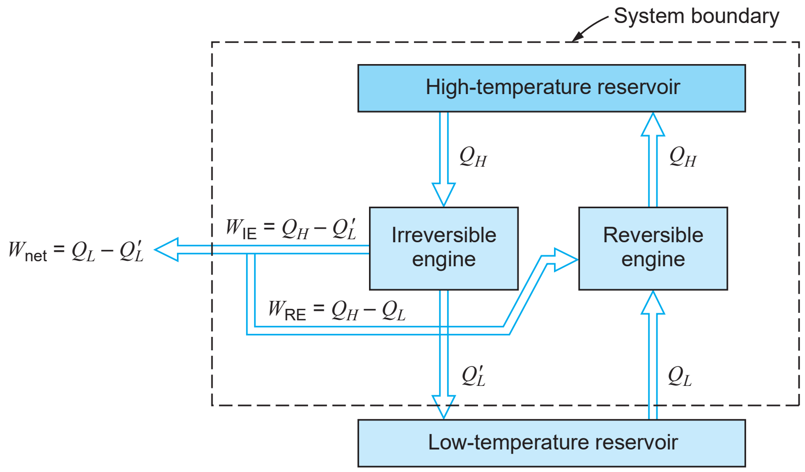



**FIGURE 7.20**
Demonstration of the fact that the Carnot cycle is the most efficient cycle operating between two fixed-temperature reservoirs.

constitute a violation of the second law, and we conclude that our initial assumption (that the irreversible engine is more efficient than a reversible engine) is incorrect. Therefore, we cannot have an irreversible engine that is more efficient than a reversible engine operating between the same two reservoirs.

### Second Proposition

All engines that operate on the Carnot cycle between two given constant-temperature reservoirs have the same efficiency. The proof of this proposition is similar to the proof just outlined, which assumes that there is one Carnot cycle that is more efficient than another Carnot cycle operating between the same temperature reservoirs. Let the Carnot cycle with the higher efficiency replace the irreversible cycle of the previous argument, and let the Carnot cycle with the lower efficiency operate as the refrigerator. The proof proceeds with the same line of reasoning as in the first proposition. The details are left as an exercise for the student.

## 7.7 THE THERMODYNAMIC TEMPERATURE SCALE

In discussing temperature in Chapter 2, we pointed out that the zeroth law of thermodynamics provides a basis for temperature measurement, but that a temperature scale must be defined in terms of a particular thermometer substance and device. A temperature scale that is independent of any particular substance, which might be called an absolute temperature scale, would be most desirable. In the preceding paragraph we noted that the efficiency of a Carnot cycle is independent of the working substance and depends only on the reservoir temperatures. This fact provides the basis for such an absolute temperature scale called the *thermodynamic scale*. Since the efficiency of a Carnot cycle is a function only of the temperature, it follows that

$$\eta_{\text{thermal}} = 1 - \frac{Q_L}{Q_H} = 1 - \psi(T_L, T_H) \tag{7.3}$$

where $\psi$ designates a functional relation.

There are many functional relations that could be chosen to satisfy the relation given in Eq. 7.3. For simplicity, the thermodynamic scale is defined as

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L} \tag{7.4}$$

Substituting this definition into Eq. 7.3 results in the following relation between the thermal efficiency of a Carnot cycle and the absolute temperatures of the two reserviors.

$$\eta_{\text{thermal}} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H} \tag{7.5}$$

It should be noted, however, that the definition of Eq. 7.4 is not complete since it does not specify the magnitude of the degree of temperature or a fixed reference point value. In the following section, we will discuss in greater detail the ideal-gas absolute temperature introduced in Section 3.6 and show that this scale satisfies the relation defined by Eq. 7.4.

## 7.8 THE IDEAL-GAS TEMPERATURE SCALE

In this section we reconsider in greater detail the ideal-gas temperature scale introduced in Section 3.6. This scale is based on the observation that as the pressure of a real gas approaches zero, its equation of state approaches that of an ideal gas:

$$Pv = RT$$

It will be shown that the ideal-gas temperature scale satisfies the definition of thermodynamic temperature given in the preceding section by Eq. 7.4. But first, let us consider how an ideal gas might be used to measure temperature in a constant-volume gas thermometer, shown schematically in Fig. 7.21.

