

19

The Second Law of Thermodynamics

New Concepts, New Skills

By the end of this chapter you should be able to

- Explain the second law of thermodynamics and the limitations it places on our ability to extract useful work from thermal-energy sources (19.2).
- Calculate the efficiencies of heat engines and refrigerators (19.2, 19.3).
- Describe the concepts of energy quality and entropy (19.4).
- Compute entropy changes for basic thermodynamic processes (19.4).

Connecting Your Knowledge

- This chapter builds on the first law of thermodynamics and the use of pV diagrams (18.1, 18.2).
- You should be familiar with the basic thermodynamic processes, particularly isothermal and adiabatic processes (18.2).



Most of the energy extracted from fuel in power plants is discarded as waste heat. The large cooling tower shown here dumps this waste heat into the environment. Why is so much energy wasted?

The first law of thermodynamics relates heat and other forms of energy. Much of our world depends on this relationship. Cars extract energy from the heat of burning gasoline. Most of our electricity originates in heat released by burning fuels or fissioning uranium. Our own bodies run on energy that begins as heat in the Sun's core. But the first law doesn't tell the whole story. Heat and mechanical energy aren't the same, and the difference makes the conversion of heat to work a more subtle task than the first law would imply.

19.1 Reversibility and Irreversibility

Figure 19.1 shows a movie of a bouncing ball. Play it backward and it still makes sense. Figure 19.2 shows a block sliding along a table, slowing because of friction—and warming in the process. Play this film backward and it makes no sense. You'll never see a block at rest suddenly start to move, cooling as it goes. Yet energy would be conserved if it did,

so the first law of thermodynamics would be satisfied. Beat an egg, blending yolk and white. Reverse the beater, and you'll never see them separate again. Put cups of cold and hot water in contact; the hot water cools and the cold water warms. The opposite never occurs—although energy would still be conserved.

Why are these events **irreversible**? In each case we start with matter in an organized state. The molecules of the sliding block share a common motion. The yolk molecules are all in one place. The hot water has more energetic molecules. Of all possible states, these *organized* ones are rare. There are many more *disorganized* states—for example, all the possible arrangements of molecules in a scrambled egg. As a system evolves, chances are it will end up less organized, simply because there are far more such states available to it. It's very unlikely to assume spontaneously a more organized state.

A key word here is “spontaneous.” We could restore organization—for example, by putting one cup of water in the refrigerator and the other in the microwave—but that requires a rather deliberate and energy-consuming process.

Irreversibility is a probabilistic notion. Events that *could* occur without violating the principles of Newtonian physics nevertheless *don't* occur because they're too improbable. As a practical consequence, harnessing the internal energy associated with random molecular motions is difficult because those motions won't spontaneously become organized. That makes much of the world's energy unavailable for doing useful work.

GOT IT? 19.1 Which of these processes is irreversible: (a) stirring sugar into coffee, (b) building a house, (c) demolishing a house with a wrecking ball, (d) demolishing a house by taking it apart piece by piece, (e) harnessing the energy of falling water to drive machinery, (f) harnessing the energy of falling water to heat a house?

19.2 The Second Law of Thermodynamics

Heat Engines

It's impossible to convert *all* the internal energy of a system to useful work. But **heat engines** extract *some* of that internal energy. Examples include gasoline and diesel engines, fossil-fueled and nuclear power plants, and jet aircraft engines.

Figure 19.3a is an energy-flow diagram for a “perfect” heat engine—one that extracts heat from a heat reservoir and converts it all to work. Such an engine would do exactly what we've just argued against: It would convert the random energy of thermal motion entirely to the ordered motion associated with mechanical work. In fact a perfect heat engine is impossible, for the same reason that we can't unscramble an egg or make a block accelerate spontaneously using its internal energy. This fact leads to one statement of the **second law of thermodynamics**:

Second law of thermodynamics (Kelvin-Planck statement) It is impossible to construct a heat engine operating in a cycle that extracts heat from a reservoir and delivers an equal amount of work.

The phrase “in a cycle” means that a practical engine goes through a repeated sequence of steps, as in the back-and-forth motions of the pistons in a gasoline engine.

A simple heat engine consists of a gas-cylinder system and a heat reservoir, the latter kept hot, perhaps, by burning a fuel. With the gas initially at high pressure, we place the cylinder in contact with the heat reservoir. The gas expands and does work W on the piston. In this isothermal process, the gas extracts heat $Q = W$ from the reservoir. Eventually the gas reaches pressure equilibrium and stops expanding. The piston must then be returned to its original position if it's to do more work.

If we just push the piston back, we'll have to do as much work as we got during the expansion, and our engine won't produce any net work. Instead we can cool the gas to reduce its volume, through contact with a cool reservoir. But then some energy leaves the

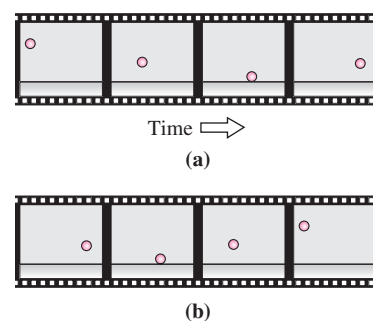


FIGURE 19.1 A movie of a bouncing ball makes sense whether it's shown forward or backward.

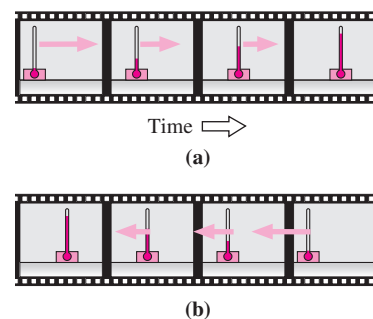


FIGURE 19.2 (a) A block warming (note thermometer) as friction dissipates its kinetic energy and it slows to a stop. (b) The reverse sequence would never happen, even though it doesn't violate energy conservation.

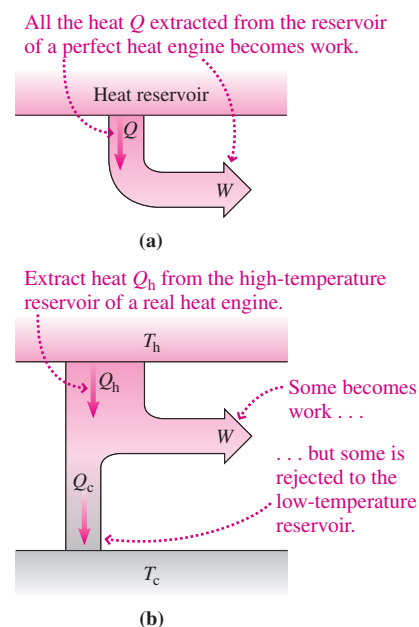


FIGURE 19.3 (a) Energy-flow diagram for a perfect heat engine. (b) A real engine delivers as work only a fraction of the energy extracted from the high-temperature reservoir.

system as heat rather than work, as shown conceptually in Fig. 19.3*b*. Our engine extracts heat from a source and delivers mechanical work, but over a full cycle the work delivered is less than the heat extracted. The remaining energy is rejected to the lower-temperature reservoir, usually the environment. That's why much of the energy released from fuels in car engines and power plants ends up as waste heat.

The second law of thermodynamics says we can't build a perfect heat engine. But how close can we come? We define the **efficiency** e of an engine as the ratio of the work W we get from it to what we have to supply—namely, the heat Q_h : $e = W/Q_h$. Since the process is cyclic, there's no net change in internal energy over one cycle. The first law of thermodynamics then shows that the work W done *by* the engine is the difference between the heat Q_h extracted from the high-temperature reservoir and the heat Q_c rejected to the cool reservoir:

$$e = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h} \quad (19.1)$$

In this chapter we'll often use W for the work done *by* an engine; in the first law it's the work done *on* a system. That's why W here is equal to the net heat $Q_h - Q_c$.

Figure 19.4 shows a heat engine whose efficiency we can calculate. The engine consists of a cylinder containing an ideal gas, sealed by a movable piston. The piston is connected to a rod that turns a wheel. The engine gets its energy from a heat reservoir at a high temperature T_h , and it rejects heat to a cooler reservoir at temperature T_c . Figure 19.5 shows how the engine works in a cycle of four steps, starting with the piston in its leftmost position (state *A* in Fig. 19.5), where the gas volume is a minimum:

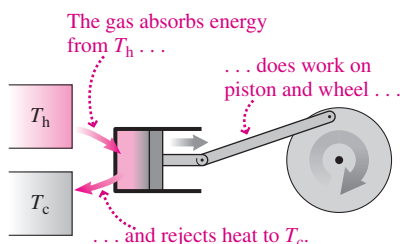


FIGURE 19.4 A simple heat engine.

1. **Isothermal expansion:** The high-temperature reservoir is placed in thermal contact with the cylinder. The gas absorbs heat Q_h from the hot reservoir and expands isothermally along path *AB*. Since temperature remains constant, so does internal energy. The first law then shows that the engine does work $W = Q$ on the piston and wheel.
2. **Adiabatic expansion:** At *B* we remove the hot reservoir, so the gas can no longer exchange heat. Thus the expansion becomes adiabatic and follows path *BC*. We design the engine so the gas has cooled to T_c when the piston reaches its rightmost position (state *C*), the point of maximum gas volume.
3. **Isothermal compression:** At *C* we bring the cool reservoir into thermal contact with the cylinder. The wheel's inertia keeps it turning, so the piston does work on the gas, compressing it isothermally from state *C* to *D*. This work ends up as heat rejected to the cool reservoir.
4. **Adiabatic compression:** At *D* we remove the cool reservoir and the compression continues adiabatically until the gas temperature is once again at T_h and the engine is back at state *A*.

