7

The Second Law of Thermodynamics

The first law of thermodynamics states that during any cycle that a system undergoes, the cyclic integral of the heat is equal to the cyclic integral of the work. The first law, however, places no restrictions on the direction of flow of heat and work. A cycle in which a given amount of heat is transferred from the system and an equal amount of work is done on the system satisfies the first law just as well as a cycle in which the flows of heat and work are reversed. However, we know from our experience that a proposed cycle that does not violate the first law does not ensure that the cycle will actually occur. It is this kind of experimental evidence that led to the formulation of the second law of thermodynamics. Thus, a cycle will occur only if both the first and second laws of thermodynamics are satisfied.

In its broader significance, the second law acknowledges that processes proceed in a certain direction but not in the opposite direction. A hot cup of coffee cools by virtue of heat transfer to the surroundings, but heat will not flow from the cooler surroundings to the hotter cup of coffee. Gasoline is used as a car drives up a hill, but the fuel in the gasoline tank cannot be restored to its original level when the car coasts down the hill. Such familiar observations as these, and a host of others, are evidence of the validity of the second law of thermodynamics.

In this chapter we consider the second law for a system undergoing a cycle, and in the next two chapters we extend the principles to a system undergoing a change of state and then to a control volume.

7.1 HEAT ENGINES AND REFRIGERATORS

Consider the system and the surroundings previously cited in the development of the first law, as shown in Fig. 7.1. Let the gas constitute the system and, as in our discussion of the first law, let this system undergo a cycle in which work is first done on the system by the paddle wheel as the weight is lowered. Then let the cycle be completed by transferring heat to the surroundings.

We know from our experience that we cannot reverse this cycle. That is, if we transfer heat to the gas, as shown by the dotted arrow, the temperature of the gas will increase but the paddle wheel will not turn and raise the weight. With the given surroundings (the container, the paddle wheel, and the weight), this system can operate in a cycle in which the heat transfer and work are both negative, but it cannot operate in a cycle in which both the heat transfer and work are positive, even though this would not violate the first law.

Consider another cycle, known from our experience to be impossible to complete. Let two systems, one at a high temperature and the other at a low temperature, undergo

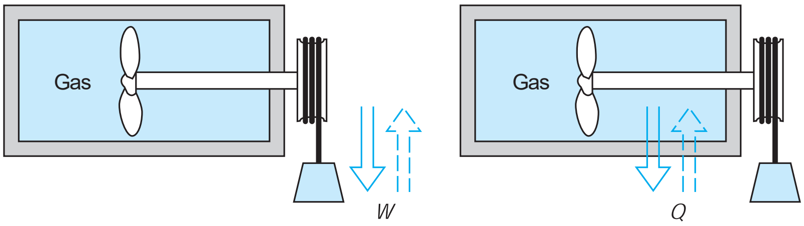

FIGURE 7.1 A system that undergoes a cycle involving work and heat.

a process in which a quantity of heat is transferred from the high-temperature system to the low-temperature system. We know that this process can take place. We also know that the reverse process, in which heat is transferred from the low-temperature system to the high-temperature system, does not occur, and that it is impossible to complete the cycle by heat transfer only. This impossibility is illustrated in Fig. 7.2.

These two examples lead us to a consideration of the heat engine and the refrigerator, which is also referred to as a heat pump. With the heat engine we can have a system that operates in a cycle and performs net positive work and net positive heat transfer. With the heat pump we can have a system that operates in a cycle and has heat transferred to it from a low-temperature body and heat transferred from it to a high-temperature body, though work is required to do this. Three simple heat engines and two simple refrigerators will be considered.

The first heat engine is shown in Fig. 7.3. It consists of a cylinder fitted with appropriate stops and a piston. Let the gas in the cylinder constitute the system. Initially the piston rests on the lower stops, with a weight on the platform. Let the system now undergo a process in which heat is transferred from some high-temperature body to the gas, causing it to expand and raise the piston to the upper stops. At this point the weight is removed. Now let the system be restored to its initial state by transferring heat from the gas to a low-temperature body, thus completing the cycle. Since the weight was raised during the cycle, it is evident that work was done by the gas during the cycle. From the first law we conclude that the net heat transfer was positive and equal to the work done during the cycle.

