CHAPTER 23

THE FIRST LAW OF THERMODYNAMICS

In earlier chapters we used the concept of heat, without defining it carefully. In this chapter we explore the nature of heat in more detail. With the concepts of work, heat, and internal energy now in hand, we return to the first law of thermodynamics—first discussed in Chapter 13—for a deeper analysis. We conclude by applying this law to a number of thermodynamic processes, once more choosing the ideal gas as our system of interest.

23-1 HEAT: ENERGY IN TRANSIT

It is a common observation that if you place a cup of hot coffee or a glass of ice water on a table at room temperature, the coffee will get colder and the ice water will get warmer, the temperature of each approaching that of the room. In each case the object will tend toward thermal equilibrium with its environment.

We have mentioned earlier that such approaches to thermal equilibrium must involve some sort of exchange of energy between the system and the environment. In Section 13-7 (which you should review) we defined the heat Q to be the energy that is transferred, such as from the coffee to the room or from the room to the ice water. Specifically:

Heat is energy that flows between a system and its environment because of a temperature difference between them.

Figure 23-1 summarizes this view. If the temperature T_S of a system is less than the temperature T_E of the system's environment, energy flows *into* the system as heat. We choose our sign convention so that Q is positive in this case, which tends to increase the internal energy E_{int} of the system. Conversely, when $T_S > T_E$, energy flows out of the system (thereby decreasing E_{int}), and we take Q for this case to be negative.

Like other forms of energy, heat can be expressed in the SI unit of joules (J). In Section 13-7 we listed the relationship of the joule to other units in which heat energy is sometimes measured.

Misconceptions about Heat

Heat is similar to work in that both represent ways of transferring energy. Neither heat nor work is an intrinsic property of a system; that is, we cannot say that a system

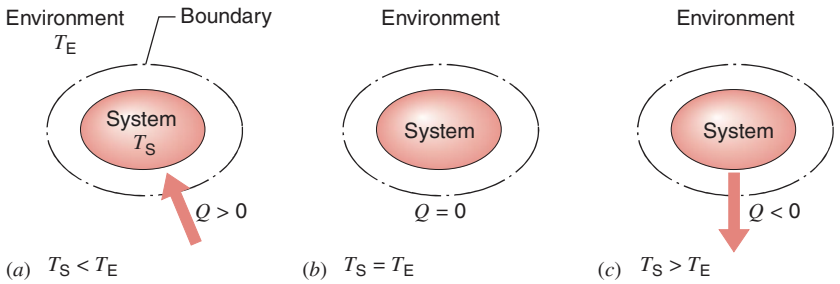

FIGURE 23-1. (*a*) If the temperature T_S of a system is less than the temperature T_E of its environment, heat is transferred into the system until thermal equilibrium is established, as in (*b*). (*c*) If the temperature of a system is greater than that of its environment, heat is transferred out of the system.

"contains" a certain amount of heat or work. Unlike properties such as pressure, temperature, and internal energy, heat and work are not properties of the state of the system; they are not *state functions.* Instead, we say that a certain amount of energy can be transferred, either into or out of the system, as heat or as work. Both heat and work are thus associated with a *thermodynamic process*—that is, with the interaction between the system and its environment as the system changes from one equilibrium state to another.

As we indicated in Section 13-7, in common usage, heat is often confused with temperature or internal energy. When cooking instructions say, "heat at 300 degrees," it is temperature (on the Fahrenheit scale!) that is being discussed. We also may hear someone refer to the "heat generated" in the brake linings of a car as it is braked to a halt. In this case, both the temperature and the internal energy of the brake linings have increased because of frictional work done on them. The rise in temperature of the brake linings did not occur because heat was transferred to the brake linings from some external object at a higher temperature. There is no such object. The only transfer of heat in this case is *from* the high-temperature brake linings *to* their immediate surroundings.

23-2 THE TRANSFER OF HEAT

We know that heat is transferred between a system and its environment when their temperatures differ. However, we have not yet described the mechanisms by which this transfer takes place. There are three of them: thermal conduction, convection, and radiation. We will discuss each in turn.

Thermal Conduction

If you leave a poker in a fire for a long enough time, its handle will become hot. Energy is transferred from the fire to the handle by *thermal conduction* along the metal shaft. In metals—as we shall learn in Chapter 49—some of the atomic electrons are free to move about within the confines of the metallic object and thus are able to pass along increases in their kinetic energy from regions of higher temperature to regions of lower temperature. In this way a region of rising temperature passes along the shaft to your hand.

Consider a thin slab of a homogeneous material of thickness Δx and area A (Fig. 23-2). One face is held at a constant temperature T and the other at a somewhat higher constant temperature $T + \Delta T$, both temperatures being uniform over their respective surfaces. Consider the rate H $(= Q/\Delta t)$ at which heat is transferred through the slab. (The SI unit for H is the joule/second, which is the watt.) Experiment shows that H is (1) directly proportional to A—the more area available, the more heat can be transferred per unit time; (2) inversely proportional to Δx—the thicker

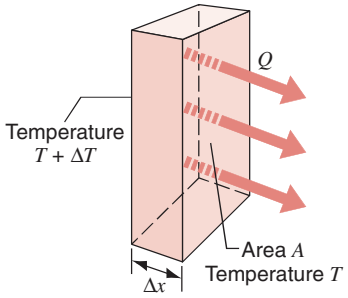

FIGURE 23-2. Heat Q flows through a rectangular slab of material of thickness Δx and area A.

the slab, the less heat will be transferred per unit time; and (3) directly proportional to ΔT—the larger the temperature difference is, the more heat will be transferred.

We can summarize these experimental findings as

$$H = kA\frac{\Delta T}{\Delta x}, \tag{23-1}$$

in which the proportionality constant k is called the *thermal conductivity* of the material. The SI unit of k is the watt per meter kelvin (W/m · K).

Table 23-1 shows some values of k for selected substances. A substance with a large value of k is a good thermal conductor; one with a small value of k is a poor thermal conductor or, equivalently, a good thermal insulator. Figure 23-3 shows a patio in which concrete slabs are separated by fir strips. As Table 23-1 shows, the thermal conductivity of concrete is more than five times that of fir; heat conduction from the (warmer) ground through the concrete

TABLE 23-1 Some Thermal Conductivities and *R*-Values[a]

Material	*Conductivity, k* (W/m · K)	*R-Value* (ft² · F° · h/Btu)
Metals		
Stainless steel	14	0.010
Lead	35	0.0041
Aluminum	235	0.00061
Copper	401	0.00036
Silver	428	0.00034
Gases		
Air (dry)	0.026	5.5
Helium	0.15	0.96
Hydrogen	0.18	0.80
Building materials		
Polyurethane foam	0.024	5.9
Rock wool	0.043	3.3
Fiberglass	0.048	3.0
Fir	0.14	1.0
Concrete	0.80	0.18
Window glass	1.0	0.14

[a] Values are for room temperature. Note that values of k are given in SI units and those of R in the customary British units. The R-values are for a 1-in. slab.

