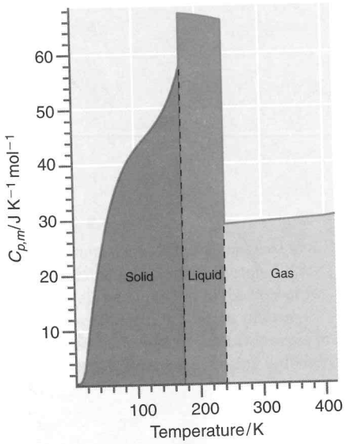

FIGURE 2.5

The variation of $C_{P,m}$ with temperature is shown for Cl_2.

where C is in the SI unit of J K^{-1}. It is an extensive quantity that, for example, doubles as the mass of the system is doubled. Often, the molar heat capacity, C_m is used in calculations. It is an intensive quantity with the units of J K^{-1} mol^{-1}. Experimentally, the heat capacity of fluids is measured by immersing a heating coil in the fluid and equating the electrical work done on the coil with the heat flow into the sample. For solids, the heating coil is wrapped around the solid. In both cases, the experimental results must be corrected for heat losses to the surroundings. The significance of the notation $đq$ for an incremental amount of heat is explained in the next section.

The value of the heat capacity depends on the experimental conditions under which it is determined. The most common conditions are constant volume or constant pressure, for which the heat capacity is denoted C_V and C_P, respectively. Values of $C_{P,m}$ at 298.15 K for pure substances are tabulated in Tables 2.2 and 2.3 (see Appendix B, Data Tables), and formulas for calculating $C_{P,m}$ at other temperatures for gases and solids are listed in Tables 2.4 and 2.5, respectively.

An example of how $C_{P,m}$ depends on T is illustrated in Figure 2.5 for Cl_2. To make the functional form of $C_{P,m}(T)$ understandable, we briefly discuss the relative magnitudes of $C_{P,m}$ in the solid, liquid, and gaseous phases using a microscopic model. A solid can be thought of as a set of interconnected harmonic oscillators, and heat uptake leads to the excitations of the collective vibrations of the solid. At very low temperatures, these vibrations cannot be activated, because the spacing of the vibrational energy levels is large compared to kT. As a consequence, energy cannot be taken up by the solid. Hence, $C_{P,m}$ approaches zero as T approaches zero. For the solid, $C_{P,m}$ rises rapidly with T because the thermal energy available as T increases is sufficient to activate the vibrations of the solid. The heat capacity increases discontinuously as the solid melts to form a liquid. This is the case because the liquid retains all the local vibrational modes of the solid, and more modes with low frequencies become available upon melting. Therefore, the heat capacity of the liquid is greater than that of the solid. As the liquid vaporizes, the local vibrational modes present in the liquid are converted to translations that cannot take up as much energy as vibrations. Therefore, $C_{P,m}$ decreases discontinuously at the vaporization temperature. The heat capacity in the gaseous state increases slowly with temperature as the vibrational modes of the individual molecules are activated. These changes in $C_{P,m}$ can be calculated for a specific substance using a microscopic model and statistical thermodynamics, as will be discussed in detail in Chapter 32.

Once the heat capacity of a variety of different substances has been determined, we have a convenient way to quantify heat flow. For example, at constant pressure, the heat flow between the system and surroundings can be written as

$$q_P = \int_{T_{sys,i}}^{T_{sys,f}} C_P^{system}(T)\,dT = -\int_{T_{surr,i}}^{T_{surr,f}} C_P^{surroundings}(T)\,dT \qquad (2.10)$$

By measuring the temperature change of a thermal reservoir in the surroundings at constant pressure, q_P can be determined. In Equation (2.10), the heat flow at constant pressure has been expressed both from the perspective of the system and from the perspective of the surroundings. A similar equation can be written for a constant volume process. Water is a convenient choice of material for a heat bath in experiments because C_P is nearly constant at the value 4.18 J g^{-1} K^{-1} or 75.3 J mol^{-1} K^{-1} over the range from 0° to 100°C.

EXAMPLE PROBLEM 2.3

The volume of a system consisting of an ideal gas decreases at constant pressure. As a result, the temperature of a 1.50-kg water bath in the surroundings increases by 14.2°C. Calculate q_P for the system.