Such a device is called a *heat engine*, and the substance to which and from which heat is transferred is called the *working substance* or *working fluid*. A heat engine may be defined as a device that operates in a thermodynamic cycle and does a certain amount of net positive work through the transfer of heat from a high-temperature body to a low-temperature body. Often the term *heat engine* is used in a broader sense to include all devices that produce work, either through heat transfer or through combustion, even though the device does not operate in a thermodynamic cycle. The internal combustion engine and the gas turbine are examples of such devices, and calling them *heat engines* is an acceptable use of the term.

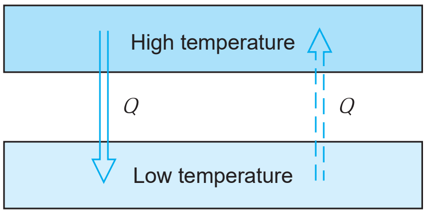

FIGURE 7.2 An example showing the impossibility of completing a cycle by transferring heat from a low-temperature body to a high-temperature body.

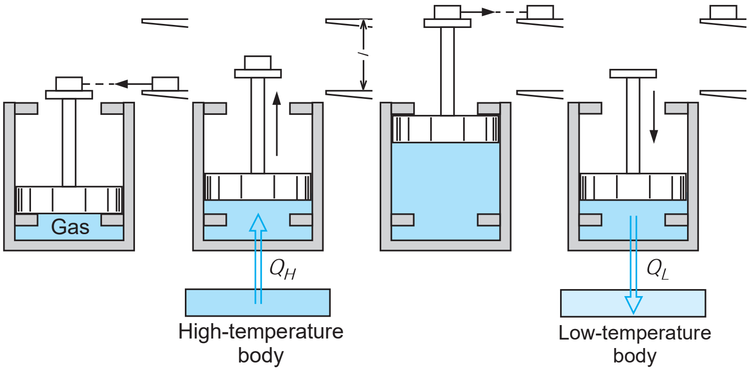

FIGURE 7.3 A simple heat engine.

In this chapter, however, we are concerned with the more restricted form of heat engine, as just defined, one that operates on a thermodynamic cycle.

A simple steam power plant is an example of a heat engine in this restricted sense. Each component in this plant may be analyzed individually as a steady-state, steady-flow process, but as a whole it may be considered a heat engine (Fig. 7.4) in which water (steam) is the working fluid. An amount of heat, Q_H, is transferred from a high-temperature body, which may be the products of combustion in a furnace, a reactor, or a secondary fluid that in turn has been heated in a reactor. In Fig. 7.4 the turbine is shown schematically as driving the pump. What is significant, however, is the net work that is delivered during the cycle. The quantity of heat Q_L is rejected to a low-temperature body, which is usually the cooling water in a condenser. Thus, the simple steam power plant is a heat engine in the restricted sense, for it has a working fluid, to which and from which heat is transferred, and which does a certain amount of work as it undergoes a cycle.

Another example of a heat engine is the thermoelectric power generation device that was discussed in Chapter 1 and shown schematically in Fig. 1.8*b*. Heat is transferred from a high-temperature body to the hot junction (Q_H), and heat is transferred from the cold junction to the surroundings (Q_L). Work is done in the form of electrical energy. Since there is no working fluid, we do not usually think of this as a device that operates in a cycle. However, if we adopt a microscopic point of view, we could regard a cycle as the

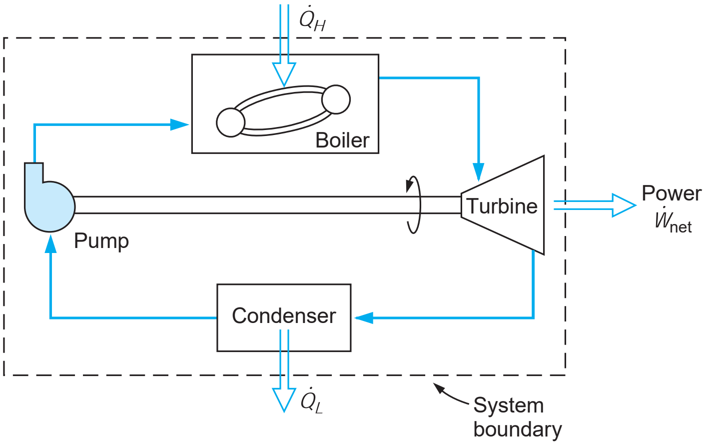

FIGURE 7.4 A heat engine involving steady-state processes.

flow of electrons. Furthermore, as with the steam power plant, the state at each point in the thermoelectric power generator does not change with time under steady-state conditions.