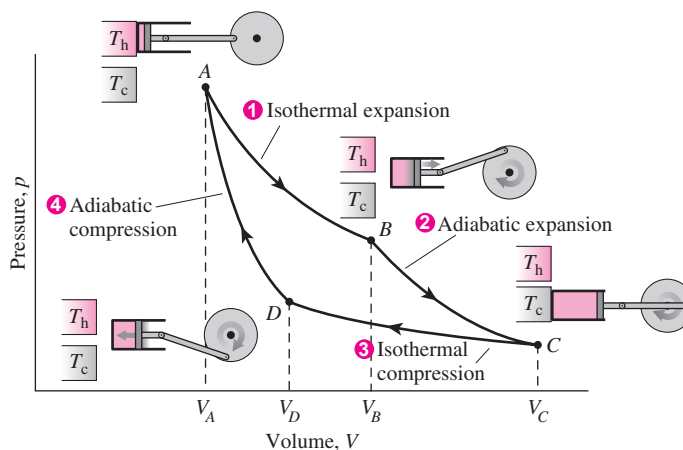


FIGURE 19.5 A pV diagram for the Carnot engine.

This cyclic process of two isothermal and two adiabatic steps is the **Carnot cycle** and the engine a **Carnot engine**, after the French engineer Sadi Carnot (1796–1832). The particular configuration of the engine isn't important, nor is the choice of an ideal gas as the engine's **working fluid**. What distinguishes the Carnot cycle from others is the sequence of thermodynamic processes and the fact that these processes are reversible. The Carnot engine is an example of a **reversible engine**—one in which thermodynamic equilibrium is maintained so that all steps could, in principle, be reversed.

What's the efficiency of a Carnot engine? To find out, we need the heats Q_h and Q_c absorbed and rejected during the isothermal parts of the cycle shown in Fig. 19.5. Equation 18.4 gives the heat Q_h absorbed during the isothermal expansion AB :

$$Q_h = nRT_h \ln\left(\frac{V_B}{V_A}\right)$$

and the heat Q_c rejected during the isothermal compression CD :

$$Q_c = -nRT_c \ln\left(\frac{V_D}{V_C}\right) = nRT_c \ln\left(\frac{V_C}{V_D}\right)$$

We put the minus sign here because the first law takes Q to be the heat *absorbed*, while Equation 19.1 for the engine efficiency requires that Q_c be the heat *rejected*. To calculate engine efficiency according to Equation 19.1, we need the ratio Q_c/Q_h :

$$\frac{Q_c}{Q_h} = \frac{T_c \ln(V_C/V_D)}{T_h \ln(V_B/V_A)} \quad (19.2)$$

This expression can be simplified by applying Equation 18.11b to the adiabatic processes BC and DA in the Carnot cycle: $T_h V_B^{\gamma-1} = T_c V_C^{\gamma-1}$ and $T_h V_A^{\gamma-1} = T_c V_D^{\gamma-1}$. Dividing the first of these two equations by the second gives

$$\left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_D}\right)^{\gamma-1} \quad \text{or} \quad \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

so Equation 19.2 becomes simply $Q_c/Q_h = T_c/T_h$. Using this result in Equation 19.1 then gives the efficiency of the Carnot engine:

$$e_{\text{Carnot}} = 1 - \frac{T_c}{T_h} \quad (\text{Carnot engine efficiency}) \quad (19.3)$$

where the temperatures are measured on an absolute scale (Kelvin or Rankine). Equation 19.3 shows that the Carnot engine's efficiency depends only on the highest and lowest temperatures of its working fluid. In practice, the low temperature is usually that of the environment; then maximizing efficiency requires making the high temperature as high as possible. Real engines trade off efficiency with the ability of materials to withstand high temperature and pressure.

EXAMPLE 19.1 Calculating Efficiency: A Carnot Engine

A Carnot engine extracts 240 J from its high-temperature reservoir during each cycle, and rejects 100 J to the environment at 15°C. How much work does the engine do in one cycle? What's its efficiency? What's the temperature of the hot reservoir?

INTERPRET This problem is about a Carnot engine, which operates via the Carnot cycle.

DEVELOP Equation 19.3, $e_{\text{Carnot}} = 1 - (T_c/T_h)$, relates the two temperatures and the efficiency. Here $Q_h = 240$ J, $Q_c = 100$ J, and $T_c = 15^\circ\text{C}$ or 288 K. The first law of thermodynamics relates work and heat flows. So our plan is to use the first law to find the work, then find the efficiency, and then use Equation 19.3 to find T_h .

EVALUATE Since there's no change in internal energy over one cycle, the first law requires that the work W done by the engine be equal to the net heat absorbed—namely, 240 J – 100 J. So $W = 140$ J. The efficiency is the ratio of work delivered to heat extracted, so $e = W/Q_h = 140 \text{ J}/240 \text{ J} = 58.3\%$. Knowing the efficiency, we solve Equation 19.3 for T_h :

$$T_h = \frac{T_c}{1 - e} = \frac{288 \text{ K}}{1 - 0.583} = 691 \text{ K} = 418^\circ\text{C}$$

ASSESS Make sense? The engine rejects somewhat less than half the 240 J as waste heat, so we should expect efficiency somewhat over 50%. And of course T_h must be greater than T_c , as our calculation confirms. ■

Engines, Refrigerators, and the Second Law

Why this emphasis on the Carnot engine? Because understanding this device will help answer the broader question of how much work we can hope to extract from thermal energy. That, in turn, will help us understand practical limitations on humankind's attempts to harness ever more energy and will lead to a deeper understanding of the second law of thermodynamics.

Why is Carnot's engine special? Couldn't we build a better engine with greater efficiency? The answer is no. The special role of the Carnot cycle is embodied in **Carnot's theorem**:

Carnot's theorem All Carnot engines operating between temperatures T_h and T_c have the same efficiency, $e_{\text{Carnot}} = 1 - (T_c/T_h)$, and no other engine operating between the same two temperatures can have a greater efficiency.

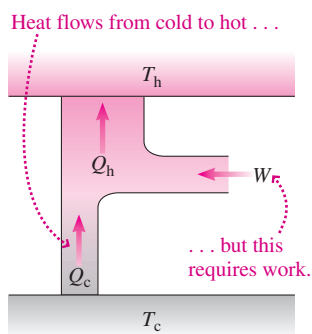


FIGURE 19.6 Energy-flow diagram for a real refrigerator.

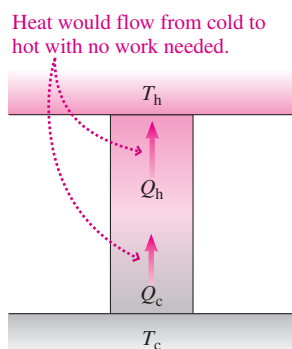


FIGURE 19.7 A perfect refrigerator is impossible.

To prove Carnot's theorem, we introduce the **refrigerator**. A refrigerator is the opposite of an engine: It extracts heat from a cool reservoir and rejects it to a hotter one, using work in the process (Fig. 19.6). A refrigerator forces heat to flow from cold to hot, but to do so it requires work. A household refrigerator cools its contents and warms the house (you can feel the heat coming out the back), but it uses electricity. That heat doesn't flow spontaneously from cold to hot leads to another statement of the second law of thermodynamics:

Second law of thermodynamics (Clausius statement) It is impossible to construct a refrigerator operating in a cycle whose sole effect is to transfer heat from a cooler object to a hotter one.

The Clausius statement rules out a perfect refrigerator (Fig. 19.7).

Suppose the Clausius statement were false. Then we could build the device of Fig. 19.8a, consisting of a reversible Carnot engine and a perfect refrigerator. In each cycle the engine would extract, say, 100 J from the hot reservoir, put out 60 J of useful work, and reject 40 J to the cool reservoir. The perfect refrigerator could transfer the 40 J back to the hot reservoir. The net effect would be to extract 60 J from the hot reservoir and convert it entirely to work (Fig. 19.8b)—and we would have a perfect heat engine, in violation of the Kelvin-Planck statement of the second law. A similar argument (Problem 38) shows that if a perfect heat engine is possible, then so is a perfect refrigerator. So the Clausius and Kelvin-Planck statements of the second law are equivalent, in that if one is false, then so is the other.

Because the Carnot engine is reversible, we could run it backward and reverse its path in Fig. 19.5. The engine would extract heat from the cool reservoir, take in work, and reject heat to the hot reservoir. It would be a refrigerator. Although real refrigerators aren't designed exactly like engines, the two are, in principle, interchangeable.

We're now ready to prove Carnot's assertion that Equation 19.3 gives the maximum engine efficiency. Consider again the Carnot engine in Fig. 19.8a. It extracts 100 J of heat and delivers 60 J of work, so it's 60% efficient. Suppose we had another engine operating between the same two reservoirs, but with 70% efficiency. Since the Carnot engine is reversible, we can run it as a refrigerator. If we put the two together, we get the device of

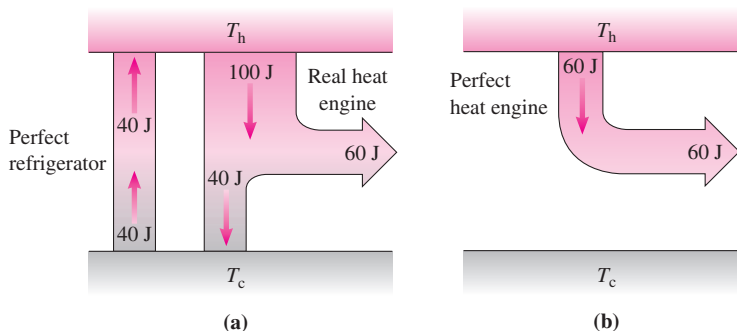


FIGURE 19.8 (a) A real heat engine combined with a perfect refrigerator is equivalent to (b) a perfect heat engine.

Fig. 19.9a. Its net effect is to extract 10 J from the cool reservoir and deliver 10 J of work—so it's a perfect heat engine, in violation of the second law (Fig. 19.9b). It's therefore impossible to make an engine that's more efficient than a Carnot engine, and thus Equation 19.3 gives the maximum possible efficiency for *any* heat engine operating between the same two fixed temperatures. For that reason the Carnot efficiency of Equation 19.3 is also called the **thermodynamic efficiency**.

