg}$. How much coal does the plant use per day, if it operates continuously? (c) At what rate is heat ejected into the cool reservoir, which is the nearby river? (d) The river is at 18.0°C before it reaches the power plant and 18.5°C after it has received the plant's waste heat. Calculate the river's flow rate, in cubic meters per second. (e) By how much does the river's entropy increase each second?

20.45 •• A Carnot engine operates between two heat reservoirs at temperatures T_H and T_C . An inventor proposes to increase the efficiency by running one engine between T_H and an intermediate temperature T' and a second engine between T' and T_C , using as input the heat expelled by the first engine. Compute the efficiency of this composite system, and compare it to that of the original engine.

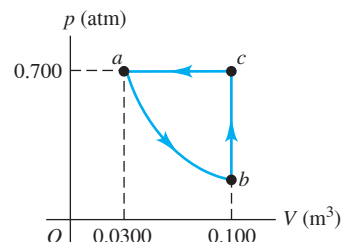
20.46 •• (a) Estimate the fuel efficiency, in miles per gallon, of a typical car. (b) The combustion of a gallon of gasoline releases 120 MJ of energy. If a typical car is driven at 40 mph and the engine is turning at 3000 revolutions per minute, then based on your estimate of fuel efficiency, how many joules of energy are released by combustion during each cycle of the engine? (c) A typical car engine runs with 20% efficiency. Based on this figure, how many watts of power does the car supply when moving at a steady 40 mph ? (d) What is that figure in horsepower?

20.47 • Automotive Thermodynamics. A Volkswagen Passat has a six-cylinder Otto-cycle engine with compression ratio $r = 10.6$. The diameter of each cylinder, called the *bore* of the engine, is 82.5 mm . The distance that the piston moves during the compression in **Fig. 20.5**, called the *stroke* of the engine, is 86.4 mm . The initial pressure of the air-fuel mixture (at point a in **Fig. 20.6**) is $8.50 \times 10^4\text{ Pa}$, and the initial temperature is 300 K (the same as the outside air). Assume that 200 J of heat is added to each cylinder in each cycle by the burning gasoline, and that the gas has $C_V = 20.5\text{ J/mol} \cdot \text{K}$ and $\gamma = 1.40$. (a) Calculate the total work done in one cycle in each cylinder of the engine, and the heat released when the gas is cooled to the temperature of the outside air. (b) Calculate the volume of the air-fuel mixture at point a in the cycle. (c) Calculate the pressure, volume, and temperature of the gas at points b , c , and d in the cycle. In a pV -diagram, show the numerical values of p , V , and T for each of the four states. (d) Compare the efficiency of this engine with the efficiency of a Carnot-cycle engine operating between the same maximum and minimum temperatures.

20.48 •• (a) Estimate the size of your room. (b) One mole of an ideal gas at STP occupies a volume of 22.4 L . Using this figure, estimate the number of moles of air in your room. (c) How many molecules is that? (d) There are N^N ways to distribute N things onto N sites. As a rough approximation, assume there are as many states for air molecules as there are air molecules in your room. Compute the entropy of the air in your room.

20.49 •• The pV -diagram in **Fig. P20.49** shows the cycle for a refrigerator operating on 0.850 mol of H_2 . Assume that the gas can be treated as ideal. Process ab is isothermal. Find the coefficient of performance of this refrigerator.

Figure P20.49



20.50 •• BIO Human Entropy. A person with skin of surface area 1.85 m^2 and temperature 30.0°C is resting in an insulated room where the ambient air temperature is 20.0°C . Assume that this person gets rid of excess heat by radiation only. By how much does the person change the entropy of the air in this room each second? (Recall that the room radiates back into the person and that the emissivity of the skin is 1.00 .)

