and

$$\int_1^2 P\,dV = P_1 V_1 \int_1^2 \frac{dV}{V} = P_1 V_1 \ln \frac{V_2}{V_1} \tag{4.6}$$

Note that in Eqs. 4.5 and 4.6 we did not say that the work is equal to the expressions given in these equations. These expressions give us the value of a certain integral, that is, a mathematical result. Whether or not that integral equals the work in a particular process depends on the result of a thermodynamic analysis of that process. It is important to keep the mathematical result separate from the thermodynamic analysis, for there are many situations in which work is not given by Eq. 4.4.

The polytropic process as described demonstrates one special functional relationship between P and V during a process. There are many other possible relations, some of which will be examined in the problems at the end of this chapter.

EXAMPLE 4.1

Consider as a system the gas in the cylinder shown in Fig. 4.7; the cylinder is fitted with a piston on which a number of small weights are placed. The initial pressure is 200 kPa, and the initial volume of the gas is 0.04 m^3.

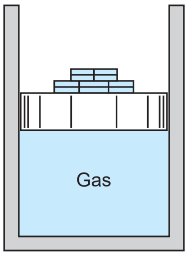

FIGURE 4.7 Sketch for Example 4.1.

a. Let a Bunsen burner be placed under the cylinder, and let the volume of the gas increase to 0.1 m^3 while the pressure remains constant. Calculate the work done by the system during this process.

$$_1W_2 = \int_1^2 P\,dV$$

Since the pressure is constant, we conclude from Eq. 4.4 that

$$_1W_2 = P \int_1^2 dV = P(V_2 - V_1)$$

$$_1W_2 = 200\ \text{kPa} \times (0.1 - 0.04)\text{m}^3 = 12.0\ \text{kJ}$$

b. Consider the same system and initial conditions, but at the same time that the Bunsen burner is under the cylinder and the piston is rising, remove weights from the piston at such a rate that, during the process, the temperature of the gas remains constant.

If we assume that the ideal-gas model is valid, then, from Eq. 3.5,

$$PV = mRT$$

We note that this is a polytropic process with exponent $n = 1$. From our analysis, we conclude that the work is given by Eq. 4.4 and that the integral in this equation is given by Eq. 4.6. Therefore,

$$_1W_2 = \int_1^2 P\,dV = P_1 V_1 \ln \frac{V_2}{V_1}$$

$$= 200\ \text{kPa} \times 0.04\ \text{m}^3 \times \ln \frac{0.10}{0.04} = 7.33\ \text{kJ}$$

c. Consider the same system, but during the heat transfer remove the weights at such a rate that the expression $PV^{1.3}$ = constant describes the relation between pressure and volume during the process. Again, the final volume is 0.1 m^3. Calculate the work.

This is a polytropic process in which $n = 1.3$. Analyzing the process, we conclude again that the work is given by Eq. 4.4 and that the integral is given by Eq. 4.5. Therefore,

$$P_2 = 200\left(\frac{0.04}{0.10}\right)^{1.3} = 60.77 \text{ kPa}$$

$$_1W_2 = \int_1^2 P\,dV = \frac{P_2V_2 - P_1V_1}{1-1.3} = \frac{60.77 \times 0.1 - 200 \times 0.04}{1-1.3} \text{ kPa m}^3$$

$$= 6.41 \text{ kJ}$$

d. Consider the system and the initial state given in the first three examples, but let the piston be held by a pin so that the volume remains constant. In addition, let heat be transferred from the system until the pressure drops to 100 kPa. Calculate the work.

Since $\delta W = P\,dV$ for a quasi-equilibrium process, the work is zero, because there is no change in volume.

The process for each of the four examples is shown on the P–V diagram of Fig. 4.8. Process 1–2a is a constant-pressure process, and area 1–2a–f–e–1 represents the work. Similarly, line 1–2b represents the process in which PV = constant, line 1–2c the process in which $PV^{1.3}$ = constant, and line 1–2d the constant-volume process. The student should compare the relative areas under each curve with the numerical results obtained for the amounts of work done.