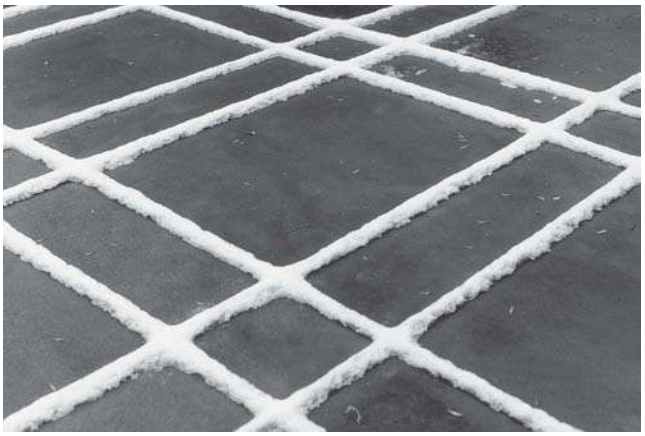

FIGURE 23-3. Snow melts on the concrete, but not on the fir strips between the concrete sections, because concrete is a better thermal conductor than wood.

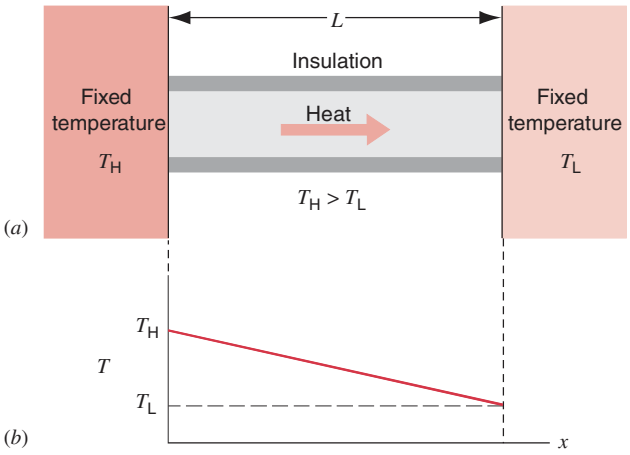

FIGURE 23-4. (*a*) Conduction of heat through an insulated conducting rod. (*b*) The variation of temperature along the rod.

and the fir to the (cooler) air causes the snow above the concrete to melt first.

In choosing building materials, one often finds them rated in terms of the *thermal resistance* or *R*-value, defined by

$$R = \frac{L}{k}, \tag{23-2}$$

where L is the thickness of the material through which the heat is transfered. Thus the lower the conductivity is, the higher is the *R*-value: good insulators have high *R*-values. Numerically, the *R*-value is evaluated according to Eq. 23-2 expressed in the British units of $\text{ft}^2 \cdot \text{F}^\circ \cdot \text{h/Btu}$. The *R*-value is determined for a certain thickness of material. For example, a 1-in. thickness of fiberglass has $R = 3$, whereas a 1-in. thickness of wood has $R = 1$ (and therefore conducts heat at three times the rate of fiberglass). One inch of air has $R = 5$, but air is a poor thermal insulator because it can transfer more heat by convection, and the thermal conductivity is thus not a good measure of the insulating value of air. Table 23-1 shows the *R*-values of one-inch slabs of some materials.

Now let us consider two applications of Eq. 23-1. We first take the case of a long rod of length L and uniform cross section A (Fig. 23-4*a*), in which one end is maintained at the high temperature T_H and the other end at the low temperature T_L.* We call this a *steady state* situation: the temperatures and the rate of heat transfer are constant in time. In this situation, every increment of energy that enters the rod at the hot end leaves it at the cold end. Put another way, through any cross section along the length of the rod, we would measure the same rate of heat transfer.

For this case, we can write Eq. 23-1 as

$$H = kA\frac{T_H - T_L}{L}. \tag{23-3}$$

Here L is the thickness of the material in the direction of heat transfer. The rate of heat flow H is a constant, and the temperature decreases in linear fashion between the ends of the rod (Fig. 23-4*b*).

We now consider the case in which the slab has infinitesimal thickness dx and temperature difference dT between its faces. In this limit, we obtain

$$H = -kA\frac{dT}{dx}. \tag{23-4}$$

The derivative dT/dx is called the *temperature gradient*. We choose the positive direction of the variable x in Eq. 23-4 to be the direction in which heat is transferred. Because heat flows in the direction of *decreasing* temperature, the gradient dT/dx is inherently negative. We introduce a minus sign into Eq. 23-4 to ensure that H, the rate of heat transfer, will be a positive quantity.

Equation 23-4 is particularly applicable in cases where the cross section of the material through which heat is being transferred is not uniform. Sample Problem 23-2 is an illustrative example.

SAMPLE PROBLEM 23-1. Consider a compound slab consisting of two materials having different thicknesses, L_1 and L_2, and different thermal conductivities, k_1 and k_2. If the temperatures of the outer surfaces are T_1 and T_2 (with $T_2 > T_1$), find the rate of heat transfer through the compound slab (Fig. 23-5) in a steady state.

* The ends of the rod can be considered to be immersed in *thermal reservoirs,* which can supply or absorb an unlimited amount of heat while maintaining a constant temperature. A thermal reservoir might be a material of such large quantity or ability to absorb heat that the heat flowing to or from the rod makes a negligible difference in its temperature. Or it might be a mixture of steam and water maintained at the boiling point or ice and water at the melting point, so that the heat absorbed causes a change in phase but no change in temperature. Other possibilities for thermal reservoirs include furnaces or refrigerators in which the heat is ultimately converted to or from mechanical work while keeping the temperature fixed.

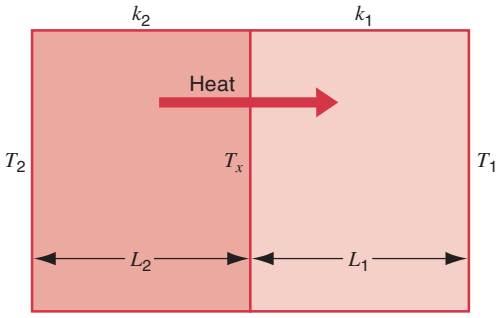

FIGURE 23-5. Sample Problem 23-1. Conduction of heat through two layers of matter with different thermal conductivities.