20.51 •• CALC An object of mass m_1 , specific heat c_1 , and temperature T_1 is placed in contact with a second object of mass m_2 , specific heat c_2 , and temperature $T_2 > T_1$. As a result, the temperature of the first object increases to T and the temperature of the second object decreases to T' . (a) Show that the entropy increase of the system is

$$\Delta S = m_1 c_1 \ln \frac{T}{T_1} + m_2 c_2 \ln \frac{T'}{T_2}$$

and show that energy conservation requires that

$$m_1 c_1 (T - T_1) = m_2 c_2 (T_2 - T')$$

(b) Show that the entropy change ΔS , considered as a function of T , is a *maximum* if $T = T'$, which is just the condition of thermodynamic equilibrium. (c) Discuss the result of part (b) in terms of the idea of entropy as a measure of randomness.

20.52 •• CALC To heat 1 cup of water (250 cm^3) to make coffee, you place an electric heating element in the cup. As the water temperature increases from 20°C to 78°C , the temperature of the heating element remains at a constant 120°C . Calculate the change in entropy of (a) the water; (b) the heating element; (c) the system of water and heating element. (Make the same assumption about the specific heat of water as in Example 20.10 in Section 20.7, and ignore the heat that flows into the ceramic coffee cup itself.) (d) Is this process reversible or irreversible? Explain.

20.53 •• DATA In your summer job with a venture capital firm, you are given funding requests from four inventors of heat engines. The inventors claim the following data for their operating prototypes:

	Prototype			
	A	B	C	D
T_C ($^\circ\text{C}$), low-temperature reservoir	47	17	-33	37
T_H ($^\circ\text{C}$), high-temperature reservoir	177	197	247	137
Claimed efficiency e (%)	21	35	56	20

(a) Based on the T_C and T_H values for each prototype, find the maximum possible efficiency for each. (b) Are any of the claimed efficiencies impossible? Explain. (c) For all prototypes with an efficiency that is possible, rank the prototypes in decreasing order of the ratio of claimed efficiency to maximum possible efficiency.

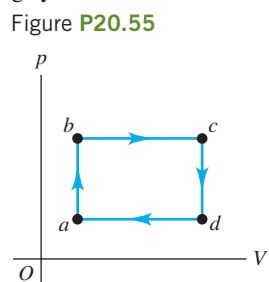
20.54 •• DATA For a refrigerator or air conditioner, the coefficient of performance K (often denoted as COP) is, as in Eq. (20.9), the ratio of cooling output $|Q_C|$ to the required electrical energy input $|W|$, both in joules. The coefficient of performance is also expressed as a ratio of powers,

$$K = \frac{|Q_C|/t}{|W|/t}$$

where $|Q_C|/t$ is the cooling power and $|W|/t$ is the electrical power input to the device, both in watts. The energy efficiency ratio (EER) is the same quantity expressed in units of Btu for $|Q_C|$ and $\text{W} \cdot \text{h}$ for $|W|$. (a) Derive a general relationship that expresses EER in terms of K . (b) For a home air conditioner, EER is generally determined for a 95°F outside temperature and an 80°F return air temperature. Calculate EER

for a Carnot device that operates between 95°F and 80°F . (c) You have an air conditioner with an EER of 10.9. Your home on average requires a total cooling output of $|Q_C| = 1.9 \times 10^{10} \text{ J}$ per year. If electricity costs you 15.3 cents per $\text{kW} \cdot \text{h}$, how much do you spend per year, on average, to operate your air conditioner? (Assume that the unit's EER accurately represents the operation of your air conditioner. A *seasonal energy efficiency ratio* (SEER) is often used. The SEER is calculated over a range of outside temperatures to get a more accurate seasonal average.) (d) You are considering replacing your air conditioner with a more efficient one with an EER of 14.6. Based on the EER, how much would that save you on electricity costs in an average year?