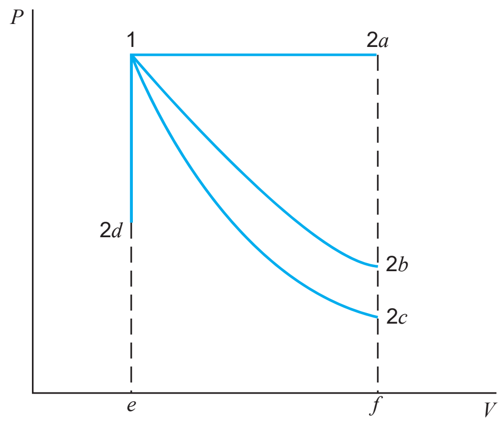

FIGURE 4.8 *P–V* diagram showing work done in the various processes of Example 4.1.

EXAMPLE 4.2 Consider a slightly different piston/cylinder arrangement, as shown in Fig. 4.9. In this example the piston is loaded with a mass m_p, the outside atmosphere P_0, a linear spring, and a single point force F_1. The piston traps the gas inside with a pressure P. A force balance on the piston in the direction of motion yields

$$m_p a \cong 0 = \sum F_\uparrow - \sum F_\downarrow$$

with a zero acceleration in a quasi-equilibrium process. The forces, when the spring is in contact with the piston, are

$$\sum F_\uparrow = PA, \qquad \sum F_\downarrow = m_p g + P_0 A + k_s(x - x_0) + F_1$$

with the linear spring constant, k_s. The piston position for a relaxed spring is x_0, which depends on how the spring is installed. The force balance then gives the gas pressure by division with area A as

$$P = P_0 + [m_p g + F_1 + k_s(x - x_0)]/A$$

To illustrate the process in a P–V diagram, the distance x is converted to volume by division and multiplication with A:

$$P = P_0 + \frac{m_p g}{A} + \frac{F_1}{A} + \frac{k_s}{A^2}(V - V_0) = C_1 + C_2 V$$

This relation gives the pressure as a linear function of the volume, with the line having a slope of $C_2 = k_s/A^2$. Possible values of P and V are as shown in Fig. 4.10 for an expansion. Regardless of what substance is inside, any process must proceed along the line in the P–V diagram. The work term in a quasi-equilibrium process then follows as

$$_1W_2 = \int_1^2 P\,dV = \text{area under the process curve}$$

$$_1W_2 = \frac{1}{2}(P_1 + P_2)(V_2 - V_1)$$

For a contraction instead of an expansion, the process would proceed in the opposite direction from the initial point 1 along a line of the same slope shown in Fig. 4.10.

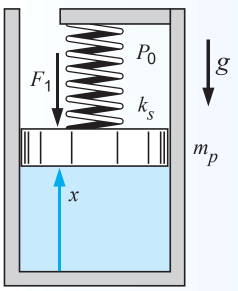

FIGURE 4.9 Sketch of the physical system for Example 4.2.

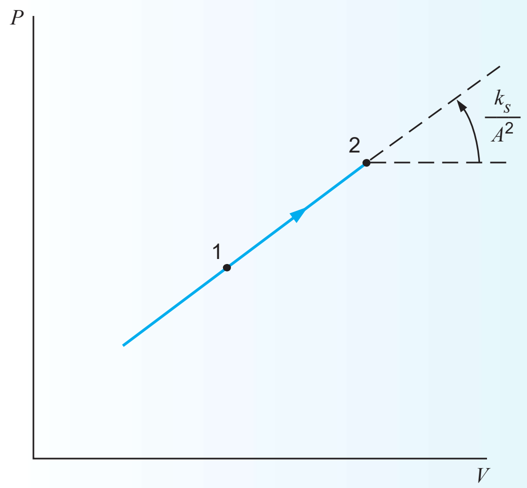

FIGURE 4.10 The process curve showing possible P–V combinations for Example 4.2.

EXAMPLE 4.3

The cylinder/piston setup of Example 4.2 contains 0.5 kg of ammonia at −20°C with a quality of 25%. The ammonia is now heated to +20°C, at which state the volume is observed to be 1.41 times larger. Find the final pressure and the work the ammonia produced.

Solution

The forces acting on the piston, the gravitation constant, the external atmosphere at constant pressure, and the linear spring give a linear relation between P and $v(V)$.