Solution Let T_x be the temperature at the interface between the two materials. Then the rate of heat transfer through slab 2 is

$$H_2 = \frac{k_2 A(T_2 - T_x)}{L_2}$$

and that through slab 1 is

$$H_1 = \frac{k_1 A(T_x - T_1)}{L_1}.$$

In a steady state $H_2 = H_1$, so that

$$\frac{k_2 A(T_2 - T_x)}{L_2} = \frac{k_1 A(T_x - T_1)}{L_1}.$$

Let H be the rate of heat transfer (the same for all sections). Then, solving for T_x and substituting into either of the equations for H_1 or H_2, we obtain

$$H = \frac{A(T_2 - T_1)}{(L_1/k_1) + (L_2/k_2)} = \frac{A(T_2 - T_1)}{R_1 + R_2}.$$

The extension to any number of sections in series is

$$H = \frac{A(T_2 - T_1)}{\Sigma\,(L_n/k_n)} = \frac{A(T_2 - T_1)}{\Sigma\,R_n}. \qquad (23\text{-}5)$$

SAMPLE PROBLEM 23-2. A thin, cylindrical metal pipe is carrying steam at a temperature of $T_S = 100°C$. The pipe has a diameter of 5.4 cm and is wrapped with a thickness of 5.2 cm of fiberglass insulation. A length $D = 6.2$ m of the pipe passes through a room in which the temperature is $T_R = 11°C$. (*a*) At what rate does heat energy pass through the insulation? (*b*) How much additional insulation must be added to reduce the heat transfer rate by half?

Solution (*a*) Figure 23-6 illustrates the geometry appropriate to the calculation. In the steady state, the rate of heat transfer H will be constant and will be the same for every thin cylindrical shell, such as the one indicated by the dashed lines in Fig. 23-6. We can regard this shell as a slab of material, having a thickness dr and an area of $2\pi rD$. Applying Eq. 23-4 to this geometry, we have

$$H = -kA\frac{dT}{dr} = -k(2\pi rD)\frac{dT}{dr}$$

or

$$H\frac{dr}{r} = -2\pi kD\,dT.$$

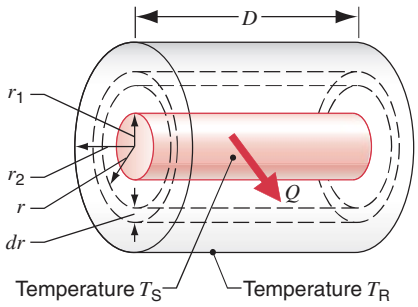

FIGURE 23-6. Sample Problem 23-2. The inner surface (radius r_1) of the insulation on a cylindrical pipe is at the temperature T_S and the outer surface (radius r_2) is at T_R. The same heat Q flows through every cylindrical shell of insulation, such as the intermediate one of thickness dr and radius r shown by the dashed lines.

We assume that the thin metal pipe is at the temperature of the steam, so it does not enter into the calculation. We integrate from the inner radius r_1 of the insulation at temperature T_S to the outer radius r_2 at temperature T_R:

$$\int_{r_1}^{r_2} H\frac{dr}{r} = -2\pi kD\int_{T_S}^{T_R} dT.$$

Removing the constant H from the integral on the left and carrying out the integrations, we obtain

$$H\ln\frac{r_2}{r_1} = -2\pi kD(T_R - T_S) = 2\pi kD(T_S - T_R).$$

Solving for H and inserting the numerical values, we find

$$H = \frac{2\pi kD(T_S - T_R)}{\ln(r_2/r_1)}$$

$$= \frac{2\pi(0.048\ \text{W/m}\cdot\text{K})(6.2\ \text{m})(89\ \text{K})}{\ln(7.9\ \text{cm}/2.7\ \text{cm})} = 155\ \text{W}.$$

Note that, if we had not inserted a minus sign into Eq. 23-4, the algebraic sign of H would not have been positive.

(*b*) To reduce the heat transfer rate by half, we must increase r_2 to the value r_2' such that the denominator in the above expression for H becomes twice as large; that is,

$$\frac{\ln(r_2'/r_1)}{\ln(r_2/r_1)} = 2.$$

Solving for r_2', we find

$$r_2' = \frac{r_2^2}{r_1} = \frac{(7.9\ \text{cm})^2}{2.7\ \text{cm}} = 23\ \text{cm}.$$

Thus we need nearly four times the thickness of insulation to reduce the heat transfer by half! This effect is due to the increase in the area, and therefore in the mass, contained in each thin slab as we increase the radius in the cylindrical geometry. There is more material available to conduct heat at the outer radii, and we must therefore supply an increasing amount of insulation as r grows larger. This differs from the linear geometry, in which the heat transferred decreases linearly as the insulation thickness increases. In the spherical geometry (which might be appropriate to calculating the heat energy transferred from the Earth's core to its surface), the calculation is still different; see Problem 3.

Convection

If you look at the flame of a candle or a match, you are watching heat energy being transported upward by *convection*. Heat transfer by convection occurs when a fluid, such as air or water, is in contact with an object whose temperature is higher than that of its surroundings. The temperature of the fluid that is in contact with the hot object increases, and (in most cases) the fluid expands. The warm fluid is less dense than the surrounding cooler fluid, so it rises because of buoyant forces; see Fig. 23-7. The surrounding cooler fluid falls to take the place of the rising warmer fluid, and a convective circulation is set up.

Atmospheric convection plays a fundamental role in determining the global climate patterns and in our daily weather variations. Glider pilots and condors alike seek the convective thermals that, rising from the warmer Earth beneath, keep them aloft. Huge energy transfers take place within the oceans by the same process. The outer region of the Sun, called the *photosphere,* contains a vast array of convection cells that transport energy to the solar surface and give the surface a granulated appearance. Finally, there are thought to be huge convective cells within the mantle of the Earth, their outermost surfaces being the tectonic plates whose motions move the continents.

We have so far been describing *free* or *natural* convection. Convection can also be forced, as when a furnace blower causes air circulation to heat the rooms of a house.