Solution

$$q_P = -\int_{T_{surr,i}}^{T_{surr,f}} C_P^{surroundings}(T)\,dT = -C_P^{surroundings}\Delta T$$
$$= -1.50\text{ kg} \times 4.18\text{ J g}^{-1}\text{K}^{-1} \times 14.2\text{ K} = -89.1\text{ kJ}$$

How are C_P and C_V related for a gas? Consider the processes shown in Figure 2.6 in which a fixed amount of heat flows from the surroundings into a gas. In the constant pressure process, the gas expands as its temperature increases. Therefore, the system does work on the surroundings. As a consequence, not all the heat flow into the system can be used to increase ΔU. No such work occurs for the corresponding constant volume process, and all the heat flow into the system can be used to increase ΔU. Therefore, $dT_P < dT_V$ for the same heat flow $đq$. For this reason, $C_P > C_V$ for gases.

The same argument applies to liquids and solids as long as V increases with T. Nearly all substances follow this behavior, although notable exceptions occur such as liquid water between 4° and 0°C for which the volume increases as T decreases. However, because ΔV_m upon heating is much smaller than for a gas, the difference between $C_{P,m}$ and $C_{V,m}$ for a liquid or solid is much smaller than for a gas.

The preceding remarks about the difference between C_P and C_V have been qualitative in nature. However, the following quantitative relationship, which will be proved in Chapter 3, holds for an ideal gas:

$$C_P - C_V = nR \quad \text{or} \quad C_{P,m} - C_{V,m} = R \qquad (2.11)$$

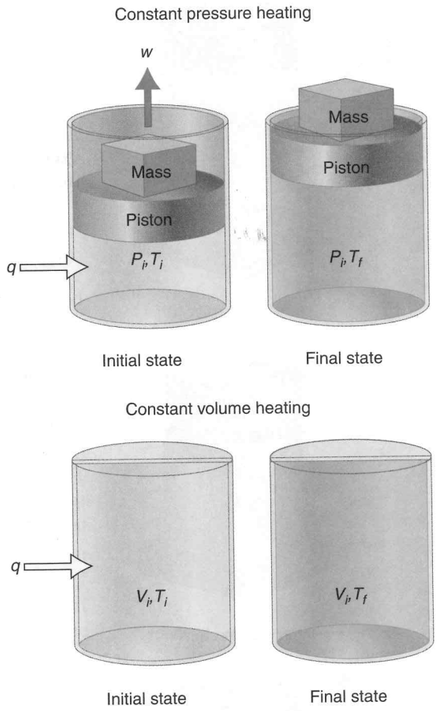

FIGURE 2.6

Not all the heat flow into the system can be used to increase ΔU in a constant pressure process, because the system does work on the surroundings as it expands. However, no work is done for constant volume heating.

2.5 STATE FUNCTIONS AND PATH FUNCTIONS

An alternate statement of the first law is that ΔU is independent of the path between the initial and final states and depends only on the initial and final states. We make this statement plausible for the kinetic energy, and the argument can be extended to the other forms of energy listed in Section 2.1. Consider a single molecule in the system. Imagine that the molecule of mass m initially has the speed v_1. We now change its speed incrementally following the sequence $v_1 \rightarrow v_2 \rightarrow v_3 \rightarrow v_4$. The change in the kinetic energy along this sequence is given by

$$\Delta E_{kinetic} = \left(\frac{1}{2}m(v_2)^2 - \frac{1}{2}m(v_1)^2\right) + \left(\frac{1}{2}m(v_3)^2 - \frac{1}{2}m(v_2)^2\right) + \left(\frac{1}{2}m(v_4)^2 - \frac{1}{2}m(v_3)^2\right)$$
$$= \left(\frac{1}{2}m(v_4)^2 - \frac{1}{2}m(v_1)^2\right) \qquad (2.12)$$

Even though v_2 and v_3 can take on any arbitrary values, they still do not influence the result. We conclude that the change in the kinetic energy depends only on the initial and final speed and that it is independent of the path between these values. Our conclusion remains the same if we increase the number of speed increments in the interval between v_1 and v_2 to an arbitrarily large number. Because this conclusion holds for all molecules in the system, it also holds for ΔU.

This example supports the assertion that ΔU depends only on the final and initial states and not on the path connecting these states. Any function that satisfies this condition is called a **state function**, because it depends only on the state of the system and