Irreversible engines, because they involve processes that dissipate organized motion, are necessarily *less* efficient. So are reversible engines, if their heat exchange doesn't take place solely at the highest and lowest temperatures. The ordinary gasoline engine is a case in point; even if it could be made perfectly reversible, its efficiency would be less than that of a comparable Carnot engine (see Problem 53).

19.3 Applications of the Second Law

The world abounds with thermal energy, but the second law of thermodynamics limits our ability to use that energy. Any device we construct that involves the interchange of heat and work is a heat engine or refrigerator, subject to the second law.

Limitations on Heat Engines

Most of our electricity is produced in large power plants that are heat engines powered by the fossil fuels coal, oil, or natural gas, or by nuclear fission. Figure 19.10 diagrams such a power plant. The working fluid is water, heated in a boiler and converted to steam at high pressure. The steam expands adiabatically to spin a fanlike turbine. The turbine turns a generator that converts mechanical work to electrical energy.

Steam leaving the turbine is still gaseous and is hotter than the water supplied to the boiler. Here's where the second law applies! Had the water returned from the turbine in its original state, we would have extracted as work all the energy acquired in the boiler, in violation of the second law. Therefore, we must run the steam through a **condenser**, where it contacts pipes carrying cool water, typically from a river, lake, or ocean. The condensed steam, now cool water, is fed back into the boiler to repeat the cycle.

The maximum steam temperature in a power plant is limited by the materials used in its construction. For a conventional fossil-fuel plant, current technology permits high temperatures of around 650 K. Potential damage to nuclear fuel rods limits the temperature in a nuclear plant to around 570 K. The average temperature of the cooling water is about 40°C (310 K), so the maximum possible efficiencies for these power plants, given by Equation 19.3, are

$$e_{\text{fossil}} = 1 - \frac{310 \text{ K}}{650 \text{ K}} = 52\% \quad \text{and} \quad e_{\text{nuclear}} = 1 - \frac{310 \text{ K}}{570 \text{ K}} = 46\%$$

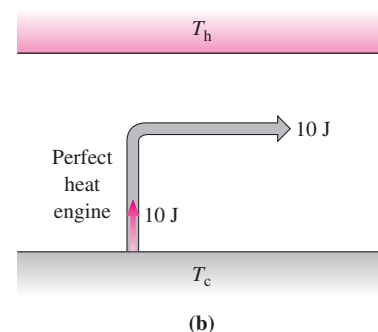
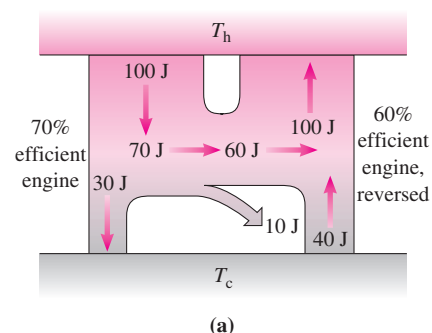
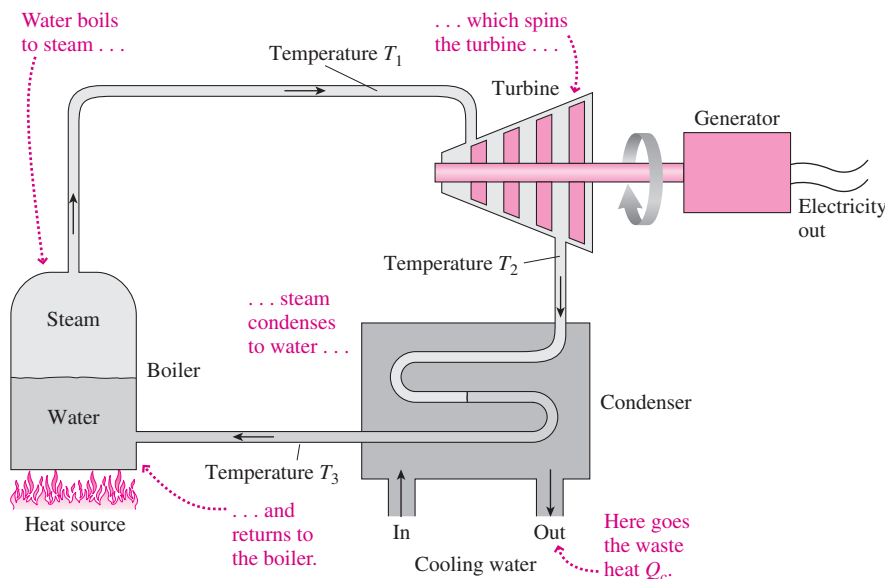


FIGURE 19.9 (a) A 60% efficient reversible engine run as a refrigerator, along with a hypothetical engine with 70% efficiency. (b) The combination is equivalent to a perfect heat engine.

FIGURE 19.10 Schematic diagram of an electric power plant.

Temperature differences between steam and cooling water, mechanical friction, and energy needed for pumps and pollution-control devices all reduce efficiency further, to about 40% for fossil-fuel plants and 34% for nuclear plants. So roughly two-thirds of the fuel energy we use to make electricity ends up as waste heat.

A typical large power plant produces 1 GW of electricity, so another 2 GW of waste heat goes into the cooling water. The resulting temperature rise can cause serious ecological problems. The huge cooling towers you see at power plants reduce such “thermal pollution” by transferring much of the waste heat to the atmosphere (see this chapter’s opening photo). Even so, a substantial fraction of all rainwater falling on the United States eventually finds its way through the condensers of power plants (see Problem 31).

EXAMPLE 19.2 Improving Efficiency: A Combined-Cycle Power Plant

The gas turbine in a combined-cycle power plant (see the Application below) operates at 1450°C . Its waste heat at 500°C is the input for a conventional steam cycle, with its average condenser temperature at 40°C . Find the thermodynamic efficiency of the combined cycle, and compare with the efficiencies of the individual components if they were operated independently.

INTERPRET This problem is about the thermodynamic efficiency of a combined-cycle power plant. As described in the Application, that means a plant using a high-temperature gas turbine whose waste heat becomes the energy input to a conventional steam turbine.

DEVELOP Figure 19.11 is a conceptual diagram of the combined-cycle power plant, based on the Application. Equation 19.3, $e = 1 - (T_c/T_h)$, gives the thermodynamic efficiencies of each cycle and of the combination. We identify the $1450^{\circ}\text{C} = 1723\text{ K}$ temperature as T_h in Equation 19.3 for the gas turbine. The intermediate temperature $500^{\circ}\text{C} = 773\text{ K}$ serves as T_c for the gas turbine but as T_h for the steam cycle. Finally, the 40°C or 313-K condenser temperature is T_c for the steam cycle.

EVALUATE To treat the entire plant as a single heat engine in Equation 19.3, we use the highest and lowest temperatures:

$$e_{\text{combined}} = 1 - \frac{T_c}{T_h} = 1 - \frac{313\text{ K}}{1723\text{ K}} = 0.82 = 82\%$$

Friction and other losses would reduce this figure substantially, but a combined-cycle plant operating at these temperatures could have a

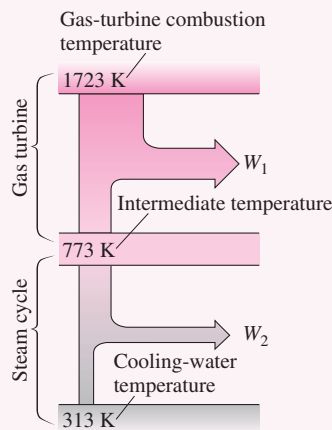


FIGURE 19.11 Conceptual diagram of a combined-cycle power plant.

practical efficiency near 60%. The efficiencies of the individual components also follow from Equation 19.3:

$$e_{\text{gas turbine}} = 1 - \frac{773\text{ K}}{1723\text{ K}} = 55\% \quad \text{and} \quad e_{\text{steam}} = 1 - \frac{313\text{ K}}{773\text{ K}} = 60\%$$

ASSESS Make sense? Because of its extreme temperatures, the combined cycle gives an efficiency that’s better than either of its parts! You can learn more about combined-cycle power plants in the Application below, and by working Problem 32. ■

APPLICATION Combined-Cycle Power Plants



Improving power-plant efficiency helps reduce air pollution and greenhouse-gas emissions, not to mention the cost of electricity. Modern *combined-cycle* power plants achieve efficiencies approaching 60% by combining a conventional steam system like that of Fig. 19.10 with a *gas turbine* similar to a jet aircraft engine. Gas turbines operate at high temperatures—between 1000 K and 2000 K—but they aren’t very efficient because their exhaust temperature (T_c in Equation 19.3) is also high. In a combined-cycle plant, exhaust from a gas turbine drives a conventional steam cycle. The overall effect is the same as that of a single heat engine operating between the gas turbine’s high combustion temperature and the low temperature of the environment (see Problem 32). The second law still limits the efficiency, but the high T_h and low T_c make for greater efficiency than in a conventional plant. The photo shows a gas-fired combined-cycle plant.

Gasoline and diesel engines provide another pervasive example of heat engines. A typical automobile engine has a theoretical maximum efficiency of around 50%, but irreversible thermodynamic processes make the actual efficiency much lower. Mechanical friction dissipates additional energy, with the end result that less than 20% of the fuel energy reaches the driving wheels. Problems 53 and 54 explore the gasoline engine.

We wouldn't be so concerned with efficiency if we didn't have to pay for fuel or worry about the environment. Engines with "free" fuel include solar-thermal power plants that concentrate sunlight to boil a fluid that drives a turbine and ocean thermal-energy conversion (OTEC) schemes that extract useful work from the modest temperature difference between tropical surface waters and the deep ocean. Neither provides significant energy today, but that could change as the world moves away from fossil fuels.