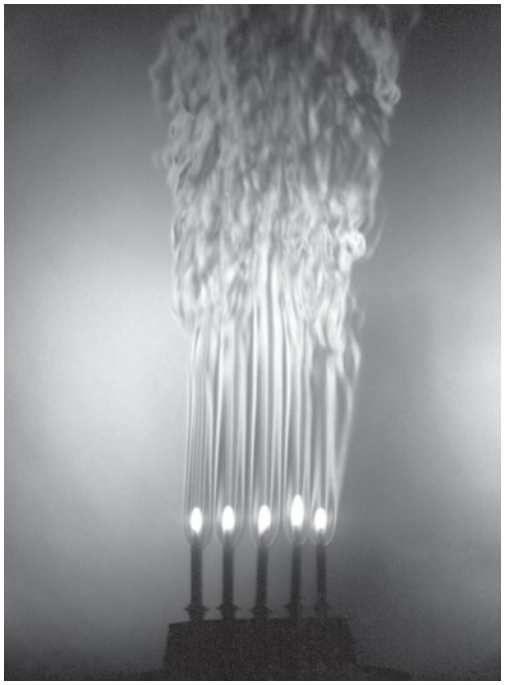

FIGURE 23-7. Air rises by convection around a heated cylinder. The dark areas represent regions of uniform temperature.

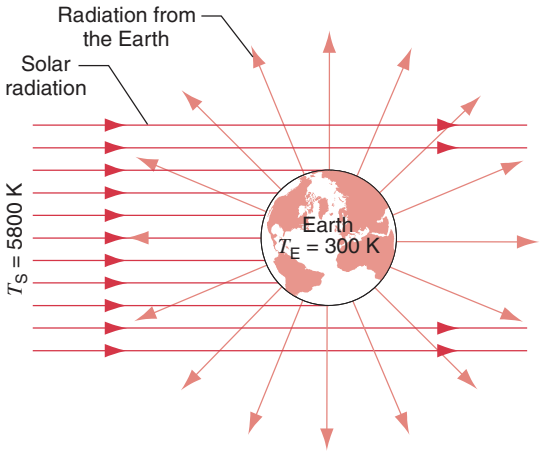

FIGURE 23-8. Solar radiation is intercepted by the Earth and is (mostly) absorbed. The temperature T_E of the Earth adjusts itself to a value at which the Earth's heat loss by radiation is just equal to the solar heat that it absorbs.

Radiation

Energy is carried from the Sun to us by electromagnetic waves that travel freely through the near vacuum of the intervening space. If you stand near a bonfire or an open fireplace, you are warmed by the same process. All objects emit such electromagnetic radiation because of their temperature and also absorb some of the radiation that falls on them from other objects. The higher the temperature of an object is, the more it radiates. We shall see in Chapter 45 of this text that the energy radiated by an object is proportional to the fourth power of its (Kelvin) temperature. The average temperature of our Earth, for example, levels off at about 300 K because at that temperature the Earth radiates energy into space at the same rate that it receives it from the Sun; see Fig. 23-8.

23-3 THE FIRST LAW OF THERMODYNAMICS

In Chapter 13 we discussed the fundamental concept of conservation of energy in a system of particles. As we did in the case of conservation of momentum in Chapter 7, we concentrated our attention on a particular collection of particles or objects that we defined as our *system.* We drew an imaginary boundary that separated the system from its *environment,* and then we carefully accounted for all interactions between the system and its environment. Sometimes, as in the case of momentum conservation, we characterize those interactions in terms of forces. Other times it is more convenient to characterize those interactions in terms of energy transfer.

We are free to define our system in any convenient way, as long as we are consistent and can account for all energy transfers to or from the system. For example, we might de-

fine the system to be a block of metal that is at a lower temperature than its environment, so that the interaction involves a transfer of heat from the environment to the block. Or we might define a system to be water and ice that are mixed together in an insulated container. In this case there is an exchange of energy *within* the system but no interaction with the environment.

For a thermodynamic system, in which internal energy is the only type of energy the system may have, the law of conservation of energy may be expressed as

$$Q + W = \Delta E_{\text{int}}. \tag{23-6}$$

In this section we examine this equation, which is a statement of the *first law of thermodynamics*. In this equation:

Q is the energy transferred (as heat) between the system and its environment because of a temperature difference between them. A heat transfer that occurs entirely within the system boundary is not included in Q.

W is the work done on (or by) the system by forces that act through the system boundary. Work done by forces that act entirely within the system boundary is not included in W.

ΔE_{int} is the change in the internal energy of the system that occurs when energy is transferred into or out of the system as heat or work.

By convention we have chosen Q to be positive when heat is transferred *into* the system and W to be positive when work is done *on* the system. With these choices, positive values of Q and W each serve to *increase* the internal energy of the system.*

Equation 23-6 is a restricted form of the general law of conservation of energy. For example, the system as a whole may be in motion in our frame of reference. That is, there may be kinetic energy associated with the motion of the center of mass of the system. If that were the case, we would have to add a term ΔK_{cm} to the right side of Eq. 23-6. However, in the systems we discuss the center of mass of the system will always be at rest in our reference frame so that no such term is needed.

Figure 23-9 suggests how Eq. 23-6 is to be applied. The system starts in an *initial equilibrium state* i in Fig. 23-9*a*, in which the properties of the system, such as its internal energy E_{int}, have definite constant values. We then permit the system to undergo a *thermodynamic process*—that is, to interact with its environment as in Fig. 23-9*b*—during which work may be done and/or heat energy exchanged. When the process is concluded, the system ends up in a *final equilibrium state* f, in which the properties of the system will, in general, have different constant values.

There are many processes by which we can take a system from a specified initial state to a specified final state. In general, the values of Q and W will differ, depending on the process we choose. However, experiment shows that, although Q and W may differ individually, their sum $Q + W$ is the same for all processes that connect the given initial and final states. As Eq. 23-6 suggests, this is the experimental basis for regarding the internal energy E_{int} as a true *state function*—that is, as just as much an inherent property of a system as pressure, temperature, and volume. To stress this point of view, we can express the first law of thermodynamics formally in these words:

In any thermodynamic process between equilibrium states i *and* f, *the quantity* $Q + W$ *has the same value for any path between* i *and* f. *This quantity is equal to the change in value of a state function called the internal energy* E_{int}.

The first law of thermodynamics is a general result that is thought to apply to every process in nature that proceeds between equilibrium states. It is not necessary that every stage of the process be an equilibrium state, only the initial and the final states. For example, we can apply the first law to the explosion of a firecracker in an insulated steel drum. We can account for the energy balance before the explosion and after the system has returned to equilibrium, and for this calculation we need not worry that the intermediate condition is turbulent and that pressure and temperature are not well defined.