Let the gas bulb be placed in the location where the temperature is to be measured, and let the mercury column be adjusted so that the level of mercury stands at the reference

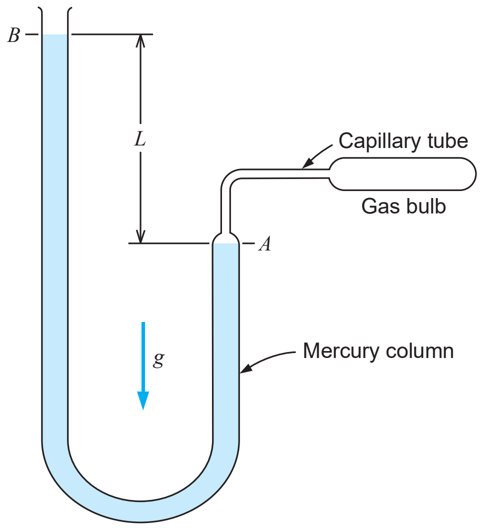



**FIGURE 7.21** Schematic diagram of a constant-volume gas thermometer.

mark $A$. Thus, the volume of the gas remains constant. Assume that the gas in the capillary tube is at the same temperature as the gas in the bulb. Then the pressure of the gas, which is indicated by the height $L$ of the mercury column, is a measure of the temperature.

Let the pressure that is associated with the temperature of the triple point of water (273.16 K) also be measured, and let us designate this pressure $P_{\text{t.p.}}$. Then, from the definition of an ideal gas, any other temperature $T$ could be determined from a pressure measurement $P$ by the relation

$$T = 273.16\left(\frac{P}{P_{\text{t.p.}}}\right)$$

## EXAMPLE 7.3

In a certain constant-volume ideal-gas thermometer, the measured pressure at the ice point (see Section 2.11) of water, 0°C, is 110.9 kPa and at the steam point, 100°C, is 151.5 kPa. Extrapolating, at what Celsius temperature does the pressure go to zero (i.e., zero absolute temperature)?

### Analysis

From the ideal-gas equation of state $PV = mRT$ at constant mass and volume, pressure is directly proportional to temperature, as shown in Fig. 7.22,

$$P = CT, \text{ where } T \text{ is the absolute ideal-gas temperature}$$

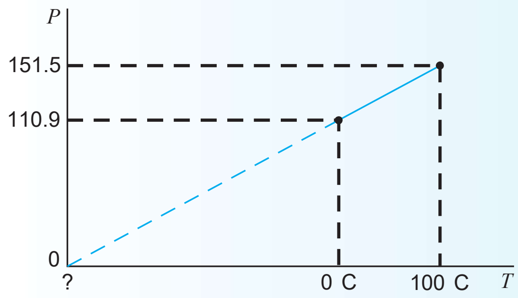



**FIGURE 7.22** Plot for Example 7.3.

### Solution

$$\text{Slope} \quad \frac{\Delta P}{\Delta T} = \frac{151.5 - 110.9}{100 - 0} = 0.406 \text{ kPa/°C}$$

Extrapolating from the 0°C point to $P = 0$,

$$T = 0 - \frac{110.9}{0.406}\,\frac{\text{kPa}}{\text{kPa/°C}} = -273.15\text{°C}$$

establishing the relation between absolute ideal-gas Kelvin and Celsius temperature scales.

(*Note:* Compatible with the subsequent present-day definition of the Kelvin and the Celsius scale in Section 2.11.)

From a practical point of view, we have the problem that no gas behaves exactly like an ideal gas. However, we do know that as the pressure approaches zero, the behavior of all gases approaches that of an ideal gas. Suppose then that a series of measurements is made with varying amounts of gas in the gas bulb. This means that the pressure measured at the triple point, and also the pressure at any other temperature, will vary. If the indicated temperature $T_i$ (obtained by assuming that the gas is ideal) is plotted against the pressure of gas with the bulb at the triple point of water, a curve like the one shown in Fig. 7.23 is obtained. When this curve is extrapolated to zero pressure, the correct ideal-gas temperature is obtained. Different curves might result from different gases, but they would all indicate the same temperature at zero pressure.

