not the path taken to reach the state. This property can be expressed in a mathematical form. Any state function, for example, U, must satisfy the equation

$$\Delta U = \int_i^f dU = U_f - U_i \tag{2.13}$$

where i and f denote the initial and final states. This equation states that in order for ΔU to depend only on the initial and final states characterized here by i and f, the value of the integral must be independent of the path. If this is the case, U can be expressed as an infinitesimal quantity, dU, that when integrated, depends only on the initial and final states. The quantity dU is called an **exact differential**. We defer a discussion of exact differentials to Chapter 3.

It is useful to define a cyclic integral, denoted by the symbol $\oint$, as applying to a **cyclic path** such that the initial and final states are identical. For U or any other state function,

$$\oint dU = U_f - U_f = 0 \tag{2.14}$$

because the initial and final states are the same in a cyclic process.

We next show that q and w are not state functions. The state of a single-phase system at fixed composition is characterized by any two of the three variables P, T, and V. The same is true of U. Therefore, for a system of fixed mass, U can be written in any of the three forms $U(V, T)$, $U(P, T)$, or $U(P, V)$. Imagine that a gas of fixed mass characterized by V_1 and T_1 is confined in a piston and cylinder system that is isolated from the surroundings. There is a thermal reservoir in the surroundings at a temperature $T_3 > T_1$. We do compression work on the system starting from an initial state in which the volume is V_1 to an intermediate state in which the volume is V_2 using a constant external pressure $P_{external}$ where $V_2 < V_1$. The work is given by

$$w = -\int_{V_i}^{V_f} P_{external}\, dV = -P_{external} \int_{V_i}^{V_f} dV$$

$$= -P_{external}(V_f - V_i) = -P_{external}\Delta V \tag{2.15}$$

Because the height of the mass in the surroundings is lower after the compression (see Figure 2.7), w is positive and U increases. Because the system consists of a uniform single phase, U is a monotonic function of T, and T also increases. The change in volume ΔV has been chosen such that the temperature of the system T_2 in the intermediate state after the compression satisfies the inequality $T_1 < T_2 < T_3$.

We next lock the piston in place and let an amount of heat q flow between the system and surroundings at constant V by bringing the system into contact with the reservoir at temperature T_3. The final state values of T and V after these two steps are T_3 and V_2.

This two-step process is repeated for different values of the mass. In each case the system is in the same final state characterized by the variables V_2 and T_3. The sequence of steps that takes the system from the initial state V_1, T_1 to the final state V_2, T_3 is referred to as a **path**. By changing the mass, a set of different paths is generated, all of which originate from the state V_1, T_1, and end in the state V_2, T_3. According to the first law, ΔU for this two-step process is

$$\Delta U = U(T_3, V_2) - U(T_1, V_1) = q + w \tag{2.16}$$

Because ΔU is a state function, its value for the two-step process just described is the same for each of the different values of the mass.

Are q and w also state functions? For this two-step process,

$$w = -P_{external}\Delta V \tag{2.17}$$

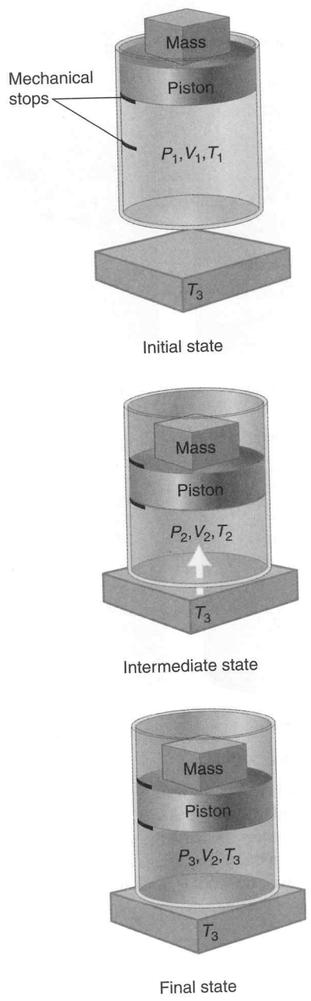

FIGURE 2.7

A system consisting of an ideal gas is contained in a piston and cylinder assembly. The gas in the initial state V_1, T_1 is compressed to an intermediate state, whereby the temperature increases to the value T_2. It is then brought into contact with a thermal reservoir at T_3, leading to a further rise in temperature. The final state is V_2, T_3. The mechanical stops allow the system volume to be only V_1 or V_2.

and $P_{external}$ is different for each value of the mass, or for each path, whereas ΔV is constant. Therefore, w is also different for each path; we can choose one path from V_1, T_1 to V_2, T_3 and a different path from V_2, T_3 back to V_1, T_1. Because the work is different along these paths, the cyclic integral of work is not equal to zero. Therefore, w is not a state function.