Because of its generality, the first law is somewhat incomplete as a description of nature. It tells us that energy must be conserved in every process, but it does not tell us whether any particular process that conserves energy can

* Some authors define work done *by* the system to be positive, in which case the first law would be written $Q - W = \Delta E_{\text{int}}$. We have chosen to define work done *on* the system to be positive, so that thermodynamic work will have the same sign convention that we used in earlier chapters for mechanical work.

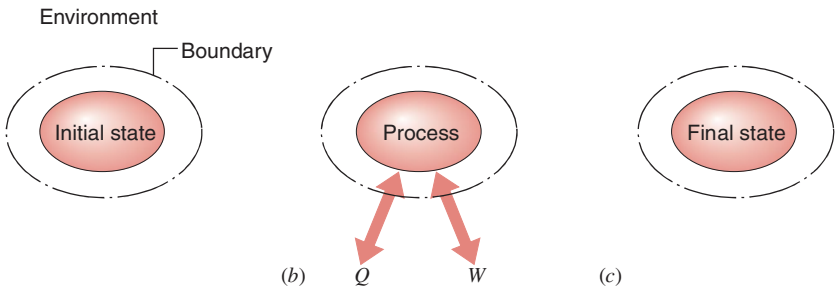

FIGURE 23-9. (*a*) A system in an initial state in equilibrium with its surroundings. (*b*) A thermodynamic process during which the system may exchange heat Q or work W with its environment. (*c*) A final equilibrium state reached as a result of the process.

actually occur. The explosion of a firecracker, for example, releases chemical energy stored in the gunpowder that eventually raises the temperature of the gas in the drum. We can imagine the hot gas giving its thermal energy back to the combustion products, turning them once again into gunpowder and reassembling the firecracker, but this never happens. Conservation of energy works either way but nature seems to go in a preferred direction. The *second* law of thermodynamics, which we discuss in Chapter 24, accounts for this distinction.

In thermal physics as in mechanics, you must be quite clear as to the system to which you are applying fundamental laws such as Eq. 23-6. Figure 23-10, for example, shows a heating coil immersed in water contained in an insulated bucket. The current through the coil is supplied by an (ideal) generator that is driven by a weight that falls with constant speed. Let us see what values of Q, W, and ΔE_{int} result for different arbitrary choices of what we choose to call our system:

1. *System = water alone.* Heat is delivered to the water from the coil so that $Q > 0$. No work is done because the water does not move under the influence of any external force that acts on it. Thus $W = 0$. From the first law, then (Eq. 23-6) $\Delta E_{int} > 0$. The heat delivered to the water causes its internal energy, and thus its temperature, to rise.

2. *System = coil + weight.* As long as the weight is falling at a constant rate the coil maintains a constant temperature. Thus the system is in a steady state, with no energy transfers occurring within the system boundary. Thus $\Delta E_{int} = 0$. Heat energy is transferred from coil to water out of this system, so that $Q < 0$. Work is done by the (external) gravitational force so that $W > 0$. The system acts as a conduit for energy, the work done by the gravitational force being delivered as heat energy to the water.

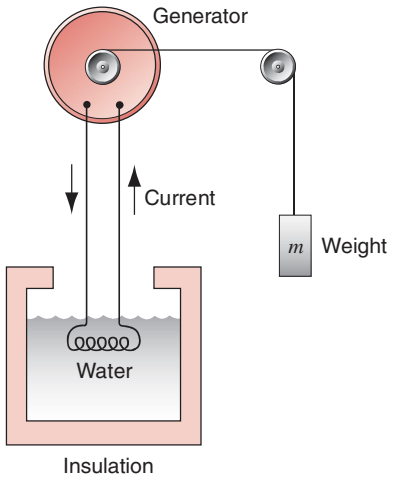

FIGURE 23-10. A heating coil is immersed in water, the electric current through the coil being provided by an (ideal) generator that is driven by a falling weight. Values of Q, W, and ΔE_{int} in Eq. 23-6 depend critically on what parts of this arrangement we choose to define as the "system."

3. *System = coil + weight + water.* Here the gravitational force does work on this system so that $W > 0$. The insulation of the bucket prevents heat transfer to the environment so that $Q = 0$. From Eq. 23-6 then, $\Delta E_{int} > 0$. Again, work done by an external force produces an increase in the internal energy, and thus the temperature, of the system.

4. *System = coil + weight + water + Earth.* In this case the gravitational force is internal to the system so that $W = 0$. Also, $Q = 0$, as for system choice 3 above. From Eq. 23-6 then, we must have $\Delta E_{int} = 0$. The internal energy of part of the system rises because of the rise in temperature of the water. However, the internal energy of another part of the system falls—and by the same amount—because the falling weight and the Earth move closer together, thus reducing their potential energy.

The lesson to learn from this analysis is to define your system carefully and stay with that definition throughout your analysis.

23-4 HEAT CAPACITY AND SPECIFIC HEAT

We can change the state of a body by transferring energy to or from it in the form of heat, or by doing work on the body. One property of a body that may change in such a process is its temperature T. The change in temperature ΔT that corresponds to the transfer of a particular quantity of heat energy Q will depend on the circumstances under which the heat was transferred. For example, in the case of a gas confined to a cylinder with a movable piston, we can add heat and keep the piston fixed (thus keeping the volume constant), or we can add heat and allow the piston to move but keep the force on the piston constant (thus keeping the gas under constant pressure). We can even change the temperature by doing work on a system, such as by rubbing together two objects that exert frictional forces on one another; in this case, no heat transfer need occur.

It is convenient to define the *heat capacity* C of a body as the ratio of the amount of heat energy Q transferred to a body in any process to its corresponding temperature change ΔT; that is,

$$C = \frac{Q}{\Delta T}. \tag{23-7}$$

The word "capacity" may be misleading because it suggests the essentially meaningless statement "the amount of heat a body can hold," whereas what is meant is simply the energy per degree of temperature change that is transferred as heat when the temperature of the body changes.

The heat capacity per unit mass of a body, called *specific heat capacity* or usually just *specific heat,* is characteristic of the material of which the body is composed:

$$c = \frac{C}{m} = \frac{Q}{m\,\Delta T}. \tag{23-8}$$

The heat capacity is characteristic of a particular object, but the specific heat characterizes a substance. Thus we speak, on one hand, of the heat capacity of a copper pot but, on the other, of the specific heat of copper.