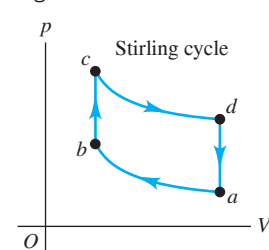
20.55 ••• DATA You are conducting experiments to study prototype heat engines. In one test, 4.00 mol of argon gas are taken around the cycle shown in **Fig. P20.55**. The pressure is low enough for the gas to be treated as ideal. You measure the gas temperature in states a , b , c , and d and find $T_a = 250.0 \text{ K}$, $T_b = 300.0 \text{ K}$, $T_c = 380.0 \text{ K}$, and $T_d = 316.7 \text{ K}$. (a) Calculate the efficiency e of the cycle. (b) Disappointed



by the cycle's low efficiency, you consider doubling the number of moles of gas while keeping the pressure and volume the same. What would e be then? (c) You remember that the efficiency of a Carnot cycle increases if the temperature of the hot reservoir is increased. So, you return to using 4.00 mol of gas but double the volume in states c and d while keeping the pressures the same. The resulting temperatures in these states are $T_c = 760.0 \text{ K}$ and $T_d = 633.4 \text{ K}$. T_a and T_b remain the same as in part (a). Calculate e for this cycle with the new T_c and T_d values. (d) Encouraged by the increase in efficiency, you raise T_c and T_d still further. But e doesn't increase very much; it seems to be approaching a limiting value. If $T_a = 250.0 \text{ K}$ and $T_b = 300.0 \text{ K}$ and you keep volumes V_a and V_b the same as in part (a), then $T_c/T_d = T_b/T_a$ and $T_c = 1.20T_d$. Derive an expression for e as a function of T_d for this cycle. What value does e approach as T_d becomes very large?

20.56 •• CP In an ideal Stirling engine, n moles of an ideal gas are isothermally compressed, pressurized at constant volume, allowed to expand isothermally, and then cooled at constant volume, as shown in **Fig. P20.56**. The expansion takes place at temperature T_H and the compression at temperature T_C . (a) Show that $p_c/p_d = p_b/p_a$. This quantity is called the compression ratio of the engine, or the CR. Determine the work

Figure P20.56



done in terms of the CR (b) during the expansion phase and (c) during the compression phase. (d) An ideal Stirling engine uses 1 mole of helium as its working substance and has a CR of 10, temperature reservoirs at 100°C and 20°C , and a frequency of operation of 100 Hz. What is its power output?

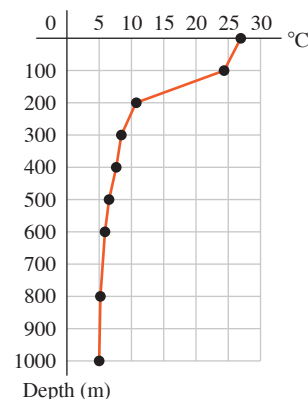
CHALLENGE PROBLEMS

20.57 ●●● On planet Tralfamadore the cool atmosphere is rich in froklom molecules. Spherical life forms called sporons feed on these molecules and obtain energy through a Carnot cycle. When a sporon that has injected froklom gas has isothermally contracted to a trigger volume, it violently squeezes itself, reducing its volume by half. At this point, its interior achieves the combustion temperature at which froklom fuses exothermically to produce klombactic acid. At the point of combustion, a sporon has radius 8.0 cm and internal pressure 20.3 kPa. The sporon swells during the reaction period, maintaining constant temperature until its injected froklom is depleted. The sporon continues to swell rapidly until its internal temperature matches the ambient temperature of 123 K and its gauge pressure is zero. Then it contracts slowly, emitting klombactic acid while simultaneously injecting froklom from the atmosphere. When its radius shrinks by a factor of 3 it reaches the trigger volume, which starts another cycle. Aside from the sporon's skin membrane, all substances behave like ideal gases. Froklom gas has a ratio of heat capacities of 1.30. (a) What is the combustion temperature at which froklom fuses? (b) What is the ambient pressure on Tralfamadore? (c) If a sporon generates 60 kJ of work each hour, how much heat does it draw in per minute? (d) How much heat is rejected back to the atmosphere per minute?

20.58 ●●● Consider a Diesel cycle that starts (at point *a* in Fig. 20.7) with air at temperature T_a . The air may be treated as an ideal gas. (a) If the temperature at point *c* is T_c , derive an expression for the efficiency of the cycle in terms of the compression ratio r . (b) What is the efficiency if $T_a = 300$ K, $T_c = 950$ K, $\gamma = 1.40$, and $r = 21.0$?