We have outlined only the general features and principles for measuring temperature on the ideal-gas scale of temperatures. Precision work in this field is difficult and laborious, and there are only a few laboratories in the world where such work is carried on. The International Temperature Scale, which was mentioned in Chapter 2, closely approximates the thermodynamic temperature scale and is much easier to work with in actual temperature measurement.

We now demonstrate that the ideal-gas temperature scale discussed earlier is, in fact, identical to the thermodynamic temperature scale, which was defined in the discussion of the Carnot cycle and the second law. Our objective can be achieved by using an ideal gas as the working fluid for a Carnot-cycle heat engine and analyzing the four processes that make up the cycle. The four state points, 1, 2, 3, and 4, and the four processes are as shown in Fig. 7.24. For convenience, let us consider a unit mass of gas inside the cylinder. Now for each of the four processes, the reversible work done at the moving boundary is given by Eq. 4.3:

$$\delta w = P\,dv$$

Similarly, for each process the gas behavior is, from the ideal-gas relation, Eq. 3.5,

$$Pv = RT$$

and the internal energy change, from Eq. 5.20, is

$$du = C_{v0}\,dT$$

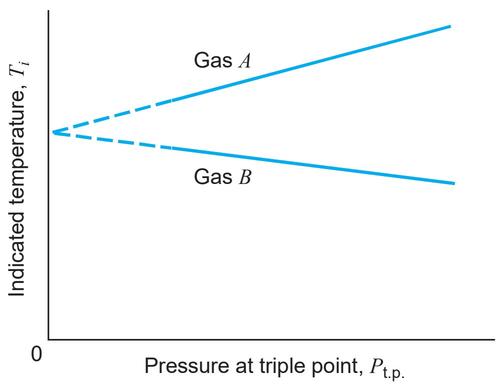



**FIGURE 7.23** Sketch showing how the ideal-gas temperature is determined.

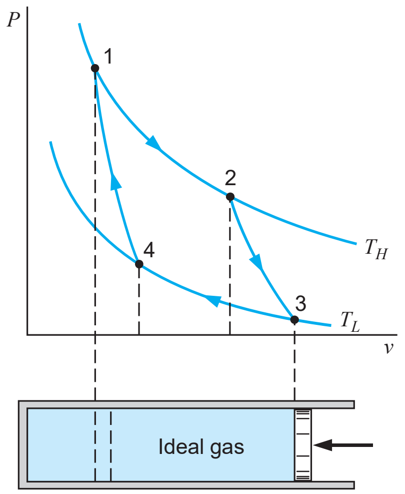



FIGURE 7.24 The ideal-gas Carnot cycle.

Assuming no changes in kinetic or potential energies, the first law is, from Eq. 5.7 at unit mass,

$$\delta q = du + \delta w$$

Substituting the three previous expressions into this equation, we have for each of the four processes

$$\delta q = C_{v0}\, dT + \frac{RT}{v}\, dv \tag{7.6}$$

The shape of the two isothermal processes shown in Fig. 7.23 is known, since $Pv$ is constant in each case. The process 1–2 is an expansion at $T_H$, such that $v_2$ is larger than $v_1$. Similarly, the process 3–4 is a compression at a lower temperature, $T_L$, and $v_4$ is smaller than $v_3$. The adiabatic process 2–3 is an expansion from $T_H$ to $T_L$, with an increase in specific volume, while the adiabatic process 4–1 is a compression from $T_L$ to $T_H$, with a decrease in specific volume. The area below each process line represents the work for that process, as given by Eq. 4.4.