Neither the heat capacity of a body nor the specific heat of a material is constant; both depend on the temperature (and possibly on other variables as well, such as the pressure). The previous equations give only average values for these quantities in the temperature range of ΔT. In the limit, as $\Delta T \rightarrow 0$, we can speak of the specific heat at a particular temperature T.

We can find the heat that must be given to a body of mass m, whose material has a specific heat c, to increase its temperature from initial temperature T_i to final temperature T_f by dividing the temperature change into N small intervals ΔT_n, assuming that c_n is constant in each small interval, and summing the contributions to the total heat transfer from all intervals $n = 1, 2, \ldots, N$. This gives

$$Q = \sum_{n=1}^{N} mc_n \Delta T_n. \tag{23-9}$$

In the differential limit this becomes

$$Q = m \int_{T_i}^{T_f} c\, dT, \tag{23-10}$$

where c may be a function of the temperature. At ordinary temperatures and over ordinary temperature intervals, specific heats can be considered to be constants. For example, the specific heat of water varies by less than 1% over the interval from 0°C to 100°C. We can therefore write Eq. 23-10 in the more generally useful form

$$Q = mc(T_f - T_i). \tag{23-11}$$

TABLE 23-2 Heat Capacities of Some Substances[a]

Substance	*Specific Heat Capacity* (J/kg·K)	*Molar Heat Capacity* (J/mol·K)
Elemental solids		
Lead	129	26.7
Tungsten	135	24.8
Silver	236	25.5
Copper	387	24.6
Carbon	502	6.02
Aluminum	900	24.3
Other solids		
Brass	380	
Granite	790	
Glass	840	
Ice (−10°C)	2220	
Liquids		
Mercury	139	
Ethyl alcohol	2430	
Seawater	3900	
Water	4190	

[a] Measured at room temperature and atmospheric pressure, except where noted.

Equation 23-8 does not define specific heat uniquely. We must also specify the conditions under which the heat Q is added to the material. One common condition is that the specimen remain at normal (constant) atmospheric pressure while we add the heat, but there are many other possibilities, each leading, in general, to a different value for c. To obtain a unique value for c we must indicate the conditions, such as specific heat at constant pressure c_p, specific heat at constant volume c_V, and so on.

Table 23-2 shows values for the specific heat capacities of a number of common substances, measured under conditions of constant pressure. Although the units are expressed in terms of K, we can also work with temperatures in °C, because a temperature *difference* in C° is equal to the same temperature difference in K.

SAMPLE PROBLEM 23-3. A cube of copper of mass $m_c = 75$ g is placed in an oven at a temperature of $T_0 = 312$°C until it comes to thermal equilibrium. The cube is then dropped quickly into an insulated beaker containing a quantity of water of mass $m_w = 220$ g. The heat capacity of the beaker alone is $C_b = 190$ J/K. Initially the water and the beaker are at a temperature of $T_i = 12.0$°C. What is the final equilibrium temperature T_f of the system consisting of the copper + water + beaker?

Solution Once the copper cube has been dropped into the beaker, no energy enters or leaves the system copper + water + beaker, either as heat or as work, so that there is no change in the internal energy of this system. However, there are changes in the internal energies of the three objects—which we now regard as subsystems—that make up the system. These three internal energy changes must add up to zero, or

$$\Delta E_{\text{int, c}} + \Delta E_{\text{int, w}} + \Delta E_{\text{int, b}} = 0.$$

However, $W = 0$ for each object (because no work is done on any object) so that, from Eq. 23-6, we must have

$$Q_c + Q_w + Q_b = 0. \tag{23-12}$$

From Eqs. 23-7 and 23-11, the heat transfers for these subsystems are:

$$\begin{aligned} \text{Copper:} \quad & Q_c = m_c c_c (T_f - T_0) \\ \text{Water:} \quad & Q_w = m_w c_w (T_f - T_i) \\ \text{Beaker:} \quad & Q_b = C_b (T_f - T_i) \end{aligned}$$

Note that we have written the temperature differences as the final temperature minus the initial temperature, so that Q_w and Q_b are positive (indicating that heat energy is transferred *into* the water and beaker subsystems, thus increasing their internal energies) and Q_c is negative (indicating that heat energy is transferred *from* this subsystem, corresponding to a decrease in its internal energy). Substituting these heat transfers into Eq. 23-12 above, we obtain

$$m_w c_w (T_f - T_i) + C_b (T_f - T_i) + m_c c_c (T_f - T_0) = 0.$$

Solving for T_f and substituting, we have

$$T_f = \frac{m_w c_w T_i + C_b T_i + m_c c_c T_0}{m_w c_w + C_b + m_c c_c}$$

$$= \frac{(0.220\text{ kg})(4190\text{ J/kg·K})(12°\text{C}) + (190\text{ J/K})(12°\text{C}) + (0.075\text{ kg})(387\text{ J/kg·K})(312°\text{C})}{(0.220\text{ kg})(4190\text{ J/kg·K}) + 190\text{ J/K} + (0.075\text{ kg})(387\text{ J/kg·K})}$$

$$= 19.6°\text{C}.$$

Note that, because all temperatures were part of temperature *differences,* we can use °C in this expression. In most thermodynamic expressions, however, only Kelvin temperatures can be used.

From the given data you can show that

$$Q_w = 7010\ \text{J}, \quad Q_b = 1440\ \text{J}, \quad \text{and} \quad Q_c = -8450\ \text{J}.$$

The algebraic sum of these three heat transfers is indeed zero, as Eq. 23-12 requires.

Heats of Transformation

When heat enters a solid or a liquid, the temperature of the sample does not necessarily rise. Instead, the sample may change from one *phase* or *state* (that is, solid, liquid, or gas) to another. Thus ice melts and water boils, absorbing heat in each case without a temperature change. In the reverse processes (water freezes, steam condenses), heat is released by the sample, again at a constant temperature.

The amount of heat per unit mass that must be transferred to produce a phase change is called the *heat of transformation* or *latent heat* (symbol L) for the process. The total heat transferred in a phase change is then

$$Q = Lm, \tag{23-13}$$

where m is the mass of the sample that changes phase. The heat transferred during melting or freezing is called the *heat of fusion* (symbol L_f), and the heat transferred during boiling or condensing is called the *heat of vaporization* (symbol L_v). Table 23-3 shows the heats of transformation of some substances.