Refrigerators and Heat Pumps

A refrigerator works like an engine in reverse; it takes in mechanical work and transfers heat from its cooler interior to its warmer surroundings. An air conditioner is a refrigerator whose "interior" is the building being cooled. A close cousin is the **heat pump**, which transfers heat either way, cooling a building in the summer and warming it in the winter (Fig. 19.12). In warmer climates, heat pumps exchange energy between a building and the outside air; in cooler climates they use groundwater, typically at about 10°C year-round. Heat pumps require electricity, but they transfer more heat energy than they consume in electricity. That makes heat pumps potentially energy-saving devices for winter heating. However, some of that gain is offset by the inefficiency of the power plant producing the electricity.

An efficient refrigerator (or any other device, for that matter) should maximize what we want from the device compared with what we have to put in. The **coefficient of performance** (COP) quantifies this ratio:

$$\text{COP} = \frac{\text{What we want}}{\text{What we put in}}$$

For a refrigerator or summertime heat pump, "what we want" is cooling, so the numerator is Q_c . For a wintertime heat pump, "what we want" is heating, so the numerator is Q_h . For either, "what we put in" is mechanical work, W , or its equivalent in electricity. Thus we have

$$\text{COP}_{\text{refrigerator}} = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c} \quad \text{COP}_{\text{heat pump}} = \frac{Q_h}{W} = \frac{Q_h}{Q_h - Q_c}$$

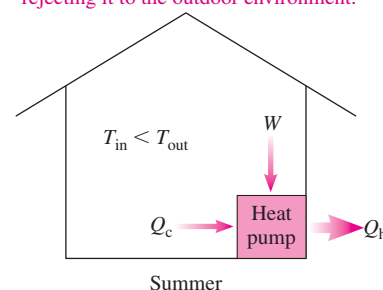
In both cases the second equality follows from the first law of thermodynamics. In deriving the maximum efficiency of a heat engine, we found that $Q_c/Q_h = T_c/T_h$. Therefore the maximum possible COPs are

$$\text{COP}_{\text{refrigerator}} = \frac{T_c}{T_h - T_c} \quad (19.4a)$$

$$\text{COP}_{\text{heat pump}} = \frac{T_h}{T_h - T_c} \quad (19.4b)$$

When the temperatures T_h and T_c are close, Equations 19.4 give high COPs—meaning the refrigerator or heat pump takes relatively little work to do its job. But as the difference increases, the COP drops and we have to supply more work. Incidentally, our COP expression works for engines as well, if we take "what we want" to be mechanical work W and "what we put in" to be the heat Q_h .

In summer the heat pump cools the house by extracting energy and rejecting it to the outdoor environment.



In winter the pump extracts energy from outside and transfers it to the inside.

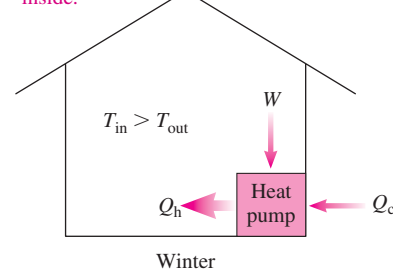


FIGURE 19.12 A heat pump.

EXAMPLE 19.3 The COP: A Home Freezer

A typical home freezer operates between a low of 0°F (−18°C or 255 K) and a high of 86°F (30°C or 303 K). What's its maximum possible COP? With this COP, how much electrical energy would it take to freeze 500 g of water initially at 0°C?

INTERPRET This problem is about a refrigerator—in this case a freezer. We identify T_h and T_c with the values 303 K and 255 K, respectively.

DEVELOP Equation 19.4a, $\text{COP} = T_c/(T_h - T_c)$, will determine the COP. Then we'll use Equation 17.5, $Q = Lm$, to find the heat Q_c that the freezer must extract to freeze the water. From there we'll be able to use $\text{COP} = Q_c/W$ to find the work—equivalently, the electrical energy—required.

(continued)

EVALUATE Equation 19.4a gives

$$\text{COP} = \frac{T_c}{T_h - T_c} = \frac{255 \text{ K}}{303 \text{ K} - 255 \text{ K}} = 5.31$$

From Equation 17.5 and Table 17.1, we find the heat that needs to be removed in freezing 500 g of ice: $Q_c = Lm = (334 \text{ kJ/kg})(0.50 \text{ kg}) = 167 \text{ kJ}$. The COP is the ratio of the heat removed to the work or electrical energy required, so we have $W = Q_c/\text{COP} = 167 \text{ kJ}/5.31 = 31 \text{ kJ}$.

ASSESS Make sense? A COP of 5.3 means that each unit of work transfers 5.3 units of heat from inside the freezer—so the electrical-energy requirement is modest. A practical freezer operating between these temperatures would have a lower COP and require more electrical energy. ■

GOT IT? 19.2 A clever engineer decides to increase the efficiency of a Carnot engine by cooling the low-temperature reservoir using a refrigerator with the maximum possible COP. Will the overall efficiency of this system (a) exceed, (b) be less than, or (c) equal that of the original engine alone?

19.4 Entropy and Energy Quality

If offered a joule of energy, would you rather it be in the form of mechanical work, heat at 1000 K, or heat at 300 K? Your answer might depend on what you want to do. To lift or accelerate a mass, you'd be smart to take your energy as work. But if you want to keep warm, heat at 300 K would be perfectly acceptable.

But which should you choose if you want to keep all your options open, making the energy available for the most possible uses? The second law of thermodynamics answers clearly: You should take the work. Why? Because you could use it directly as mechanical energy, or you could, through friction or other irreversible processes, use it to raise the temperature of something.

If you chose 300 K heat for your joule of energy, then you could supply a full joule only to objects cooler than 300 K. You couldn't do mechanical work unless you ran a heat engine. With its T_h only a little above the ambient temperature, your engine would be inefficient, and you could extract only a small fraction of a joule of mechanical energy. You would be better off with 1000-K heat since you could transfer it to anything cooler than 1000 K, or you could run a heat engine to produce up to 0.70 joule of mechanical energy.

CONCEPTUAL EXAMPLE 19.1 Energy Quality and Cogeneration

You need a new water heater, and you're trying to decide between gas and electric. The gas heater is 85% efficient, meaning 85% of the fuel energy goes into heating water. The electric heater is essentially 100% efficient. Thermodynamically, which heater makes the most sense?

EVALUATE Your electricity is energy of the highest quality. It probably comes from a thermal power plant, which typically discards as waste heat twice as much energy as it produces in electricity. The electric heater may be 100% efficient in your home, but when you consider the big picture, only about one-third of the fuel energy consumed at the power plant ends up heating your water. With 85% efficiency, the gas heater is the wiser choice.

ASSESS It makes sense to match energy sources to their end uses. Electricity is high-quality energy, so it's best for running motors, light sources, electronics, and other devices requiring high-quality energy.

Turning it into low-grade heat is a thermodynamic folly! A really smart strategy is **cogeneration**, in which the waste heat from electric power generation is used to heat buildings. In Europe, whole communities are heated that way, and institutions in the United States are increasingly turning to cogeneration to reduce energy costs and carbon emissions.

MAKING THE CONNECTION If the electricity comes from a more efficient gas-fired power plant with $e = 48\%$, compare the gas consumption of your two heater choices.

EVALUATE The gas heater turns 1 unit of fuel energy into 0.85 unit of thermal energy in the water. The power plant turns 1 unit of fuel energy into 0.48 unit of electrical energy, which the electric heater converts to 0.48 unit of thermal energy. The electric heater is therefore responsible for $0.85/0.48 = 1.8$ times as much gas consumption.

Taking your energy in the form of work gives you the most options. Anything you can do with a joule of energy, you can do with the work. Heat is less versatile, with 300 K heat the least useful of the three. We're not talking here about the quantity of energy—we have exactly 1 joule in each case—but about **energy quality** (Fig. 19.13). We can readily convert an entire amount of energy from higher to lower quality, but the second law precludes going in the opposite direction with 100% efficiency.

Entropy

Mix hot and cold water, and you get lukewarm water. There's no energy loss, but you *have* lost something—namely, the ability to do useful work. In the initial state, we could have run a heat engine using the ΔT between the hot and cold water. In the final state, there's no temperature difference, so we couldn't run a heat engine. The *quantity* of energy hasn't changed, but its *quality* has decreased. **Entropy**, S , quantifies the loss of quality associated with energy transformations. In his Ninth Memoir, Clausius coined the term for its similarity to the word “energy” and its Greek root “troph,” meaning *transformation*.

To motivate the definition of entropy, consider an ideal gas undergoing a Carnot cycle. Recall that a Carnot cycle consists of two isothermal and two adiabatic processes (Fig. 19.5). In deriving Equation 19.3 for the Carnot efficiency, we found that $Q_c/Q_h = T_c/T_h$, where Q_c was the heat *rejected* from the system to the low-temperature reservoir at T_c , and Q_h the heat *added* from the reservoir at T_h .

Let's focus on the ideal gas itself and define all heats as the heat *added* to the gas, so Q_c changes sign. The relationship between heats and temperatures can now be expressed as

$$\frac{Q_c}{T_c} + \frac{Q_h}{T_h} = 0 \quad (\text{Carnot cycle})$$

We can generalize this result to *any* reversible cycle by approximating the cycle as a sequence of Carnot cycles, as shown in Fig. 19.14. For each segment, we have $\sum Q/T = 0$. As we increase the number of cycles, the volume change associated with each isothermal segment shrinks and the edges get less jagged. We can approximate the closed cycle ever closer by using more and more Carnot cycles. In the limit, the approximation becomes exact and the sum becomes an integral:

$$\oint \frac{dQ}{T} = 0 \quad (\text{any reversible cycle}) \quad (19.5)$$

where the circle indicates integration over a *closed* path.

Equation 19.5 holds for *any* closed path in the pV diagram—that is, for any *reversible cycle*. That means we can define the *entropy change*, ΔS , between an initial state 1 and a final state 2 as

$$\Delta S_{12} = \int_1^2 \frac{dQ}{T} \quad (\text{entropy change}) \quad (19.6)$$

Note that entropy has the units J/K, the same units as Boltzmann's constant k_B .

