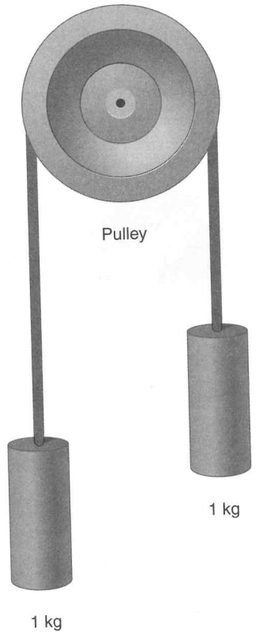

FIGURE 2.9

Two masses of exactly 1 kg each are connected by a wire of zero mass running over a frictionless pulley. The system is in mechanical equilibrium and the masses are stationary.

Next, consider a process in which the system changes from an initial state characterized by P_i, V_i, and T_i to a final state characterized by P_f, V_f, and T_f as shown in Figure 2.8. If the rate of change of the macroscopic variables is negligibly small, the system passes through a succession of states of internal equilibrium as it goes from the initial to the final state. Such a process is called a **quasi-static process**, and internal equilibrium is maintained in a quasi-static process. If the rate of change is sufficiently large, the rates of diffusion and intermolecular collisions may not be high enough to maintain the system in a state of internal equilibrium. Thermodynamic calculations for such a process are valid only if it is meaningful to assign a single value of the macroscopic variables *P, V, T,* and concentration to the system undergoing change. The same considerations hold for the surroundings. We only consider quasi-static processes in this text as state variables such as P and T are only meaningful in this limit.

We now visualize a process in which the system undergoes a major change in terms of a directed path consisting of a sequence of quasi-static processes and distinguish between two very important classes of quasi-static processes, namely, reversible and irreversible processes. It is useful to consider the mechanical system shown in Figure 2.9 when discussing reversible and irreversible processes. Because the two masses have the same value, the net force acting on each end of the wire is zero, and the masses will not move. If an additional mass is placed on either of the two masses, the system is no longer in mechanical equilibrium and the masses will move. In the limit that the incremental mass approaches zero, the velocity at which the initial masses move approaches zero. In this case, one refers to the process as being **reversible**, meaning that the direction of the process can be reversed by placing the infinitesimal mass on the other side of the pulley.

Reversibility in a chemical system can be illustrated by a system consisting of liquid water in equilibrium with gaseous water that is surrounded by a thermal reservoir. The system and surroundings are both at temperature T. An infinitesimally small increase in T results in a small increase of the amount of water in the gaseous phase, and a small decrease in the liquid phase. An equally small decrease in the temperature has the opposite effect. Therefore, fluctuations in T give rise to corresponding fluctuations in the composition of the system. If an infinitesimal opposing change in the variable that drives the process (temperature in this case) causes a reversal in the direction of the process, the process is reversible.

If an infinitesimal change in the driving variable does not change the direction of the process, one says that the process is **irreversible**. For example, if a large stepwise temperature increase is induced in the system using a heat pulse, the amount of water in the gas phase increases abruptly. In this case, the composition of the system cannot be returned to its initial value by an infinitesimal temperature decrease. This relationship is characteristic of an irreversible process. Although any process that takes place at a rapid rate in the real world is irreversible, real processes can approach reversibility in the appropriate limit. For example, a slow increase in the electrical potential in an electrochemical cell can convert reactants to products in a nearly reversible process.

2.7 COMPARING WORK FOR REVERSIBLE AND IRREVERSIBLE PROCESSES

We concluded in Section 2.5 that w is not a state function and that the work associated with a process is path dependent. This statement can be put on a quantitative footing by comparing the work associated with the reversible and irreversible expansion and compression of an ideal gas. This process is discussed next and illustrated in Figure 2.10.

Consider the following irreversible process, meaning that the internal and external pressures are not equal. A quantity of an ideal gas is confined in a cylinder with a weightless movable piston. The walls of the system are diathermal, allowing heat to flow between the system and surroundings. Therefore, the process is isothermal at the temperature of the surroundings, T. The system is initially defined by the variables T, P_1, and V_1. The position of the piston is determined by $P_{external} = P_1$, which can be changed by adding or removing weights from the piston. Because the weights are moved horizontally, no work is done in adding or removing them. The gas is first expanded at constant temperature by decreasing $P_{external}$ abruptly to the value P_2 (weights are removed), where $P_2 < P_1$. A sufficient amount of heat flows into the system through the diathermal walls to keep the temperature at the constant value T. The system is now in the state defined by T, P_2, and V_2, where $V_2 > V_1$. The system is then returned to its original state in an **isothermal process** by increasing $P_{external}$ abruptly to its original value P_1 (weights are added). Heat flows out of the system into the surroundings in this step. The system has been restored to its original state and, because this is a cyclic process, $\Delta U = 0$. Are q_{total} and w_{total} also zero for the cyclic process? The total work associated with this cyclic process is given by the sum of the work for each individual step:

$$\begin{aligned} w_{total} &= \sum_i -P_{external,\,i}\Delta V_i = w_{expansion} + w_{compression} \\ &= -P_2(V_2 - V_1) - P_1(V_1 - V_2) \\ &= -(P_2 - P_1) \times (V_2 - V_1) > 0 \quad \text{because } P_2 < P_1 \quad \text{and } V_2 > V_1 \end{aligned} \tag{2.20}$$

The relationship between P and V for the process under consideration is shown graphically in Figure 2.10, in what is called an **indicator diagram**. An indicator diagram is useful because the work done in the expansion and contraction steps can be evaluated from the appropriate area in the figure, which is equivalent to evaluating the integral $w = -\int P_{external}\, dV$. Note that the work done in the expansion is negative because $\Delta V > 0$, and that done in the compression is positive because $\Delta V < 0$. Because $P_2 < P_1$, the magnitude of the work done in the compression process is more than that done in the expansion process and $w_{total} > 0$. What can one say about q_{total}? The first law states that because $\Delta U = q_{total} + w_{total} = 0$, $q_{total} < 0$.

The same cyclical process is carried out in a reversible cycle. A necessary condition for reversibility is that $P = P_{external}$ at every step of the cycle. This means that P changes during the expansion and compression steps. The work associated with the expansion is

$$w_{expansion} = -\int P_{external}\, dV = -\int P\, dV = -nRT\int \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1} \tag{2.21}$$

This work is shown schematically as the red area in the indicator diagram of Figure 2.11.

If this process is reversed and the compression work is calculated, the following result is obtained:

$$w_{compression} = -nRT \ln \frac{V_1}{V_2} \tag{2.22}$$

It is seen that the magnitudes of the work in the forward and reverse processes are equal. The total work done in this cyclical process is given by

$$\begin{aligned} w &= w_{expansion} + w_{compression} = -nRT \ln \frac{V_2}{V_1} - nRT \ln \frac{V_1}{V_2} \\ &= -nRT \ln \frac{V_2}{V_1} + nRT \ln \frac{V_2}{V_1} = 0 \end{aligned} \tag{2.23}$$

Therefore, the work done in a reversible isothermal cycle is zero. Because $\Delta U = q + w$ is a state function, $q = -w = 0$ for this reversible isothermal process. Looking at the heights of the weights in the surroundings at the end of the process, we find that they are the same as at the beginning of the process. To compare the work for reversible and irreversible processes, the state variables need to be given specific values as is done in Example Problem 2.4.

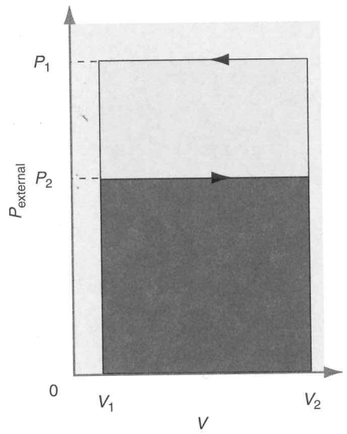

FIGURE 2.10

The work for each step and the total work can be obtained from an indicator diagram. For the compression step, w is given by the total area in red and yellow; for the expansion step, w is given by the red area. The arrows indicate the direction of change in V in the two steps. The sign of w is opposite for these two processes. The total work in the cycle is the yellow area.

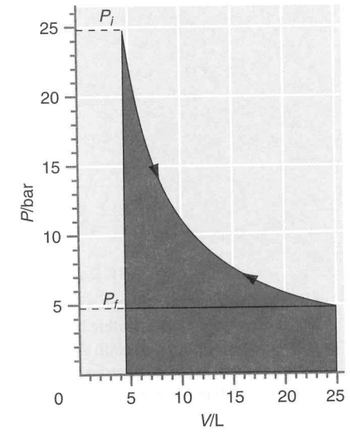

FIGURE 2.11

Indicator diagram for a reversible process. Unlike Figure 2.10, the areas under the *P–V* curves are the same in the forward and reverse directions.