Thus, by means of a heat engine, we are able to have a system operate in a cycle and have both the net work and the net heat transfer positive, which we were not able to do with the system and surroundings of Fig. 7.1.

We note that in using the symbols Q_H and Q_L, we have departed from our sign connotation for heat, because for a heat engine Q_L is negative when the working fluid is considered as the system. In this chapter, it will be advantageous to use the symbol Q_H to represent the heat transfer to or from the high-temperature body and Q_L to represent the heat transfer to or from the low-temperature body. The direction of the heat transfer will be evident from the context.

At this point, it is appropriate to introduce the concept of thermal efficiency of a heat engine. In general, we say that efficiency is the ratio of output, the energy sought, to input, the energy that costs, but the output and input must be clearly defined. At the risk of oversimplification, we may say that in a heat engine the energy sought is the work and the energy that costs money is the heat from the high-temperature source (indirectly, the cost of the fuel). Thermal efficiency is defined as

$$\eta_{\text{thermal}} = \frac{W(\text{energy sought})}{Q_H(\text{energy that costs})} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \tag{7.1}$$

Heat engines vary greatly in size and shape, from large steam engines, gas turbines, or jet engines, to gasoline engines for cars and diesel engines for trucks or cars, to much smaller engines for lawn mowers or hand-held devices such as chain saws or trimmers. Typical values for the thermal efficiency of real engines are about 35–50% for large power plants, 30–35% for gasoline engines, and 30–40% for diesel engines. Smaller utility-type engines may have only about 20% efficiency, owing to their simple carburetion and controls and to the fact that some losses scale differently with size and therefore represent a larger fraction for smaller machines.

EXAMPLE 7.1

An automobile engine produces 136 hp on the output shaft with a thermal efficiency of 30%. The fuel it burns gives 35 000 kJ/kg as energy release. Find the total rate of energy rejected to the ambient and the rate of fuel consumption in kg/s.

Solution

From the definition of a heat engine efficiency, Eq. 7.1, and the conversion of hp from Table A.1 we have

$$\dot{W} = \eta_{\text{eng}} \dot{Q}_H = 136 \text{ hp} \times 0.7355 \text{ kW/hp} = 100 \text{ kW}$$

$$\dot{Q}_H = \dot{W}/\eta_{\text{eng}} = 100/0.3 = 333 \text{ kW}$$

The energy equation for the overall engine gives

$$\dot{Q}_L = \dot{Q}_H - \dot{W} = (1 - 0.3)\,\dot{Q}_H = 233 \text{ kW}$$

From the energy release in the burning we have $\dot{Q}_H = \dot{m} q_H$, so

$$\dot{m} = \dot{Q}_H / q_H = \frac{333 \text{ kW}}{35\,000 \text{ kJ/kg}} = 0.0095 \text{ kg/s}$$

An actual engine shown in Fig. 7.5 rejects energy to the ambient through the radiator cooled by atmospheric air as heat transfer from the exhaust system and the exhaust flow of hot gases.

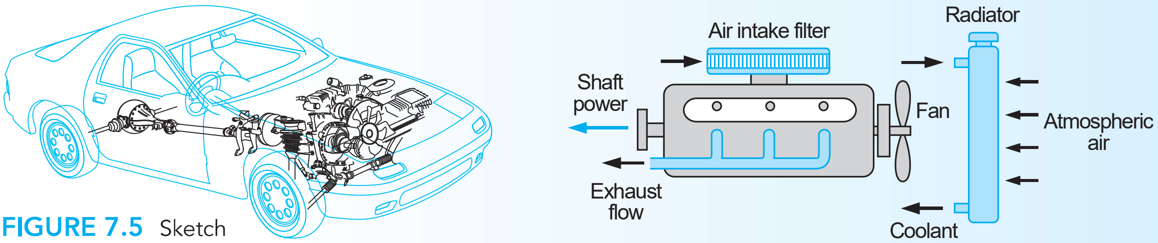

FIGURE 7.5 Sketch for Example 7.1.