Take a system along a path from state 1 to state 2 in its pV diagram; Equation 19.6 gives the corresponding entropy change ΔS_{12} . Go back to state 1 by any other reversible path, and the resulting entropy change ΔS_{21} must be $-\Delta S_{12}$ so that there's no entropy change around the closed path (Fig. 19.15). Thus the entropy change of Equation 19.6 is independent of path; it depends only on the initial and final states. The only restriction is that we integrate over a reversible path. Like pressure and temperature, entropy is therefore a *thermodynamic state variable*—a quantity that characterizes a given state independently of how the system got into that state.

We restricted ourselves to reversible paths in Equation 19.6 since irreversible processes take a system out of thermodynamic equilibrium and therefore aren't described by paths in the pV diagram. But because entropy depends only on the initial and final states, we can calculate the entropy change in an *irreversible* process by using Equation 19.6 for a *reversible* process that goes between the same two states.

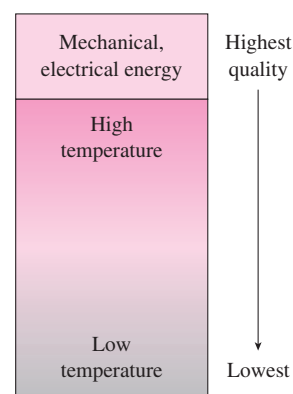


FIGURE 19.13 Energy quality measures the versatility of different energy forms.

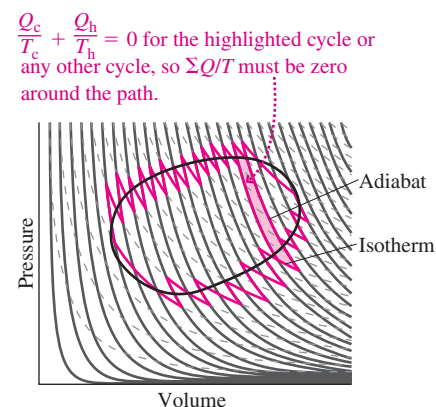


FIGURE 19.14 An arbitrary cycle approximated by isothermal (dashed curves) and adiabatic (solid curves) steps. Heat transfer occurs only during the isothermal steps.

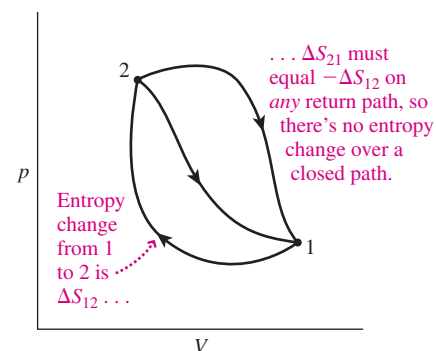


FIGURE 19.15 Entropy change is path-independent.

Note also that Equation 19.6 gives the entropy change of *just* the working fluid. The fluid—perhaps in an engine—is thermally connected to its surroundings, and if we’re interested in the *total* entropy change resulting from the engine’s operation, we’ll need to add the entropy changes for its environment—in this case the hot and cold reservoirs.

Adiabatic Free Expansion

In Fig. 19.16a, a partition confines an ideal gas to one side of a box; the other side is vacuum. Remove the partition, and the gas undergoes a **free expansion**, filling the box. Consider the box to be insulated, so there’s no heat flow and the expansion is therefore adiabatic. But this expansion is *irreversible*, so it’s significantly different from the adiabatic expansions we considered in Chapter 18. In our free expansion, the vacuum doesn’t exert pressure to oppose the gas, so the gas does no work and therefore its internal energy doesn’t change. Figure 19.16c shows how we could have used the expanding gas to turn a paddle wheel, extracting useful work. We can’t do that with the uniform-pressure gas of Fig. 19.16b, so the free expansion results in the system’s losing its ability to do work.

Let’s determine the entropy change for this irreversible process. We do that by finding a reversible process that takes the gas between the same two states. Since the gas’s internal energy doesn’t change, neither does its temperature. So the corresponding reversible process is an isothermal expansion, for which Equation 18.4 gives the heat added: $Q = nRT \ln(V_2/V_1)$. With the temperature constant, the entropy change of Equation 19.6 becomes

$$\Delta S = \int \frac{dQ}{T} = \frac{1}{T} \int dQ = \frac{Q}{T} = nR \ln\left(\frac{V_2}{V_1}\right)$$

The final volume V_2 is larger than V_1 , so entropy has *increased*. Although we computed this result for the reversible process, it holds for *any* process that takes the system between the same initial and final states—including our irreversible free expansion.

Entropy and the Availability of Work

Entropy increases during irreversible expansion—and energy quality decreases, in that the system loses its ability to do work. Had we let the gas in Fig. 19.16 undergo a reversible isothermal expansion instead of free expansion, it would have done work equal to the heat gained:

$$W = Q = nRT \ln\left(\frac{V_2}{V_1}\right)$$

After the irreversible free expansion, the gas can no longer do this work, even though its energy is unchanged. Comparing W with the entropy change ΔS we calculated above, we see that the energy that becomes unavailable to do work is $E_{\text{unavailable}} = T \Delta S$. This illustrates a more general relation between entropy and energy quality:

During an irreversible process in which the entropy of a system increases by ΔS , energy $E = T_{\text{min}} \Delta S$ becomes unavailable to do work, where T_{min} is the lowest temperature available to the system.

This statement shows that entropy provides our measure of energy quality. Given two systems with identical energy content, the one with the lower entropy contains the higher-quality energy. An entropy increase corresponds to a degradation in energy quality, as energy becomes unavailable to do work.

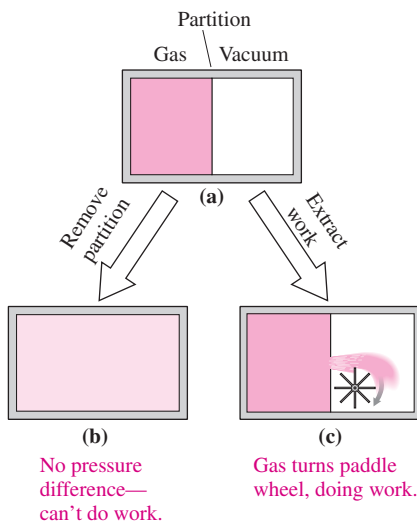


FIGURE 19.16 Two ways for a gas to expand into a vacuum.

EXAMPLE 19.4 Increasing Entropy: The Loss of Energy Quality

A 2.0-L cylinder contains 5.0 mol of compressed gas at 300 K. If the cylinder is discharged into a 150-L vacuum chamber and its temperature remains 300 K, how much energy has become unavailable to do work?

INTERPRET This problem asks about the loss of energy quality during an irreversible and therefore entropy-increasing process—namely, an adiabatic free expansion.

DEVELOP Figure 19.17 is a sketch of the situation, similar to Fig. 19.16 except that here the gas volume changes more dramatically. In analyzing the free expansion of Fig. 19.16, we found $\Delta S = nR \ln(V_2/V_1)$. Our statement relating entropy and energy quality says that the energy made unavailable to do work is $T_{\min} \Delta S$. So our plan is to calculate ΔS and multiply by T_{\min} to find that unavailable energy.

EVALUATE Because the temperature doesn't change, T_{\min} is the 300 K temperature we're given, and we have

$$\begin{aligned} E_{\text{unavailable}} &= T \Delta S = nRT \ln\left(\frac{V_2}{V_1}\right) \\ &= (5.0 \text{ mol})(8.314 \text{ J/K} \cdot \text{mol})(300 \text{ K}) \ln\left(\frac{152 \text{ L}}{2.0 \text{ L}}\right) = 54 \text{ kJ} \end{aligned}$$

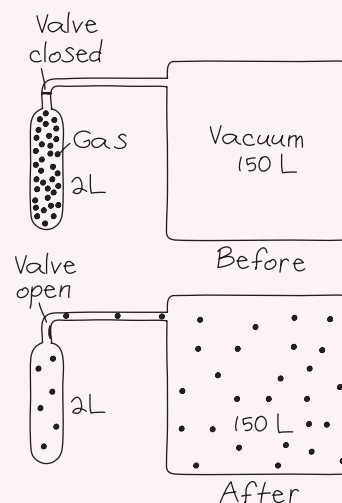


FIGURE 19.17 Our sketch for Example 19.4. Note that the final volume is 152 L.

ASSESS Make sense? Yes: This is the work we could have extracted from a reversible isothermal expansion. By letting the gas undergo an irreversible process, we gave up the possibility of extracting this work. ■

A Statistical Interpretation of Entropy

We began this chapter arguing that systems naturally evolve from ordered to disordered states. Entropy increase measures that loss of order, which is what makes energy unavailable to do work. Here we'll explore the meaning of entropy further, based on the partitioned box we used for adiabatic free expansion.

Suppose we have a gas with just two identical molecules. The left side of Fig. 19.18 shows that, with the partition removed, there are four possible **microstates**—specific arrangements of the individual molecules in the box. But say we only care about the number of molecules in each side of the box. Then two of these arrangements are indistinguishable, because they both have one molecule in each half of the box. Those two correspond to a single **macrostate**, specified by giving the number of molecules in each half of the box, without regard to which molecules they are. This is shown on the right in Fig. 19.18.

With four available microstates, the probability of being in any one microstate is $\frac{1}{4}$. There's only one microstate with both molecules on the left, so the chances of being in the macrostate with two molecules on the left is also $\frac{1}{4}$; the same is true for the macrostate with two molecules on the right. But two of the possible microstates have one molecule on each side, so the probability for this macrostate is $\frac{1}{2}$.

Now consider a gas of four molecules. Figure 19.19 (next page) shows 16 possible microstates, corresponding to 5 macrostates. Again, the probability of finding the system in a given macrostate depends on the associated number of microstates; Fig. 19.19 enumerates these probabilities. Clearly, we're most likely to find the system in the macrostate with the molecules evenly divided; the states with all the molecules on one side are now quite improbable.