MCAT-STYLE PASSAGE PROBLEMS

Power from the Sea. *Ocean thermal energy conversion* is a process that uses the temperature difference between the warm surface water of tropical oceans and the cold deep-ocean water to run a heat engine. The graph shows a typical decrease of temperature with depth below the surface in tropical oceans. In the heat engine, the warmer surface water vaporizes a low-boiling-point fluid, such as ammonia. The heat of vaporization of ammonia is 260 cal/g at 27°C, the surface-water temperature. The vapor is used to turn a turbine and is then condensed back into a liquid by means of cold water



brought from deep below the surface through a large intake pipe. A power plant producing 10 MW of useful power would require a cold seawater flow rate of about 30,000 kg/s.

20.59 If the power plant uses a Carnot cycle and the desired theoretical efficiency is 6.5%, from what depth must cold water be brought? (a) 100 m; (b) 400 m; (c) 800 m; (d) deeper than 1000 m.

20.60 What is the change in entropy of the ammonia vaporized per second in the 10 MW power plant, assuming an ideal Carnot efficiency of 6.5%? (a) $+6 \times 10^6$ J/K per second; (b) $+5 \times 10^5$ J/K per second; (c) $+1 \times 10^5$ J/K per second; (d) 0.

20.61 Compare the entropy change of the warmer water to that of the colder water during one cycle of the heat engine, assuming an ideal Carnot cycle. (a) The entropy does not change during one cycle in either case. (b) The entropy of both increases, but the entropy of the colder water increases by more because its initial temperature is lower. (c) The entropy of the warmer water decreases by more than the entropy of the colder water increases, because some of the heat removed from the warmer water goes to the work done by the engine. (d) The entropy of the warmer water decreases by the same amount that the entropy of the colder water increases.

20.62 If the proposed plant is built and produces 10 MW but the rate at which waste heat is exhausted to the cold water is 165 MW, what is the plant's actual efficiency? (a) 5.7%; (b) 6.1%; (c) 6.5%; (d) 16.5%.

ANSWERS

Chapter Opening Question ?

(i) This is what a refrigerator does: It makes heat flow from the cold interior of the refrigerator to the warm outside. The second law of thermodynamics says that heat cannot *spontaneously* flow from a cold object to a hot one. A refrigerator has a motor that does work on the system to *force* the heat to flow in that way.

Key Example VARIATION Problems

VP20.1.1 (a) 6.89×10^4 J (b) 5.65×10^4 J

VP20.1.2 0.173

VP20.1.3 (a) 6.17×10^8 J (b) 1.21×10^8 J

VP20.1.4 (a) 3.96×10^8 J (b) 1.7×10^9 J (c) 0.23

VP20.4.1 (a) 0.210 (b) 6.32×10^4 J (c) 104°C

VP20.4.2 (a) 0.60

(b) $W_{ab} = 576$ J, $W_{bc} = 1250$ J, $W_{cd} = -231$ J, $W_{da} = -1250$ J

VP20.4.3 (a) 7.52 (b) 5.32×10^5 J

VP20.4.4 (a) $nRT_H \ln 2$ (b) $\frac{3}{2}nR(T_H - T_C)$

(c) $T_C/T_H = 1 - \frac{2}{3} \ln 2 = 0.538$, $e = \frac{2}{3} \ln 2 = 0.462$

VP20.10.1 (a) 6.55×10^2 J/K (b) 1.92×10^3 J/K (c) 2.43×10^3 J/K

VP20.10.2 (a) +45.7 J/K (b) +45.7 J/K

VP20.10.3 (a) zero (b) -150 J/K (c) +218 J/K (d) +68 J/K; increase

VP20.10.4 (a) $+1.22 \times 10^3$ J/K (b) -1.05×10^3 J/K

(c) $+1.7 \times 10^2$ J/K; increase

Bridging Problem

(a) 34.8°C

(b) +10 J/K