State 1: (T_1, x_1) from Table B.2.1

$$P_1 = P_{sat} = 190.2 \text{ kPa}$$

$$v_1 = v_f + x_1 v_{fg} = 0.001\,504 + 0.25 \times 0.621\,84 = 0.156\,96 \text{ m}^3/\text{kg}$$

State 2: $(T_2, v_2 = 1.41\, v_1 = 1.41 \times 0.156\,96 = 0.2213 \text{ m}^3/\text{kg})$

Table B.2.2 state very close to $P_2 = 600$ kPa

Process: $P = C_1 + C_2 v$

The work term can now be integrated, knowing P versus v, and can be seen as the area in the P–v diagram, shown in Fig. 4.11.

$$_1W_2 = \int_1^2 P\,dV = \int_1^2 Pm\,dv = \text{area} = m\frac{1}{2}(P_1 + P_2)(v_2 - v_1)$$

$$= 0.5 \text{ kg}\,\frac{1}{2}\,(190.2 + 600) \text{ kPa}\,(0.2213 - 0.156\,96) \text{ m}^3/\text{kg}$$

$$= 12.71 \text{ kJ}$$

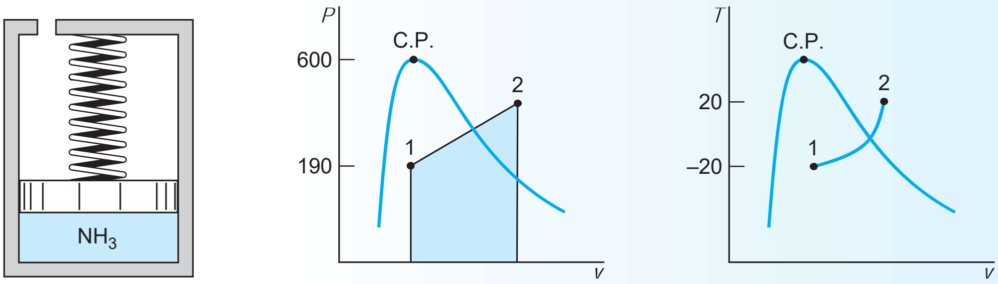

FIGURE 4.11 Diagrams for Example 4.3.

EXAMPLE 4.4

The piston/cylinder setup shown in Fig. 4.12 contains 0.1 kg of water at 1000 kPa, 500°C. The water is now cooled with a constant force on the piston until it reaches half the initial volume. After this it cools to 25°C while the piston is against the stops. Find the final water pressure and the work in the overall process, and show the process in a P–v diagram.

Solution

We recognize that this is a two-step process, one of constant P and one of constant V. This behavior is dictated by the construction of the device.

State 1: (P, T) From Table B.1.3; $v_1 = 0.354\ 11\ \text{m}^3/\text{kg}$

Process 1–1a: $P = \text{constant} = F/A$

1a–2: $v = \text{constant} = v_{1a} = v_2 = v_1/2$

State 2: $(T,\ v_2 = v_1/2 = 0.177\ 06\ \text{m}^3/\text{kg})$

From Table B.1.1, $v_2 < v_g$, so the state is two phase and $P_2 = P_{\text{sat}} = 3.169$ kPa.

$$
{}_1W_2 = \int_1^2 P\,dV = m\int_1^2 P\,dv = mP_1(v_{1a} - v_1) + 0
$$

$$
= 0.1\ \text{kg} \times 1000\ \text{kPa}\ (0.177\ 06 - 0.345\ 11)\ \text{m}^3/\text{kg} = -17.7\ \text{kJ}
$$

Note that the work done from 1a to 2 is zero (no change in volume), as shown in Fig. 4.13.

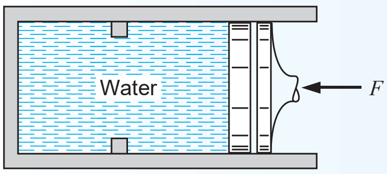

FIGURE 4.12 Sketch for Example 4.4.

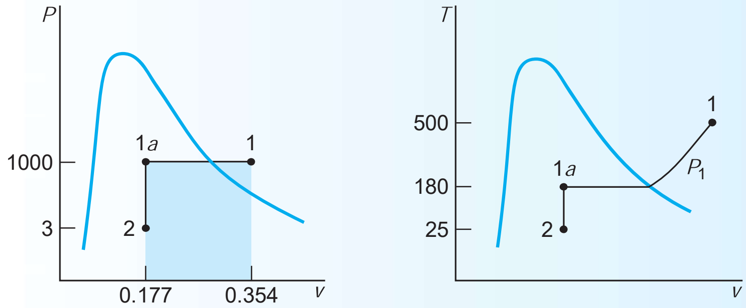

FIGURE 4.13 Diagrams for Example 4.4.