Raise the number of molecules to 100, and the number of microstates becomes huge— 2^{100} , or more than 10^{30} . That makes the macrostates with all or nearly all the molecules on one side extremely improbable. The macrostate with half the molecules on each side

Microstates (ways of distributing the two atoms in the two halves of the box)	Macrostates (number of atoms in each half)
	2 0
	1 1
	1 1
	0 2

FIGURE 19.18 A gas of two molecules has four possible microstates and three macrostates.

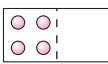
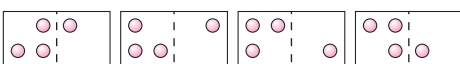
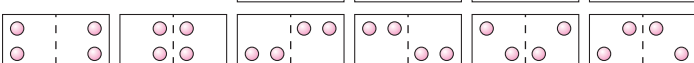
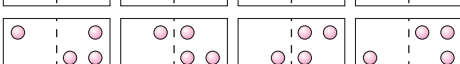

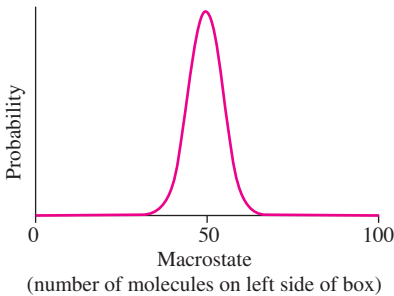
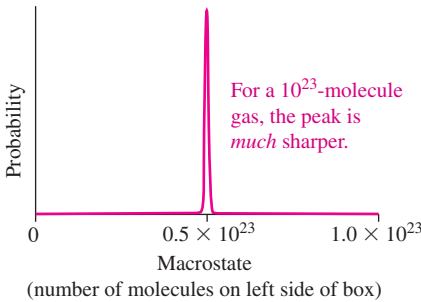
Microstates (16 total)				Macrostates	Probability of macrostate		
				<table><tr><td>4</td><td>0</td></tr></table>	4	0	$\frac{1}{16} = 0.06$
4	0						
				<table><tr><td>3</td><td>1</td></tr></table>	3	1	$\frac{4}{16} = 0.25$
3	1						
				<table><tr><td>2</td><td>2</td></tr></table>	2	2	$\frac{6}{16} = 0.38$
2	2						
				<table><tr><td>1</td><td>3</td></tr></table>	1	3	$\frac{4}{16} = 0.25$
1	3						
				<table><tr><td>0</td><td>4</td></tr></table>	0	4	$\frac{1}{16} = 0.06$
0	4						

FIGURE 19.19 Microstates, macrostates, and probabilities for a gas of four molecules.



(a)



(b)

FIGURE 19.20 (a) Probability distributions for a gas of (a) 100 molecules and (b) 10^{23} molecules.

remains the most likely, although states with nearly equal divisions of molecules are also quite probable. Rather than enumerate these probabilities, we graph them (Fig. 19.20).

Typical gas samples have roughly 10^{23} molecules, and that makes macrostates with anything other than a nearly equal distribution of molecules extremely unlikely—as suggested by the spike-like probability distribution in Fig. 19.20. You could sit in your room for many times the age of the universe, and you’d never see all the air molecules spontaneously end up on one side of the room!

Entropy and the Second Law of Thermodynamics

The statistical improbability of more ordered states—in our example, those with significantly more molecules on one side of the box—is at the root of the second law of thermodynamics. Although we defined entropy in terms of heat flow and temperature (Equation 19.6), a more fundamental definition involves the probabilities of individual microstates. In that sense, entropy is indeed a measure of disorder.

Systems naturally evolve toward disordered or higher-entropy states simply because there are far more of these states available. So a general statement of the second law is:

Second law of thermodynamics The entropy of a closed system can never decrease.

At best, the entropy of a closed system remains constant—and that’s only in an ideal, reversible process. If anything irreversible occurs—friction, or any deviation from thermodynamic equilibrium—then entropy increases. As it does, energy becomes unavailable to do work, and nothing within the closed system can restore that energy to its original quality. This new statement of the second law subsumes our previous statements about the impossibility of perfect heat engines and refrigerators, for their operation would require an entropy decrease.

We *can* decrease the entropy of a system that isn’t closed—but only by supplying high-quality energy from outside. Running a refrigerator decreases the entropy of its contents, but this requires electrical energy to make heat flow from cold to hot. That high-quality electrical energy deteriorates into additional heat that’s rejected to the refrigerator’s environment. If we consider the entire system, not just the refrigerator’s contents, the overall entropy has increased.

Any system whose entropy seems to decrease—that gets more rather than less organized—can’t be closed. If we enlarge a system’s boundaries to encompass the entire universe, then we have the ultimate statement of the second law:

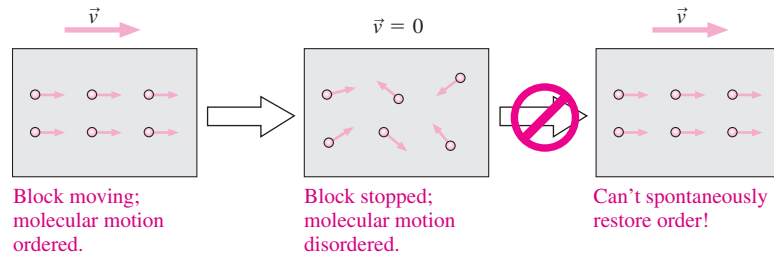
Second law of thermodynamics The entropy of the universe can never decrease.

Examples include the growth of a living thing from the random mix of molecules in its environment, the construction of a skyscraper from materials that were originally dispersed about Earth, and the appearance of ordered symbols on a printed page from a bottle of ink. All these are entropy-decreasing processes in which matter goes from near chaos to a highly organized state—akin to separating yolk and white from a scrambled egg. But Earth isn't a closed system. It gets high-quality energy from the Sun, energy that's ultimately responsible for life. If we consider the Earth-Sun system, the entropy decrease associated with life and civilization is more than balanced by the entropy increase associated with the degradation of high-quality solar energy. We living things represent a remarkable phenomenon—the organization of matter in a universe governed by a tendency toward disorder. But we can't escape the second law of thermodynamics. Our highly organized selves and society, and the entropy decreases they represent, come into being only at the expense of greater entropy increases elsewhere.

GOT IT? 19.3 In each of the following processes, does the entropy of the named system alone increase, decrease, or stay the same? (a) A balloon deflates; (b) cells differentiate in a growing embryo, forming different physiological structures; (c) an animal dies, and its remains gradually decay; (d) an earthquake demolishes a building; (e) a plant utilizes sunlight, carbon dioxide, and water to manufacture sugar; (f) a power plant burns coal and produces electrical energy; (g) a car's friction-based brakes stop the car.

Big Picture

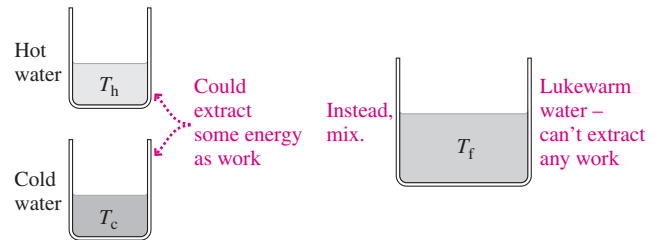
The big idea behind this chapter is the **second law of thermodynamics**—ultimately, the statement that systems tend naturally toward disorder, or states of higher **entropy**. The second law is manifest in the real world by forbidding the construction of perfect heat engines and perfect refrigerators—therefore preventing us from extracting as useful work all the energy that’s contained in random thermal motions. Ultimately, the second law says that the entropy of any closed system, including the entire universe, cannot decrease.



Key Concepts and Equations

Entropy is a quantitative measure of energy quality and of disorder; the higher the entropy, the lower the energy quality and the greater the disorder. The highest-quality energy is mechanical or electrical energy, followed by the internal energy of systems at high temperature, and finally low-temperature internal energy. Whenever entropy increases, energy becomes unavailable to do work.

- $\Delta S = \int_1^2 \frac{dQ}{T}$ gives the entropy change as a system goes from state 1 to state 2.
- $E_{\text{unavailable}} = T_{\text{min}} \Delta S$ is the energy that becomes unavailable as a result of entropy increase ΔS .

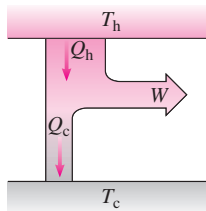


Applications

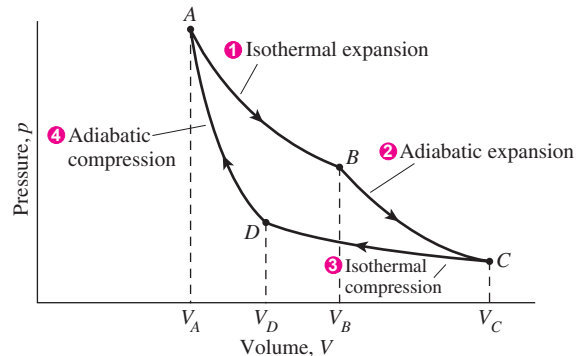
The second law sets the maximum possible efficiency of any heat engine as that of the **Carnot engine**, an engine that combines adiabatic and isothermal processes.

$$e = \frac{W}{Q_h} \leq e_{\text{max}} = 1 - \frac{T_c}{T_h}$$

This defines the engine's efficiency. This is the maximum possible efficiency.



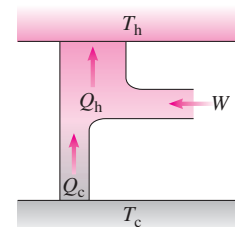
Energy-flow diagram for an engine



pV diagram for Carnot engine

Similarly, the second law limits the **coefficient of performance** of refrigerators and heat pumps:

$$\text{COP}_{\text{refrigerator}} = \frac{T_c}{T_h - T_c} \quad \text{COP}_{\text{heat pump}} = \frac{T_h}{T_h - T_c}$$



For Thought and Discussion

1. Could you cool the kitchen by leaving the refrigerator open? Explain.
2. Could you heat the kitchen by leaving the oven open? Explain.
3. Should a car get better mileage in the summer or the winter? Explain.
4. Is there a limit to the maximum temperature that can be achieved by focusing sunlight with a lens? If so, what is it?
5. Name some irreversible processes that occur in a real engine.
6. Your power company claims that electric heat is 100% efficient. Discuss.
7. A hydroelectric power plant, using the energy of falling water, can operate with efficiency arbitrarily close to 100%. Why?
8. A heat-pump manufacturer claims the device will heat your home using only energy already available in the ground. Is this true?
9. Why do refrigerators and heat pumps have different definitions of COP?
10. The heat Q added during adiabatic free expansion is zero. Why can't we then argue from Equation 19.6 that the entropy change is zero?
11. Energy is conserved, so why can't we recycle it as we do materials?
12. Why doesn't the evolution of human civilization violate the second law of thermodynamics?