We now proceed to integrate Eq. 7.6 for each of the four processes that make up the Carnot cycle. For the isothermal heat addition process 1–2, we have

$$q_H = {}_1q_2 = 0 + RT_H \ln \frac{v_2}{v_1} \tag{7.7}$$

For the adiabatic expansion process 2–3 we divide by T to get,

$$0 = \int_{T_H}^{T_L} \frac{C_{v0}}{T}\, dT + R \ln \frac{v_3}{v_2} \tag{7.8}$$

For the isothermal heat rejection process 3–4,

$$\begin{aligned} q_L = -{}_3q_4 &= -0 - RT_L \ln \frac{v_4}{v_3} \\ &= +RT_L \ln \frac{v_3}{v_4} \end{aligned} \tag{7.9}$$

and for the adiabatic compression process 4–1 we divide by T to get,

$$0 = \int_{T_L}^{T_H} \frac{C_{v0}}{T}\, dT + R \ln \frac{v_1}{v_4} \tag{7.10}$$

From Eqs. 7.8 and 7.10, we get

$$\int_{T_L}^{T_H} \frac{C_{v0}}{T}\, dT = R \ln \frac{v_3}{v_2} = -R \ln \frac{v_1}{v_4}$$

Therefore,

$$\frac{v_3}{v_2} = \frac{v_4}{v_1}, \qquad \text{or} \qquad \frac{v_3}{v_4} = \frac{v_2}{v_1} \tag{7.11}$$

Thus, from Eqs. 7.7 and 7.9 and substituting Eq. 7.11, we find that

$$\frac{q_H}{q_L} = \frac{RT_H \ln \dfrac{v_2}{v_1}}{RT_L \ln \dfrac{v_3}{v_4}} = \frac{T_H}{T_L}$$

which is Eq. 7.4, the definition of the thermodynamic temperature scale in connection with the second law.

## 7.9 IDEAL VERSUS REAL MACHINES

Following the definition of the thermodynamic temperature scale by Eq. 7.4, it was noted that the thermal efficiency of a Carnot cycle heat engine is given by Eq. 7.5. It also follows that a Carnot cycle operating as a refrigerator or heat pump will have a COP expressed as

$$\beta = \frac{Q_L}{Q_H - Q_L} \underset{\text{Carnot}}{=} \frac{T_L}{T_H - T_L} \tag{7.12}$$

$$\beta' = \frac{Q_H}{Q_H - Q_L} \underset{\text{Carnot}}{=} \frac{T_H}{T_H - T_L} \tag{7.13}$$

For all three "efficiencies" in Eqs. 7.5, 7.12, and 7.13, the first equality sign is the definition with the use of the energy equation and thus is always true. The second equality sign is valid only if the cycle is reversible, that is, a Carnot cycle. Any real heat engine, refrigerator, or heat pump will be less efficient, such that

$$\eta_{\text{real thermal}} = 1 - \frac{Q_L}{Q_H} \le 1 - \frac{T_L}{T_H}$$

$$\beta_{\text{real}} = \frac{Q_L}{Q_H - Q_L} \le \frac{T_L}{T_H - T_L}$$

$$\beta'_{\text{real}} = \frac{Q_H}{Q_H - Q_L} \le \frac{T_H}{T_H - T_L}$$

A final point needs to be made about the significance of absolute zero temperature in connection with the second law and the thermodynamic temperature scale. Consider a Carnot-cycle heat engine that receives a given amount of heat from a given high-temperature reservoir. As the temperature at which heat is rejected from the cycle is lowered, the net work output increases and the amount of heat rejected decreases. In the limit, the heat rejected is zero, and the temperature of the reservoir corresponding to this limit is absolute zero.

Similarly, for a Carnot-cycle refrigerator, the amount of work required to produce a given amount of refrigeration increases as the temperature of the refrigerated space decreases. Absolute zero represents the limiting temperature that can be achieved, and the amount of work required to produce a finite amount of refrigeration approaches infinity as the temperature at which refrigeration is provided approaches zero.

## EXAMPLE 7.4

Let us consider the heat engine, shown schematically in Fig. 7.25, that receives a heat-transfer rate of 1 MW at a high temperature of 550°C and rejects energy to the ambient surroundings at 300 K. Work is produced at a rate of 450 kW. We would like to know how much energy is discarded to the ambient surroundings and the engine efficiency and compare both of these to a Carnot heat engine operating between the same two reservoirs.