In this section we have discussed boundary movement work in a quasi-equilibrium process. We should also realize that there may very well be boundary movement work in a nonequilibrium process. Then the total force exerted on the piston by the gas inside the cylinder, PA, does not equal the external force, F_{ext}, and the work is not given by Eq. 4.3. The work can, however, be evaluated in terms of F_{ext} or, dividing by area, an equivalent external pressure, P_{ext}. The work done at the moving boundary in this case is

$$\delta W = F_{ext}\, dL = P_{ext}\, dV \tag{4.7}$$

Evaluation of Eq. 4.7 in any particular instance requires a knowledge of how the external force or pressure changes during the process.

EXAMPLE 4.5 Consider the system shown in Fig. 4.14, in which the piston of mass m_p is initially held in place by a pin. The gas inside the cylinder is initially at pressure P_1 and volume V_1. When the pin is released, the external force per unit area acting on the system (gas) boundary is comprised of two parts:

$$P_{ext} = F_{ext}/A = P_0 + m_p g/A$$

Calculate the work done by the system when the piston has come to rest.

After the piston is released, the system is exposed to the boundary pressure equal to P_{ext}, which dictates the pressure inside the system, as discussed in Section 2.8 in connection with Fig. 2.9. We further note that neither of the two components of this external force will change with a boundary movement, since the cylinder is vertical (gravitational force) and the top is open to the ambient surroundings (movement upward merely pushes the air out of the way). If the initial pressure P_1 is greater than that resisting the boundary, the piston will move upward at a finite rate, that is, in a nonequilibrium process, with the cylinder pressure eventually coming to equilibrium at the value P_{ext}. If we were able to trace the average cylinder pressure as a function of time, it would typically behave as shown in Fig. 4.15. However, the work done by the system during this process is done against the force resisting the boundary movement and is therefore given by Eq. 4.7. Also, since the external force is constant during this process, the result is

$$_1W_2 = \int_1^2 P_{ext}\, dV = P_{ext}(V_2 - V_1)$$

where V_2 is greater than V_1, and the work done by the system is positive. If the initial pressure had been less than the boundary pressure, the piston would have moved downward,

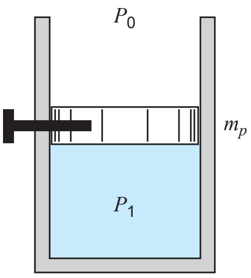

FIGURE 4.14 Example of a nonequilibrium process.

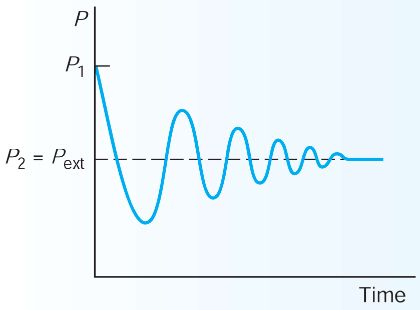

FIGURE 4.15
Cylinder pressure as a function of time.

compressing the gas, with the system eventually coming to equilibrium at P_{ext}, at a volume less than the initial volume, and the work would be negative, that is, done on the system by its surroundings.

In-Text Concept Questions

c. What is roughly the relative magnitude of the work in process 1–2*c* versus process 1–2*a* shown in Fig. 4.8?

d. Helium gas expands from 125 kPa, 350 K, and 0.25 m^3 to 100 kPa in a polytropic process with $n = 1.667$. Is the work positive, negative, or zero?

e. An ideal gas goes through an expansion process in which the volume doubles. Which process will lead to the larger work output: an isothermal process or a polytropic proces with $n = 1.25$?

4.4 OTHER SYSTEMS THAT INVOLVE WORK

In the preceding section we considered the work done at the moving boundary of a simple compressible system during a quasi-equilibrium process and during a nonequilibrium process. There are other types of systems in which work is done at a moving boundary. In this section we briefly consider three such systems: a stretched wire, a surface film, and electrical work.