Using the first law to calculate q for each of the paths, we obtain the result

$$q = \Delta U - w = \Delta U + P_{external}\Delta V \tag{2.18}$$

Because ΔU is the same for each path, and w is different for each path, we conclude that q is also different for each path. Just as for work, the cyclic integral of heat is not equal to zero. Therefore, neither q nor w are state functions, and they are called **path functions**.

Because both q and w are path functions, there are no exact differentials for work and heat. Incremental amounts of these quantities are denoted by $đq$ and $đw$, rather than dq and dw, to emphasize the fact that incremental amounts of work and heat are not exact differentials. This is an important result that can be expressed mathematically.

$$\Delta q \neq \int_i^f đq \neq q_f - q_i \quad \text{and} \quad \Delta w \neq \int_i^f đw \neq w_f - w_i \tag{2.19}$$

because there are no such quantities as Δq, q_f, q_i and Δw, w_f, w_i. This is an important result. One cannot refer to the work or heat possessed by a system. After a process involving the transfer of heat and work between the system and surroundings is completed, the system and surroundings possess internal energy, but neither possesses heat or work.

The preceding discussion emphasizes that it is important to use the terms *work* and *heat* in a way that reflects the fact that they are not state functions. Examples of systems of interest to us are batteries, fuel cells, refrigerators, and internal combustion engines. In each case, the utility of these systems is that work and/or heat flows between the system and surroundings. For example, in a refrigerator, electrical energy is used to extract heat from the inside of the device and to release it in the surroundings. One can speak of the refrigerator as having the capacity to extract heat, but it would be wrong to speak of it as having heat. In the internal combustion engine, chemical energy contained in the bonds of the fuel molecules and in O_2 is released in forming CO_2 and H_2O. This change in internal energy can be used to rotate the wheels of the vehicle, thereby inducing a flow of work between the vehicle and the surroundings. One can refer to the capability of the engine to do work, but it would be incorrect to refer to the vehicle or the engine as containing or having work.

2.6 EQUILIBRIUM, CHANGE, AND REVERSIBILITY

Thermodynamics can only be applied to systems in internal equilibrium, and a requirement for equilibrium is that the overall rate of change of all processes such as diffusion or chemical reaction be zero. How do we reconcile these statements with our calculations of q, w, and ΔU associated with processes in which there is a macroscopic change in the system? To answer this question, it is important to distinguish between the system and surroundings each being in internal equilibrium, and the system and surroundings being in equilibrium with one another.

We first discuss the issue of internal equilibrium. Consider a system made up of an ideal gas, which satisfies the equation of state, $P = nRT/V$. All combinations of P, V, and T consistent with this equation of state form a surface in P–V–T space as shown in Figure 2.8. All points on the surface correspond to equilibrium states of the system. Points that are not on the surface do not correspond to any physically realizable state of the system. Nonequilibrium situations cannot be represented on such a plot, because P, V, and T do not have unique values for a system that is not in internal equilibrium.

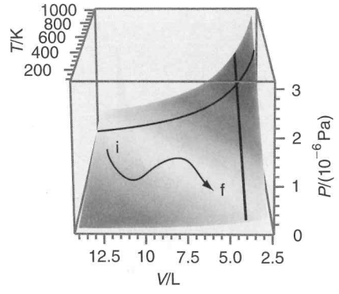

FIGURE 2.8

All combinations of pressure, volume, and temperature consistent with 1 mol of an ideal gas lie on the colored surface. All combinations of pressure and volume consistent with $T = 800$ K and all combinations of pressure and temperature consistent with a volume of 4.0 L are shown as black curves that lie in the P–V–T surface. The third curve corresponds to a path between an initial state i and a final state f that is neither a constant temperature nor a constant volume path.