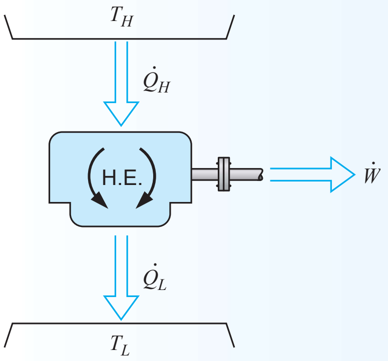



**FIGURE 7.25** A heat engine operating between two constant-temperature energy reservoirs for Example 7.4.

**Solution**

If we take the heat engine as a control volume, the energy equation gives

$$\dot{Q}_L = \dot{Q}_H - \dot{W} = 1000 - 450 = 550\ \text{kW}$$

and from the definition of efficiency

$$\eta_{\text{thermal}} = \dot{W}/\dot{Q}_H = 450/1000 = 0.45$$

For the Carnot heat engine, the efficiency is given by the temperature of the reservoirs:

$$\eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H} = 1 - \frac{300}{550 + 273} = 0.635$$

The rates of work and heat rejection become

$$\dot{W} = \eta_{\text{Carnot}}\,\dot{Q}_H = 0.635 \times 1000 = 635\ \text{kW}$$

$$\dot{Q}_L = \dot{Q}_H - \dot{W} = 1000 - 635 = 365\ \text{kW}$$

The actual heat engine thus has a lower efficiency than the Carnot (ideal) heat engine, with a value of 45% typical for a modern steam power plant. This also implies that the actual engine rejects a larger amount of energy to the ambient surroundings (55%) compared with the Carnot heat engine (36%).

EXAMPLE 7.5

As one mode of operation of an air conditioner is the cooling of a room on a hot day, it works as a refrigerator, shown in Fig. 7.26. A total of 4 kW should be removed from a room at 24°C to the outside atmosphere at 35°C. We would like to estimate the magnitude of the required work. To do this we will not analyze the processes inside the refrigerator, which is deferred to Chapter 11, but we can give a lower limit for the rate of work, assuming it is a Carnot-cycle refrigerator.

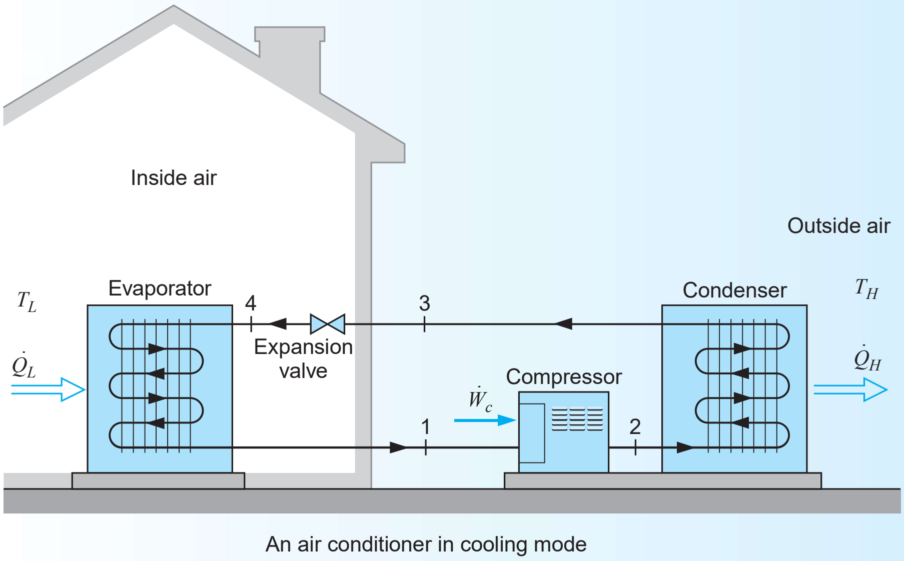



FIGURE 7.26 An air conditioner in cooling mode where $T_L$ is the room.