The second cycle that we were not able to complete was the one indicating the impossibility of transferring heat directly from a low-temperature body to a high-temperature body. This can, of course, be done with a refrigerator or heat pump. A vapor-compression refrigerator cycle, which was introduced in Chapter 1 and shown in Fig. 1.7, is shown again in Fig. 7.6. The working fluid is the refrigerant, such as R-134a or ammonia, which goes through a thermodynamic cycle. Heat is transferred to the refrigerant in the evaporator, where its pressure and temperature are low. Work is done on the refrigerant in the compressor, and heat is transferred from it in the condenser, where its pressure and temperature are high. The pressure drops as the refrigerant flows through the throttle valve or capillary tube.

Thus, in a refrigerator or heat pump, we have a device that operates in a cycle, that requires work, and that transfers heat from a low-temperature body to a high-temperature body.

The thermoelectric refrigerator, which was discussed in Chapter 1 and shown schematically in Fig. 1.8*a*, is another example of a device that meets our definition of a refrigerator. The work input to the thermoelectric refrigerator is in the form of electrical energy, and heat is transferred from the refrigerated space to the cold junction (Q_L) and from the hot junction to the surroundings (Q_H).

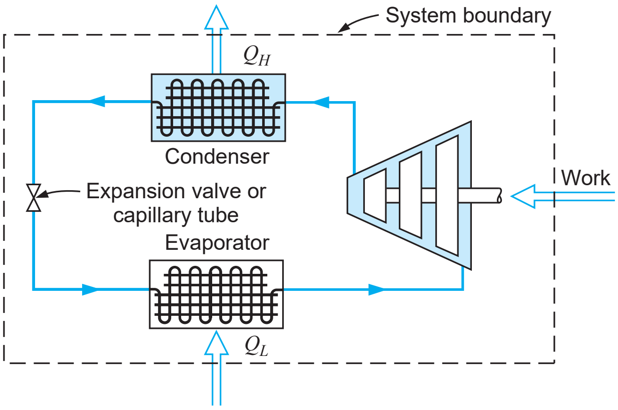

FIGURE 7.6 A simple refrigeration cycle.

The "efficiency" of a refrigerator is expressed in terms of the coefficient of performance (COP), which we designate with the symbol β. For a refrigerator the objective, that is, the energy sought, is Q_L, the heat transferred from the refrigerated space. The energy that costs is the work, W. Thus, the COP, β,[1] is

$$\beta = \frac{Q_L \text{(energy sought)}}{W \text{(energy that costs)}} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{Q_H/Q_L - 1} \tag{7.2}$$

A household refrigerator may have a COP of about 2.5, whereas a deep-freeze unit will be closer to 1.0. Lower cold-temperature space or higher warm-temperature space will result in lower values of COP, as will be seen in Section 7.6. For a heat pump operating over a moderate temperature range, a value of its COP can be around 4, with this value decreasing sharply as the heat pump's operating temperature range is broadened.

EXAMPLE 7.2

The refrigerator in a kitchen shown in Fig. 7.7 receives electrical input power of 150 W to drive the system, and it rejects 400 W to the kitchen air. Find the rate of energy taken out of the cold space and the COP of the refrigerator.

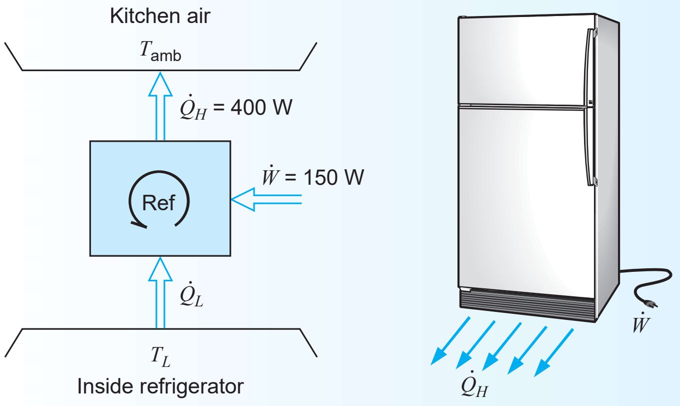

FIGURE 7.7 Sketch for Example 7.2.