Consider as a system a stretched wire that is under a given tension $\mathcal{T}$. When the length of the wire changes by the amount dL, the work done by the system is

$$\delta W = -\mathcal{T}\, dL \qquad (4.8)$$

The minus sign is necessary because work is done by the system when dL is negative. This equation can be integrated to have

$$_1W_2 = -\int_1^2 \mathcal{T}\, dL \qquad (4.9)$$

The integration can be performed either graphically or analytically if the relation between $\mathcal{T}$ and L is known. The stretched wire is a simple example of the type of problem in solid-body mechanics that involves the calculation of work.

EXAMPLE 4.6 A metallic wire of initial length L_0 is stretched. Assuming elastic behavior, determine the work done in terms of the modulus of elasticity and the strain.

Let σ = stress, e = strain, and E = the modulus of elasticity.

$$\sigma = \frac{\mathcal{T}}{A} = Ee$$

Therefore,

$$\mathcal{T} = AEe$$

From the definition of strain,

$$de = \frac{dL}{L_0}$$

Therefore,

$$\delta W = -\mathcal{T}\,dL = -AEeL_0\,de$$

$$W = -AEL_0 \int_{e=0}^{e} e\,de = -\frac{A\,EL_0}{2}(e)^2$$

Now consider a system that consists of a liquid film with a surface tension $\mathcal{S}$. A schematic arrangement of such a film, maintained on a wire frame, one side of which can be moved, is shown in Fig. 4.16. When the area of the film is changed, for example, by sliding the movable wire along the frame, work is done on or by the film. When the area changes by an amount dA, the work done by the system is

$$\delta W = -\mathcal{S}\,dA \tag{4.10}$$

For finite changes,

$$_1W_2 = -\int_1^2 \mathcal{S}\,dA \tag{4.11}$$

We have already noted that electrical energy flowing across the boundary of a system is work. We can gain further insight into such a process by considering a system in which the only work mode is electrical. Examples of such a system include a charged condenser, an electrolytic cell, and the type of fuel cell described in Chapter 1. Consider a quasi-equilibrium process for such a system, and during this process let the potential difference be $\mathcal{E}$ and the amount of electrical charge that flows into the system be dZ. For this quasi-equilibrium process the work is given by the relation

$$\delta W = -\mathcal{E}\,dZ \tag{4.12}$$

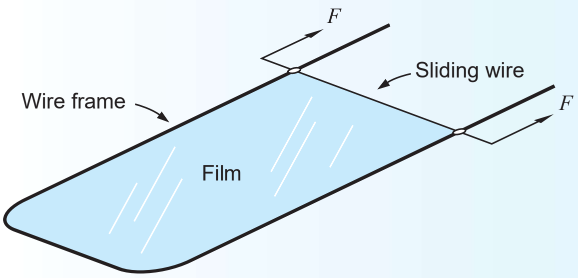

FIGURE 4.16 Schematic arrangement showing work done on a surface film.

Since the current, i, equals dZ/dt (where $t =$ time), we can also write

$$\delta W = -\mathscr{E} i\, dt$$

$$_1W_2 = -\int_1^2 \mathscr{E} i\, dt \tag{4.13}$$

Equation 4.13 may also be written as a rate equation for work (power):

$$\dot{W} = \frac{\delta W}{dt} = -\mathscr{E} i \tag{4.14}$$

Since the ampere (electric current) is one of the fundamental units in the International System and the watt was defined previously, this relation serves as the definition of the unit for electric potential, the volt (V), which is one watt divided by one ampere.

4.5 CONCLUDING REMARKS REGARDING WORK

The similarity of the expressions for work in the three processes discussed in Section 4.4 and in the processes in which work is done at a moving boundary should be noted. In each of these quasi-equilibrium processes, work is expressed by the integral of the product of an intensive property and the change of an extensive property. The following is a summary list of these processes and their work expressions:

Simple compressible system	$_1W_2 = \int_1^2 P\, dV$
Stretched wire	$_1W_2 = -\int_1^2 \mathscr{T}\, dL$
Surface film	$_1W_2 = -\int_1^2 \mathscr{S}\, dA$
System in which the work is completely electrical	$_1W_2 = -\int_1^2 \mathscr{E}\, dZ$ (4.15)