Knowledge of heat capacities and heats of transformation is important because we can measure a heat transfer by determining either the temperature change of a material of known heat capacity or the amount of a substance of known heat of transformation converted from one phase to another. For example, in low-temperature systems involving liquid helium at 4 K, the rate at which helium gas boils from the liquid gives a measure of the rate at which heat enters the system.

TABLE 23-3 Some Heats of Transformation

Substance[a]	*Melting Point* (K)	*Heat of Fusion* (kJ/kg)	*Boiling Point* (K)	*Heat of Vaporization* (kJ/kg)
Hydrogen	14.0	58.6	20.3	452
Oxygen	54.8	13.8	90.2	213
Mercury	234	11.3	630	296
Water	273	333	373	2256
Lead	601	24.7	2013	858
Silver	1235	105	2485	2336
Copper	1356	205	2840	4730

[a] Substances are listed in order of increasing melting points.

Heat Capacities of Solids

Recall that the *specific heat capacity* of any material (SI unit: J/kg · K) is the heat capacity per unit mass. In Table 23-2 we see that the values of this quantity vary widely from one solid material to another. If we multiply the specific heat capacity by the molar mass M we obtain the *molar heat capacity* (SI unit: J/mol · K) or the heat capacity per mole. Table 23-2 shows that, with few exceptions (see carbon) the molar heat capacities of all solids have values close to 25 J/mol · K. This remarkable experimental observation was first pointed out in 1819 by the French scientists P. L. Dulong (1785–1838) and A. T. Petit (1791–1820).

In comparing molar heat capacities, we are, in effect, comparing samples that contain the same number of moles rather than samples that have the same mass. Samples with the same number of moles have the same number of atoms, and we conclude that the heat energy required *per atom* to raise the temperature of a solid by a given amount seems—with a few exceptions—to be about the same for all solids. This is striking evidence for the atomic theory of matter.

Actually, molar heat capacities vary with temperature, approaching zero as $T \to 0$ and approaching the so-called Dulong–Petit value only at relatively high temperatures. Figure 23-11 shows the variation for lead, aluminum, and carbon. The low value of the molar heat capacity for carbon listed in Table 23-2 occurs because, at room temperature, carbon has not yet achieved its limiting value.*

* The data plotted in Fig. 23-11 are the molar heat capacities at constant volume. It is almost impossible to keep a solid from expanding as you increase its temperature so the direct measurements of molar heat capacity are made under conditions of constant pressure. The constant-volume values plotted in the figure are found by making a small theory-based correction to the measured constant-pressure values.

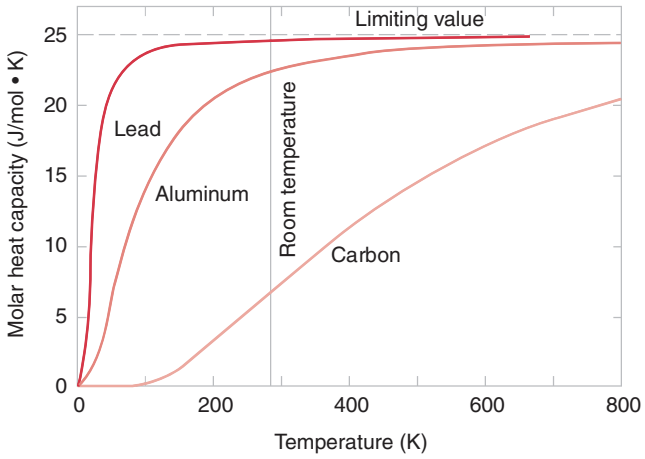

FIGURE 23-11. The molar heat capacity of three elements as a function of temperature. At high temperatures, the heat capacities of all solids approach the same limiting value. For lead and aluminum, that value is nearly reached at room temperature; for carbon it is not.

We will learn in Section 23-6 that the Dulong–Petit high-temperature limit for the molar heat capacity can be understood on the basis of classical physics. However, to understand the complete temperature variation of the molar heat capacity requires an analysis based on quantum physics. Einstein was quick to realize that measurements of the molar heat capacity provide a sensitive probe of the manner in which atoms absorb energy—a matter of deep significance. Understanding the temperature variation of the molar heat capacities of solids was the first problem to which Einstein turned his attention after the introduction of quantum theory, and he provided a preliminary but insightful solution in 1906.*

The data plotted in Fig. 23-11 vary smoothly and characterize materials that do not change their state in that temperature range. That is, they do not melt or change from one crystal structure to another. Measurements of heat capacity are useful in studying such changes. For example, Fig. 23-12*a* shows the variation of the molar heat capacity of tantalum for temperatures in the range 3–5.5 K. It seems likely that something is happening to tantalum at $T = 4.4$ K and indeed it is. Above that temperature, tantalum conducts electricity in the same way that copper and other familiar electrical conductors do. Below that temperature, however, the electrical resistance of tantalum completely disappears; it becomes a so-called *superconductor.*

For another example, Fig. 23-12*b* shows the specific heat capacity of brass in the range 300–600°C. X-ray analysis shows that a change in the crystal structure of brass occurs at about 460°C, from a very ordered structure below that temperature to a rather disordered structure above it.

* Details of Einstein's calculation can be found in *Modern Physics,* by Kenneth S. Krane (Wiley, 1996), Chapter 10.

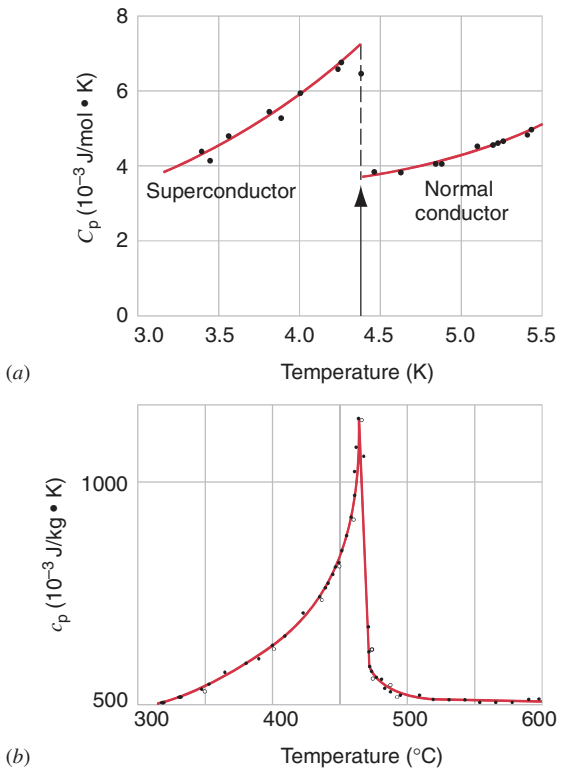

FIGURE 23-12. (*a*) The molar heat capacity of tantalum near its superconducting transition temperature. (*b*) The specific heat capacity of brass.