**Solution**

The COP is

$$\beta = \frac{\dot{Q}_L}{\dot{W}} = \frac{\dot{Q}_L}{\dot{Q}_H - \dot{Q}_L} = \frac{T_L}{T_H - T_L} = \frac{273 + 24}{35 - 24} = 27$$

so the rate of work or power input will be

$$\dot{W} = \dot{Q}_L/\beta = 4/27 = 0.15 \text{ kW}$$

Since the power was estimated assuming a Carnot refrigerator, it is the smallest amount possible. Recall also the expressions for heat-transfer rates in Chapter 4. If the refrigerator should push 4.15 kW out to the atmosphere at 35°C, the high-temperature side of it should be at a higher temperature, maybe 45°C, to have a reasonably small-sized heat exchanger. As it cools the room, a flow of air of less than, say, 18°C would be needed. Redoing the COP with a high of 45°C and a low of 18°C gives 10.8, which is more realistic. A real refrigerator would operate with a COP of the order of 5 or less.

In the previous discussion and examples, we considered the constant-temperature energy reservoirs and used those temperatures to calculate the Carnot-cycle efficiency. However, if we recall the expressions for the rate of heat transfer by conduction, convection, or radiation in Chapter 4, they can all be shown as

$$\dot{Q} = C\,\Delta T \tag{7.14}$$

The constant $C$ depends on the mode of heat transfer as

$$\text{Conduction:} \quad C = \frac{kA}{\Delta x} \qquad \text{Convection: } C = hA$$

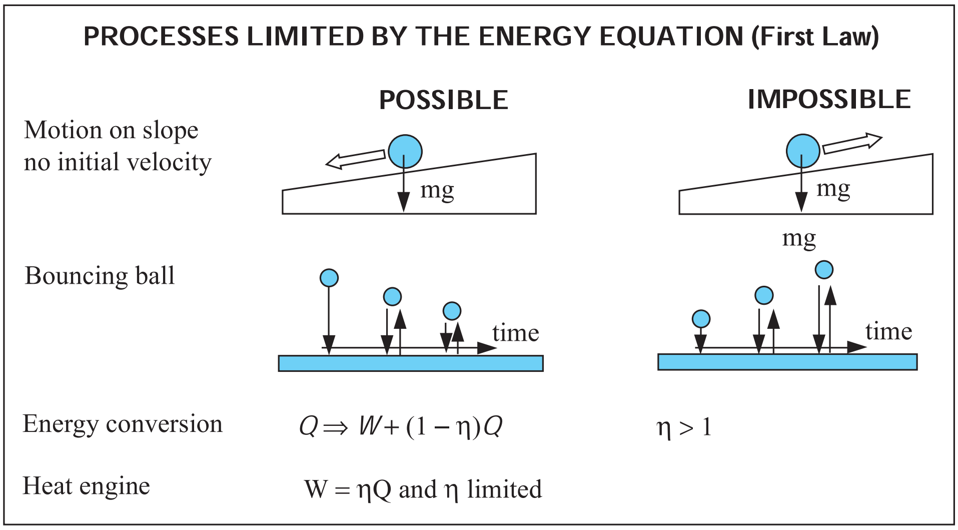
$$\text{Radiation:} \quad C = \varepsilon\sigma A(T_s^2 + T_\infty^2)(T_s + T_\infty)$$

For more complex situations with combined layers and modes, we also recover the form in Eq. 7.14, but with a value of $C$ that depends on the geometry, materials, and modes of heat transfer. To have a heat transfer, we therefore must have a temperature difference so that the working substance inside a cycle cannot attain the reservoir temperature unless the area is infinitely large.

## 7.10 ENGINEERING APPLICATIONS

The second law of thermodynamics is presented as it was developed, with some additional comments and in a modern context. The main implication is the limits it imposes on processes: Some processes will not occur but others will, with a constraint on the operation of complete cycles such as heat engines and heat pumps.

Nearly all energy conversion processes that generate work (typically converted further from mechanical to electrical work) involve some type of cyclic heat engine. These include the engine in a car, a turbine in a power plant, or a windmill. The source of energy can be a storage reservoir (fossil fuels that can burn, such as gasoline or natural gas) or a more temporary form, for example, the wind kinetic energy that ultimately is driven by heat input from the sun.




Machines that violate the energy equation, say generate energy from nothing, are called perpetual-motion machines of the first kind. Such machines have been "demonstrated" and investors asked to put money into their development, but most of them had some kind of energy input not easily observed (such as a small, compressed air line or a hidden fuel supply). Recent examples are cold fusion and electrical phase imbalance;