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[1] It should be noted that a refrigeration or heat pump cycle can be used with either of two objectives. It can be used as a refrigerator, in which case the primary objective is Q_L, the heat transferred to the refrigerant from the refrigerated space. It can also be used as a heating system (in which case it is usually referred to as a *heat pump*), the objective being Q_H, the heat transferred from the refrigerant to the high-temperature body, which is the space to be heated. Q_L is transferred to the refrigerant from the ground, the atmospheric air, or well water. The coefficient of performance for this case, β', is

$$\beta' = \frac{Q_H \text{(energy sought)}}{W \text{(energy that costs)}} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - Q_L/Q_H}$$

It also follows that for a given cycle,

$$\beta' - \beta = 1$$

Unless otherwise specified, the term *COP* will always refer to a refrigerator as defined by Eq. 7.2.

Solution

C.V. refrigerator. Assume a steady state, so there is no storage of energy. The information provided is $\dot{W} = 150$ W, and the heat rejected is $\dot{Q}_H = 400$ W.

The energy equation gives

$$\dot{Q}_L = \dot{Q}_H - \dot{W} = 400 - 150 = 250 \text{ W}$$

This is also the rate of energy transfer into the cold space from the warmer kitchen due to heat transfer and exchange of cold air inside with warm air when you open the door.

From the definition of the coefficient of performance, Eq. 7.2,

$$\beta_{\text{REFRIG}} = \frac{\dot{Q}_L}{\dot{W}} = \frac{250}{150} = 1.67$$

Before we state the second law, the concept of a *thermal reservoir* should be introduced. A thermal reservoir is a body to which and from which heat can be transferred indefinitely without change in the temperature of the reservoir. Thus, a thermal reservoir always remains at constant temperature. The ocean and the atmosphere approach this definition very closely. Frequently, it will be useful to designate a high-temperature reservoir and a low-temperature reservoir. Sometimes a reservoir from which heat is transferred is called a *source*, and a reservoir to which heat is transferred is called as *sink*.

7.2 THE SECOND LAW OF THERMODYNAMICS

On the basis of the matter considered in the previous section, we are now ready to state the second law of thermodynamics. There are two classical statements of the second law, known as the *Kelvin–Planck statement* and the *Clausius statement*.

> *The Kelvin–Planck statement*: It is impossible to construct a device that will operate in a cycle and produce no effect other than the raising of a weight and the exchange of heat with a single reservoir. See Fig. 7.8.

This statement ties in with our discussion of the heat engine. In effect, it states that it is impossible to construct a heat engine that operates in a cycle, receives a given amount of heat from a high-temperature body, and does an equal amount of work. The only alternative is that some heat must be transferred from the working fluid at a lower temperature to a

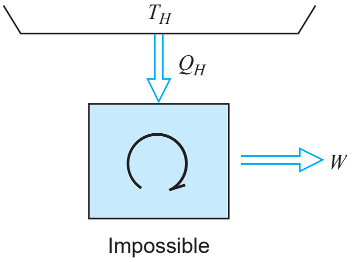

FIGURE 7.8 The Kelvin–Planck statement.

low-temperature body. Thus, work can be done by the transfer of heat only if there are two temperature levels, and heat is transferred from the high-temperature body to the heat engine and also from the heat engine to the low-temperature body. This implies that it is impossible to build a heat engine that has a thermal efficiency of 100%.

> *The Clausius statement*: It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a cooler body to a hotter body. See Fig. 7.9.

This statement is related to the refrigerator or heat pump. In effect, it states that it is impossible to construct a refrigerator that operates without an input of work. This also implies that the COP is always less than infinity.

Three observations should be made about these two statements. The first observation is that both are negative statements. It is, of course, impossible to prove these negative statements. However, we can say that the second law of thermodynamics (like every other law of nature) rests on experimental evidence. Every relevant experiment that has been conducted, either directly or indirectly, verifies the second law, and no experiment has ever been conducted that contradicts the second law. The basis of the second law is therefore experimental evidence.

