On the basis of these calculations for the reversible and irreversible cycles, we introduce another criterion to distinguish between reversible and irreversible processes. Suppose that a system undergoes a change through one or a number of individual steps, and that the system is restored to its initial state by following the same steps in reverse order. The system is restored to its initial state because the process is cyclical. If the surroundings are also returned to their original state (all masses at the same height and all reservoirs at their original temperatures), the process is reversible. If the surroundings are not restored to their original state, the process is irreversible.

We are often interested in extracting work from a system. For example, it is the expansion of the fuel–air mixture in an automobile engine upon ignition that provides the torque that eventually drives the wheels. Is the capacity to do work similar for reversible and irreversible processes? This question is answered using the indicator diagrams of Figures 2.10 and 2.11 for the specific case of isothermal expansion work, noting that the work can be calculated from the area under the P–V curve. We compare the work for expansion from V_1 to V_2 in a single stage at constant pressure to that for the reversible case. For the single-stage expansion, the constant external pressure is given by $P_{external} = nRT/V_2$. However, if the expansion is carried out reversibly, the system pressure is always greater than this value. By comparing the areas in the indicator diagrams of Figure 2.12, it is seen that

$$|w_{reversible}| \geq |w_{irreversible}| \tag{2.24}$$

By contrast, for the compression step,

$$|w_{reversible}| \leq |w_{irreversible}| \tag{2.25}$$

The reversible work is the lower bound for the compression work and the upper bound for the expansion work. This result for the expansion work can be generalized to an important statement that holds for all forms of work: *The maximum work that can be extracted from a process between the same initial and final states is that obtained under reversible conditions.*

Although the preceding statement is true, it suggests that it would be optimal to operate an automobile engine under conditions in which the pressure inside the cylinders differs only infinitesimally from the external atmospheric pressure. This is clearly not possible. A practical engine must generate torque on the drive shaft, and this can only occur if the cylinder pressure is appreciably greater than the external pressure. Similarly, a battery is only useful if one can extract a sizable rather than an infinitesimal current. To operate such devices under useful irreversible conditions, the work output is less than the theoretically possible limit set by the reversible process.

2.8 DETERMINING ΔU AND INTRODUCING ENTHALPY, A NEW STATE FUNCTION

How can the ΔU for a thermodynamic process be measured? This will be the topic of Chapter 4, in which calorimetry is discussed. However, this topic is briefly discussed here in order to enable you to carry out calculations on ideal gas systems in the end-of-chapter problems. The first law states that $\Delta U = q + w$. Imagine that the process is carried out under constant volume conditions and that nonexpansion work is not possible. Because under these conditions, $w = -\int P_{external}\, dV = 0$,

$$\Delta U = q_V \tag{2.26}$$

Equation (2.26) states that ΔU can be experimentally determined by measuring the heat flow between the system and surroundings in a constant volume process.

What does the first law look like under reversible and constant pressure conditions? We write

$$dU = \not{d} q_P - P_{external}\, dV = \not{d} q_P - P\, dV \tag{2.27}$$

and integrate this expression between the initial and final states:

$$\int_i^f dU = U_f - U_i = \int \not{d} q_P - \int P\, dV = q_P - P(V_f - V_i)$$

$$= q_P - (P_f V_f - P_i V_i) \tag{2.28}$$

In order to evaluate the integral involving P, we must know $P(V)$, which in this case is $P_i = P_f = P$ where P is constant. The integral over $\not{d} q_P$ has a unique value because the path (P = constant) is defined. Rearranging the last equation, we obtain

$$(U_f + P_f V_f) - (U_i + P_i V_i) = q_P \tag{2.29}$$

Because P, V, and U are all state functions, $U + PV$ is a state function. This new state function is called **enthalpy** and is given the symbol H. [A more rigorous demonstration that H is a state function can be given by invoking the first law for U and applying the criterion of Equation (3.5) to the product PV.]

$$H \equiv U + PV \tag{2.30}$$

As is the case for U, H has the units of energy, and it is an extensive property. As shown in Equation (2.29), ΔH for a process involving only P–V work can be determined by measuring the heat flow between the system and surroundings at constant pressure:

$$\Delta H = q_P \tag{2.31}$$

This equation is the constant pressure analogue of Equation (2.26). Because chemical reactions are much more frequently carried out at constant P than constant V, the energy change measured experimentally by monitoring the heat flow is ΔH rather than ΔU.

2.9 CALCULATING q, w, ΔU, AND ΔH FOR PROCESSES INVOLVING IDEAL GASES

In this section, we discuss how ΔU and ΔH, as well as q and w, can be calculated from the initial and final state variables if the path between the initial and final state is known. The problems at the end of this chapter ask you to calculate q, w, ΔU, and ΔH for simple and multistep processes. Because an equation of state is often needed to carry out such calculations, the system will generally be an ideal gas. Using an ideal gas as a surrogate for more complex systems has the significant advantage that the mathematics is simplified, allowing one to concentrate on the process rather than the manipulation of equations and the evaluation of integrals.

What does one need to know to calculate ΔU? The following discussion is restricted to processes that do not involve chemical reactions or changes in phase. Because U is a state function, ΔU is independent of the path between the initial and final states. To describe a fixed amount of an ideal gas (i.e., n is constant), the values of two of the variables P, V, and T must be known. Is this also true for ΔU for processes involving ideal gases? To answer this question, consider the expansion of an ideal gas from an initial state V_1, T_1 to a final state V_2, T_2. We first assume that U is a function of both V and T. Is this assumption correct? Because U does not depend on V for an ideal gas, ΔU must be a function of T only for an ideal gas, $\Delta U = \Delta U(T)$.

We also know that for a temperature range over which C_V is constant,

$$\Delta U = q_V = C_V(T_f - T_i) \tag{2.32}$$

Is this equation only valid for constant V? Because U is a function of T only for an ideal gas, Equation (2.32) is also valid for processes involving ideal gases in which V is not constant. Therefore, if one knows C_V, T_1, and T_2, ΔU can be calculated, regardless of the path between the initial and final states.

2.1 Heat Capacity