Although we will deal primarily with systems in which there is only one mode of work, it is quite possible to have more than one work mode in a given process. Thus, we could write

$$\delta W = P\, dV - \mathscr{T}\, dL - \mathscr{S}\, dA - \mathscr{E}\, dZ + \cdots \tag{4.16}$$

where the dots represent other products of an intensive property and the derivative of a related extensive property. In each term the intensive property can be viewed as the driving force that causes a change to occur in the related extensive property, which is often termed the *displacement*. Just as we can derive the expression for power for the single point force in Eq. 4.2, the rate form of Eq. 4.16 expresses the power as

$$\dot{W} = \frac{dW}{dt} = P\dot{V} - \mathscr{T}\mathbf{V} - \mathscr{S}\dot{A} - \mathscr{E}\dot{Z} + \cdots \tag{4.17}$$

It should also be noted that many other forms of work can be identified in processes that are not quasi-equilibrium processes. For example, there is the work done by shearing

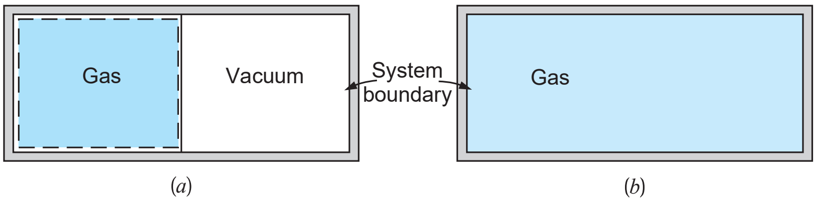

FIGURE 4.17 Example of a process involving a change of volume for which the work is zero.

forces in the friction in a viscous fluid or the work done by a rotating shaft that crosses the system boundary.

The identification of work is an important aspect of many thermodynamic problems. We have already noted that work can be identified only at the boundaries of the system. For example, consider Fig. 4.17, which shows a gas separated from the vacuum by a membrane. Let the membrane rupture and the gas fill the entire volume. Neglecting any work associated with the rupturing of the membrane, we can ask whether work is done in the process. If we take as our system the gas and the vacuum space, we readily conclude that no work is done because no work can be identified at the system boundary. If we take the gas as a system, we do have a change of volume, and we might be tempted to calculate the work from the integral

$$\int_1^2 P\,dV$$

However, this is not a quasi-equilibrium process, and therefore the work cannot be calculated from this relation. Because there is no resistance at the system boundary as the volume increases, we conclude that for this system no work is done in this process of filling the vacuum.

Another example can be cited with the aid of Fig. 4.18. In Fig. 4.18*a* the system consists of the container plus the gas. Work crosses the boundary of the system at the point where the system boundary intersects the shaft, and this work can be associated with the shearing forces in the rotating shaft. In Fig. 4.18*b* the system includes the shaft and the weight as well as the gas and the container. Therefore, no work crosses the system boundary as the weight moves downward. As we will see in the next chapter, we can identify a change of potential energy within the system, but this should not be confused with work crossing the system boundary.

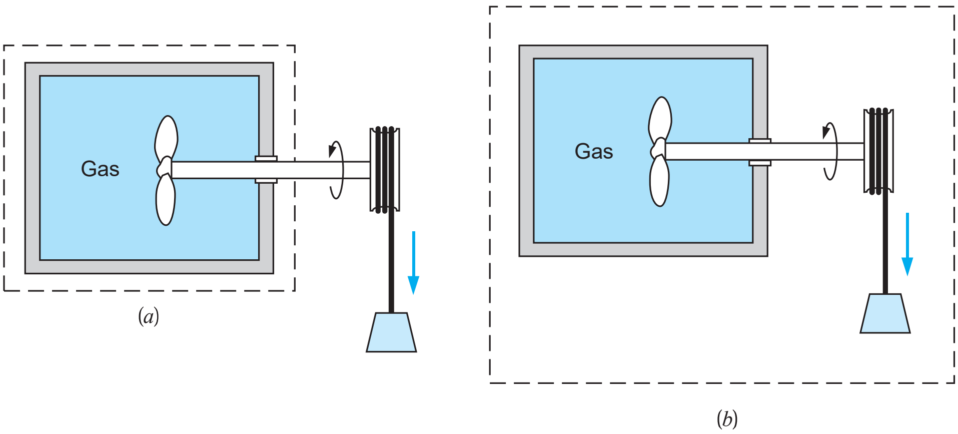

FIGURE 4.18 Example showing how selection of the system determines whether work is involved in a process.