A second observation is that these two statements of the second law are equivalent. Two statements are equivalent if the truth of either statement implies the truth of the other or if the violation of either statement implies the violation of the other. That a violation of the Clausius statement implies a violation of the Kelvin–Planck statement may be shown. The device at the left in Fig. 7.10 is a refrigerator that requires no work and thus violates the Clausius statement. Let an amount of heat Q_L be transferred from the low-temperature reservoir to this refrigerator, and let the same amount of heat Q_L be transferred to the high-temperature reservoir. Let an amount of heat Q_H that is greater than Q_L be transferred from the high-temperature reservoir to the heat engine, and let the engine reject the amount of heat Q_L as it does an amount of work, W, that equals $Q_H - Q_L$. Because there is no net heat transfer to the low-temperature reservoir, the low-temperature reservoir, along with the heat engine and the refrigerator, can be considered together as a device that operates in a cycle and produces no effect other than the raising of a weight (work) and the exchange of heat with a single reservoir. Thus, a violation of the Clausius statement implies a violation of the Kelvin–Planck statement. The complete equivalence of these two statements is established when it is also shown that a violation of the Kelvin–Planck statement implies a violation of the Clausius statement. This is left as an exercise for the student.

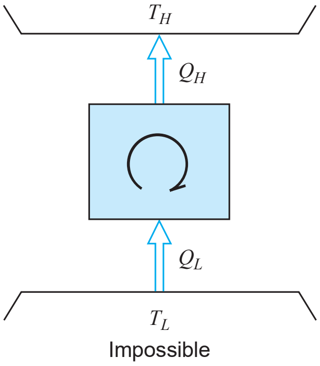

FIGURE 7.9 The Clausius statement.

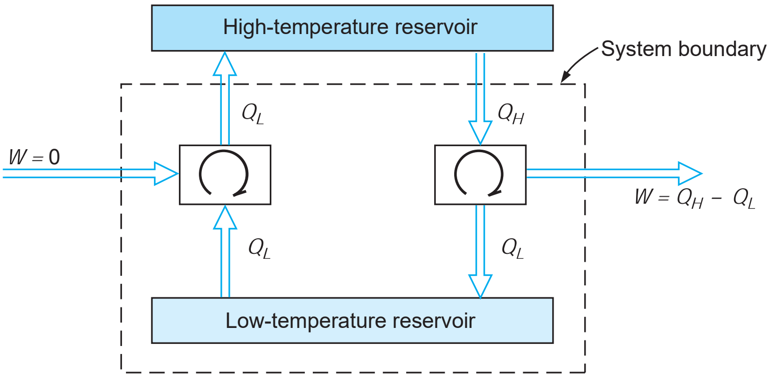

FIGURE 7.10 Demonstration of the equivalence of the two statements of the second law.

The third observation is that frequently the second law of thermodynamics has been stated as the impossibility of constructing a perpetual-motion machine of the second kind. A perpetual-motion machine of the first kind would create work from nothing or create mass or energy, thus violating the first law. A perpetual-motion machine of the second kind would extract heat from a source and then convert this heat completely into other forms of energy, thus violating the second law. A perpetual-motion machine of the third kind would have no friction, and thus would run indefinitely but produce no work.

A heat engine that violated the second law could be made into a perpetual-motion machine of the second kind by taking the following steps. Consider Fig. 7.11, which might be the power plant of a ship. An amount of heat Q_L is transferred from the ocean to a high-temperature body by means of a heat pump. The work required is W', and the heat transferred to the high-temperature body is Q_H. Let the same amount of heat be transferred to a heat engine that violates the Kelvin–Planck statement of the second law and does an amount of work $W = Q_H$. Of this work, an amount $Q_H - Q_L$ is required to drive the heat pump, leaving the net work ($W_{\text{net}} = Q_L$) available for driving the ship. Thus, we have a perpetual-motion machine in the sense that work is done by utilizing freely available sources of energy such as the ocean or atmosphere.

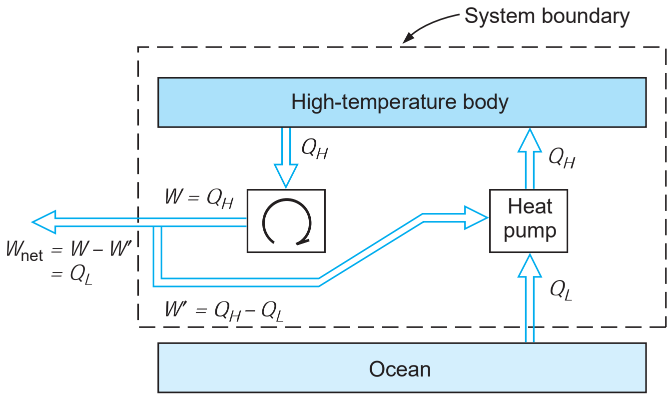

FIGURE 7.11 A perpetual-motion machine of the second kind.