Exercises and Problems

Exercises

Sections 19.2 and 19.3 The Second Law of Thermodynamics and Its Applications

13. What are the efficiencies of reversible heat engines operating between (a) the normal freezing and boiling points of water, (b) the 25°C temperature at the surface of a tropical ocean and deep water at 4°C , and (c) a 1000°C flame and room temperature?
14. A cosmic heat engine might operate between the Sun's 5600 K surface and the 2.7 K temperature of intergalactic space. What would be its maximum efficiency?
15. A reversible Carnot engine operating between helium's melting point and its 4.25 K boiling point has an efficiency of 77.7% . What's the melting point?
16. A Carnot engine absorbs 900 J of heat each cycle and provides 350 J of work. (a) What's its efficiency? (b) How much heat is rejected each cycle? (c) If the engine rejects heat at 10°C , what's its maximum temperature?
17. Find the COP of a reversible refrigerator operating between 0°C and 30°C .
18. How much work does a refrigerator with $\text{COP} = 4.2$ require to freeze 670 g of water already at its freezing point?
19. The human body can be 25% efficient at converting chemical energy of fuel to mechanical work. Can the body be considered a heat engine, operating on the temperature difference between body temperature and the environment?

Section 19.4 Entropy and Energy Quality

20. Calculate the entropy change associated with melting 1.0 kg of ice at 0°C .
21. You metabolize a 650-kcal burger at your 37°C body temperature. What's the associated entropy increase?
22. You heat 250 g of water from 10°C to 95°C . By how much does the entropy of the water increase?

23. Melting a block of lead already at its melting point results in an entropy increase of 900 J/K . What's the mass of the lead? (*Hint:* Consult Table 17.1.)
24. How much energy becomes unavailable for work in an isothermal process at 440 K , if the entropy increase is 25 J/K ?
25. For a gas of 6 molecules confined to a box, find the probability that (a) all the molecules will be found on one side of the box and (b) half the molecules will be found on each side.

Problems

26. A Carnot engine extracts 890 J from a 550 K reservoir during each cycle and rejects 470 J to a cooler reservoir. It operates at 22 cycles per second. Find (a) the work done during each cycle, (b) its efficiency, (c) the temperature of the cool reservoir, and (d) its mechanical power output.
27. The maximum steam temperature in a nuclear power plant is 570 K . The plant rejects heat to a river whose temperature is 0°C in the winter and 25°C in the summer. What are the maximum possible efficiencies for the plant during these seasons?
28. You're engineering an energy-efficient house that will require an average of 4.6 kW to heat on cold winter days. You've designed a photovoltaic system for electric power, which will supply on average 2.0 kW . You propose to heat the house with an electrically operated groundwater-based heat pump. What should you specify as the minimum acceptable COP for the pump if the photovoltaic system supplies its energy?
29. A power plant's electrical output is 750 MW . Cooling water at 15°C flows through the plant at $2.8 \times 10^4\text{ kg/s}$, and its temperature rises by 8.5°C . Assuming that the plant's only energy loss is to the cooling water, which serves as its low-temperature reservoir, find (a) the rate of energy extraction from the fuel, (b) the plant's efficiency, and (c) its highest temperature.
30. A power plant extracts energy from steam at 250°C and delivers 800 MW of electric power. It discharges waste heat to a river at 30°C . The plant's overall efficiency is 28% . (a) How does this efficiency compare with the maximum possible at these temperatures? (b) Find the rate of waste-heat discharge to the river. (c) How many houses, each requiring 18 kW of heating power, could be heated with the waste heat from this plant?
31. The electric power output of all the thermal electric power plants in the United States is about $2 \times 10^{11}\text{ W}$, and these plants operate at an average efficiency of around 33% . Find the rate at which all these plants use cooling water, assuming an average 5°C rise in cooling-water temperature. Compare with the $1.8 \times 10^7\text{ kg/s}$ average flow at the mouth of the Mississippi River.
32. Consider a Carnot engine operating between temperatures T_h and T_i , where T_i is intermediate between T_h and the ambient temperature T_c (Fig. 19.21). It should be possible to operate a second engine between T_i and T_c . Show that the maximum overall

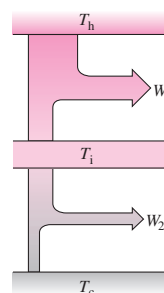


FIGURE 19.21 Problem 32

efficiency of such a two-stage engine is the same as that of a single engine operating between T_h and T_c (which is why combined-cycle power plants achieve high efficiencies).

33. An industrial freezer operates between 0°C and 32°C , consuming electrical energy at the rate of 12 kW. Assuming the freezer is perfectly reversible, (a) what's its COP? (b) How much water at 0°C can it freeze in 1 hour?
34. Use appropriate energy-flow diagrams to analyze the situation in Got It? 19.2; that is, show that using a refrigerator to cool the low-temperature reservoir can't increase the overall efficiency of a Carnot engine when the work input to the refrigerator is included.
35. It costs \$180 to heat a house with electricity in a typical winter month. (Electric heat simply converts all the incoming electrical energy to heat.) What would the monthly heating bill be after switching to an electrically powered heat-pump system with $\text{COP} = 3.1$?
36. A refrigerator maintains an interior temperature of 4°C while its exhaust temperature is 30°C . The refrigerator's insulation is imperfect, and heat leaks in at the rate of 340 W. Assuming the refrigerator is reversible, at what rate must it consume electrical energy to maintain a constant 4°C interior?
37. You operate a store that's heated by an oil furnace supplying 30 kWh of heat from each gallon of oil. You're considering switching to a heat-pump system. Oil costs \$1.75/gallon, and electricity costs 16.5¢/kWh. What's the minimum heat-pump COP that will reduce your heating costs?
38. Use energy-flow diagrams to show that the existence of a perfect heat engine would permit the construction of a perfect refrigerator, thus violating the Clausius statement of the second law.
39. A heat pump extracts energy from groundwater at 10°C and transfers it to water at 70°C to heat a building. Find (a) its COP and (b) its electric power consumption if it supplies heat at the rate of 20 kW. (c) Compare the pump's hourly operating cost with that of an oil furnace if electricity costs 15.5¢/kWh and oil costs \$2.60/gallon and releases about 30 kWh/gal when burned.
40. A reversible engine contains 0.20 mol of ideal monatomic gas, initially at 600 K and confined to 2.0 L. The gas undergoes the following cycle:
 - Isothermal expansion to 4.0 L
 - Isovolumic cooling to 300 K
 - Isothermal compression to 2.0 L
 - Isovolumic heating to 600 K
 (a) Calculate the net heat added during the cycle and the net work done. (b) Determine the engine's efficiency, defined as the ratio of the work done to the heat *absorbed* during the cycle.

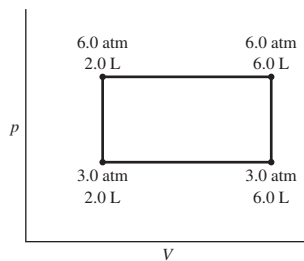


FIGURE 19.22 Problem 41

42. A 0.20-mol sample of an ideal gas goes through the Carnot cycle of Fig. 19.23. Calculate (a) the heat Q_h absorbed, (b) the heat Q_c

rejected, and (c) the work done. (d) Use these quantities to determine the efficiency. (e) Find the maximum and minimum temperatures, and show explicitly that the efficiency as defined in Equation 19.1 is equal to the Carnot efficiency of Equation 19.3.

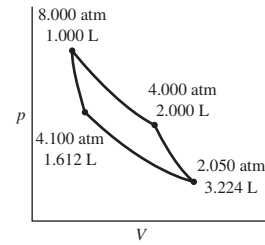


FIGURE 19.23 Problem 42

43. A shallow pond contains 94 Mg of water. In winter, it's entirely frozen. By how much does the entropy of the pond increase when the ice, already at 0°C , melts and then heats to its summer temperature of 15°C ?
44. Estimate the rate of entropy increase associated with your body's **BIO** normal metabolism.
45. The temperature of n moles of ideal gas is changed from T_1 to T_2 at constant volume. Show that the corresponding entropy change is $\Delta S = nC_V \ln(T_2/T_1)$.
46. The temperature of n moles of ideal gas is changed from T_1 to T_2 with pressure held constant. Show that the corresponding entropy change is $\Delta S = nC_p \ln(T_2/T_1)$.
47. A 5.0-mol sample of an ideal diatomic gas is at 1.0 atm pressure and 300 K. Find the entropy change if the gas is heated to 500 K (a) at constant volume, (b) at constant pressure, and (c) adiabatically.
48. A 250-g sample of water at 80°C is mixed with 250 g of water at 10°C . Find the entropy changes for (a) the hot water, (b) the cool water, and (c) the system.
49. An ideal gas undergoes a process that takes it from pressure p_1 and volume V_1 to p_2 and V_2 , such that $p_1 V_1^\gamma = p_2 V_2^\gamma$, where γ is the specific heat ratio. Find the entropy change if the process consists of constant-pressure and constant-volume segments. Why does your result make sense?
50. In an adiabatic free expansion, 8.7 mol of ideal gas at 288 K expand 10-fold in volume. How much energy becomes unavailable to do work?
51. Find the entropy change when a 2.4-kg aluminum pan at 155°C is plunged into 3.5 kg of water at 15°C .
52. An engine with mechanical power output 8.5 kW extracts heat from a source at 420 K and rejects it to a 1000-kg block of ice at its melting point. (a) What's its efficiency? (b) How long can it maintain this efficiency if the ice isn't replenished?
53. Gasoline engines operate approximately on the Otto cycle, consisting of two adiabatic and two constant-volume segments. Figure 19.24 shows the Otto cycle for a particular engine. (a) If

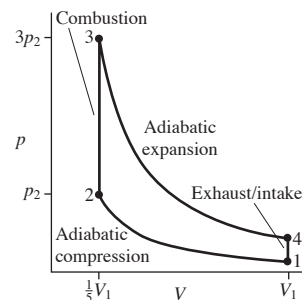


FIGURE 19.24 Problem 53

the gas in the engine has specific heat ratio γ , find the engine's efficiency, assuming all processes are reversible. (b) Find the maximum temperature in terms of the minimum temperature T_{\min} . (c) How does the efficiency compare with that of a Carnot engine operating between the same temperature extremes?

54. The compression ratio r of an engine is the ratio of maximum to minimum gas volume. For the engine of the preceding problem, Fig. 19.24 shows that the compression ratio is 5. Find an expression for the engine's efficiency as a function of compression ratio, assuming that pressure continues to triple during the combustion phase.
55. The 54-MW wood-fired McNeil Generating Station in Burlington, Vermont, produces steam at 950°F to drive its turbines, and condensed steam returns to the boiler as 90°F water. (Note the temperatures in °F, used in U.S. engineering situations.) Find McNeil's maximum thermodynamic efficiency, and compare with its actual efficiency of 25%.
56. A 500-g copper block at 80°C is dropped into 1.0 kg of water at 10°C. Find (a) the final temperature and (b) the entropy change of the system.
57. An object's heat capacity is inversely proportional to its absolute temperature: $C = C_0(T_0/T)$, where C_0 and T_0 are constants. Find the entropy change when the object is heated from T_0 to T_1 .
58. A Carnot engine extracts heat from a block of mass m and specific heat c initially at temperature T_{h0} but without a heat source to maintain that temperature. The engine rejects heat to a reservoir at constant temperature T_c . The engine is operated so its mechanical power output is proportional to the temperature difference $T_h - T_c$:

$$P = P_0 \frac{T_h - T_c}{T_{h0} - T_c}$$

where T_h is the instantaneous temperature of the hot block and P_0 is the initial power. (a) Find an expression for T_h as a function of time, and (b) determine how long it takes for the engine's power output to reach zero.

59. In an alternative universe, you've got the impossible: an infinite heat reservoir, containing infinite energy at temperature T_h . But you've only got a finite cool reservoir, with initial temperature T_{c0} and heat capacity C . Find an expression for the maximum work you can extract if you operate an engine between these two reservoirs.
60. You're the environmental protection officer for a 35% efficient nuclear power plant that produces 750 MW of electric power, situated on a river whose minimum flow rate is 110 m³/s. State environmental regulations limit the rise in river temperature from your plant's cooling system to 5°C. Can you achieve this standard if you use river water for all your cooling, or will you need to install cooling towers that transfer some of your waste heat to the atmosphere?
61. Find an expression for the entropy gain when hot and cold water are irreversibly mixed. A corresponding reversible process you can use to calculate this change is to bring each water sample slowly to their common final temperature T_f and then mix them. Express your answer in terms of the initial temperatures T_h and T_c . Assume equal masses of hot and cold water, with constant specific heat c . What's the sign of your answer?
62. Problem 74 of Chapter 16 provided an approximate expression for the specific heat of copper at low absolute temperatures: $c = 31(T/343 \text{ K})^3 \text{ J/kg}\cdot\text{K}$. Use this to find the entropy change when 40 g of copper are cooled from 25 K to 10 K. Why is the change negative?
63. The molar specific heat at constant pressure for a certain gas is given by $C_p = a + bT + cT^2$, where $a = 33.6 \text{ J/mol}\cdot\text{K}$,

$b = 2.93 \times 10^{-3} \text{ J/mol}\cdot\text{K}^2$, and $c = 2.13 \times 10^{-5} \text{ J/mol}\cdot\text{K}^3$. Find the entropy change when 2 moles of this gas are heated from 20°C to 200°C.

64. Consider a gas containing an even number N of molecules, distributed among the two halves of a closed box. Find expressions for (a) the total number of microstates and (b) the number of microstates with half the molecules on each side of the box. (You can either work out a formula, or explore the term "combinations" in a math reference source.) (c) Use these results to find the ratio of the probability that all the molecules will be found on one side of the box to the probability that there will be equal numbers on both sides. (d) Evaluate for $N = 4$ and $N = 100$.

Passage Problems

Refrigerators remain among the greatest consumers of electrical energy in most homes, although mandated efficiency standards have decreased their energy consumption by some 80% in the past four decades. In the course of a day, one kitchen refrigerator removes 30 MJ of energy from its contents, in the process consuming 10 MJ of electrical energy. The electricity comes from a 40% efficient coal-fired power plant.

65. The electrical energy
 - a. is used to run the light bulb inside the refrigerator.
 - b. wouldn't be necessary if the refrigerator had enough insulation.
 - c. retains its high-quality status after the refrigerator has used it.
 - d. ends up as waste heat rejected to the kitchen environment.
66. The refrigerator's COP is
 - a. $\frac{1}{3}$.
 - b. 2.
 - c. 3.
 - d. 4.
67. The fuel energy consumed at the power plant to run this refrigerator for the day is
 - a. 12 MJ.
 - b. 25 MJ.
 - c. 40 MJ.
 - d. 75 MJ.
68. The total energy rejected to the surrounding kitchen during the course of the day is
 - a. 10 MJ.
 - b. 30 MJ.
 - c. 40 MJ.
 - d. 75 MJ.

Answers to Chapter Questions

Answer to Chapter Opening Question

The second law of thermodynamics prevents us from converting thermal energy to mechanical energy with 100% efficiency, and practical limits on temperature make it hard to achieve 50% efficiency in conventional power plants.

Answers to GOT IT? Questions

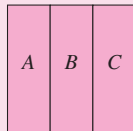
- 19.1. (a), (c), and (f).
- 19.2. (c); see Problem 34 for a proof.
- 19.3. (a) increase; (b) decrease; (c) increase; (d) increase; (e) decrease; (f) increase; (g) increase.

Thermodynamics

Thermodynamics is the study of heat, temperature, and related phenomena—and their relation to the all-important concept of energy. Thermodynamics provides a macroscopic description in terms of parameters like temperature and pressure.

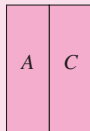
Thermodynamic equilibrium occurs when two systems are brought into thermal contact and no further changes occur in any macroscopic properties. The **zeroth law of thermodynamics** says that two systems each in thermodynamic equilibrium with a third are also in thermodynamic equilibrium with each other. This law allows us to establish temperature scales and construct thermometers.

Systems A and C are each in thermodynamic equilibrium with B.



(a)

If A and C are placed in thermal contact, their macroscopic properties don't change—showing that they're already in equilibrium.



(b)

Ideal gases exhibit a simple relation among temperature, pressure, and volume:

$$pV = NkT = nRT$$

This is the **ideal gas law**, with $k = 1.38 \times 10^{-23} \text{ J/K}$ and $R = 8.314 \text{ J/K} \cdot \text{mol}$.

The **first law of thermodynamics** relates the change ΔU in a system's internal energy to the heat Q added to the system and the work W done by the system:

$$\Delta U = Q - W$$

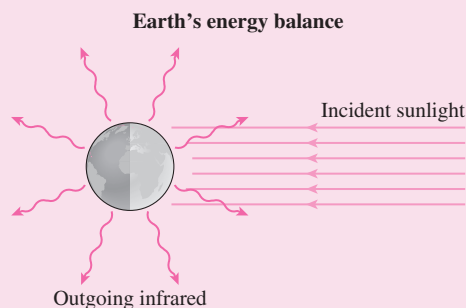
For an ideal gas, **reversible thermodynamic processes** are described by curves in the pressure–volume diagram. Common processes include **isothermal** (constant temperature), **constant volume**, **constant pressure**, and **adiabatic** (no heat flow).

Part Three Challenge Problem

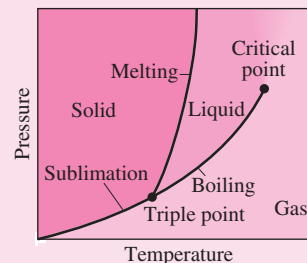
The ideal Carnot engine shown in the figure at right operates between a heat reservoir and a block of ice with mass M . An external energy source maintains the reservoir at a constant temperature T_h . At time $t = 0$, the ice is at its melting point T_0 , but it's insulated from everything except the engine, so it's free to change state and temperature. The engine is operated in such a way that it extracts heat from the reservoir at a constant rate P_h . (a) Find an expression for the time t_1 at which the ice is all melted, in terms of the quantities given and any other appropriate thermodynamic parameters. (b) Find an expression for the mechanical power output of the engine as a function of time for times $t > t_1$. (c) Your expression in part (b) holds up only to some maximum time t_2 . Why? Find an expression for t_2 .

This contrasts with **statistical mechanics**, which provides a microscopic description in terms of the properties and behavior of molecules.

Heat is energy that's flowing because of a temperature difference. Important heat-transfer mechanisms include **conduction**, **convection**, and **radiation**. A system is in **thermal-energy balance** at a fixed temperature when its energy input balances heat transfer to its surroundings.



Real substances undergo **phase changes** among liquid, solid, and gaseous phases. Substantial **heats of transformation** describe the energies involved in phase changes.



Entropy is a measure of disorder. The **second law of thermodynamics** states that the entropy of a closed system can never decrease. Applied to the heat engines that provide most of humankind's electrical and transportation energy, the second law shows that it's impossible to extract as useful work all the random internal energy of hot objects.

Maximum efficiency (Carnot):

$$e = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$$