23-5 WORK DONE ON OR BY AN IDEAL GAS

So far in this chapter we have explored energy transfers as heat in relation to the first law of thermodynamics. In this section we explore energy transfers as work and—as we have done before—we choose the ideal gas as our thermodynamic system of interest. The stylized apparatus of Fig. 21-13 suggests how work might be done either on an ideal gas or by it under various conditions.

If we increase the temperature of the gas in the cylinder of Fig. 21-13, the gas expands and raises the piston against gravity; the gas does (positive) work on the piston. The upward force exerted on the piston by the gas due to its pressure p is given by pA, where A is the area of the piston. By Newton's third law, the force exerted *on* the gas *by* the piston is equal and opposite to the force exerted *on* the piston *by* the gas. Using Eq. 11-14, we can therefore write the work W done on the gas as

$$W = \int F_x\,dx = \int (-pA)dx. \qquad (23\text{-}14)$$

Here dx represents the displacement of the piston, and the minus sign enters because the force exerted on the gas by the piston is in a direction opposite to the displacement of the piston. If we *reduce* the temperature of the gas, it contracts instead of expanding; the work done on the gas in that case is positive. We assume that the process described by Eq. 23-14 is carried out slowly, so that the gas can be considered to be in thermal equilibrium at all intermediate stages. Otherwise, the pressure would not be clearly defined during the process, and the integral in Eq. 23-14 could not easily be evaluated.

We can write Eq. 23-14 in a more general form that turns out to be very useful. If the piston moves through a distance dx, then the volume of the gas changes by an amount $dV = A\,dx$. Thus the work done on the gas is

$$W = -\int p\,dV. \qquad (23\text{-}15)$$

The integral is carried out between the initial volume V_i and the final volume V_f.

Equation 23-15 is the most general result for the work done on a gas. It makes no reference to the outside agent that does the work; it states simply that the work done on the gas can be calculated from the pressure and the change in volume of the gas itself. Note that the algebraic sign of the work is implicitly contained in Eq. 23-15; if the gas expands, dV is

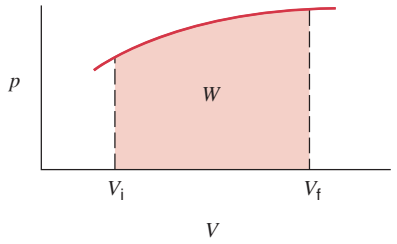

FIGURE 23-13. The magnitude of the work W done on a gas by a process of arbitrarily varying pressure is equal to the area under the pressure curve on a pV diagram between the initial volume V_i and the final volume V_f.

positive and W is negative, p being a scalar quantity having only positive values. Conversely, if the gas is compressed, dV is negative and the work done on the gas is positive.

Equation 23-15 is analogous to the general result for the work done on a system by a variable force F. You will recall from Fig. 11-12 that if we plot F against x, the work done by F is simply the area under the curve between x_i and x_f. Figure 23-13 shows the similar situation for the work done on the gas. A graph in the form of Fig. 23-13 is called a *pV diagram,* with p plotted on the vertical axis (like F) and V plotted on the horizontal axis (like x). *The magnitude of the work done on the gas is equal to the area under the curve representing the process on a pV diagram.* The sign of W is determined according to whether $V_f > V_i$ (in which case W is negative, as in Fig. 23-13), or $V_f < V_i$ (in which case W is positive). Once again, the work done *on* the gas is negative if the process increases the volume of the gas and positive if the process reduces the volume of the gas.

The pressure force is clearly nonconservative, as Fig. 23-14 demonstrates. Let us suppose we wish to take our ideal gas from the initial conditions V_i and p_i (point A) to the final conditions V_f and p_f (point D). There are many different paths we can take between A and D, of which two are shown in Fig. 23-14. Along path 1 (ABD), we first increase the pressure from p_i to p_f at constant volume. (We might accomplish this by turning up the control knob on the thermal reservoir, increasing the temperature of the gas, while we simultaneously add just the right amount of additional weight to the piston to keep it from moving.) We then follow path BD by increasing the temperature but adding no additional weight to the piston, so that the pressure remains constant at the value p_f while the volume increases from V_i to V_f. The work done in this entire procedure is the area of the rectangle $BDFE$ (the area below the line BD).

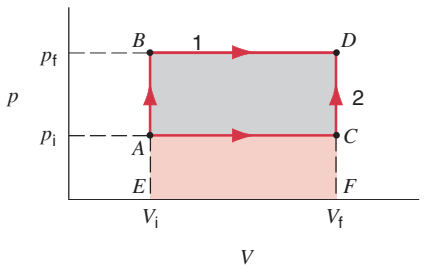

FIGURE 23-14. A gas is taken from the pressure and volume at point A to the pressure and volume at point D along two different paths, ABD and ACD. Along path 1 (ABD) the work is equal to the area of the rectangle $BDFE$, whereas along path 2 (ACD) the work is equal to the area of the rectangle $ACFE$.

We can find W_1, the work done on the gas along path 1, by considering the work done along the two segments AB and BD:

$$W_1 = W_{AB} + W_{BD}.$$

Because the volume is constant along AB, it follows from Eq. 23-15 that $W_{AB} = 0$. Along BD, the pressure is constant (at the value p_f) and comes out of the integral. The result is

$$W_1 = W_{AB} + W_{BD} = 0 - \int p\,dV = -p_f \int_{V_i}^{V_f} dV = -p_f(V_f - V_i).$$

To follow path 2 (ACD), we first increase the temperature while holding the pressure constant at p_i (that is, adding no additional weight to the piston), so that the volume increases from V_i to V_f. We then increase the pressure from p_i to p_f at the constant volume V_f by increasing the temperature and adding weight to the piston to keep it from moving. The work done in this case is the area under the line AC or the rectangle $ACFE$. We can compute this as

$$W_2 = W_{AC} + W_{CD} = -\int p\,dV + 0 = -p_i \int_{V_i}^{V_f} dV = -p_i(V_f - V_i).$$

Clearly $W_1 \neq W_2$, and the work depends on the path.

We can perform a variety of operations on the gas and evaluate the work done in each case.

Work Done at Constant Volume

The work is zero for any process in which the volume remains constant (as in segments AB and CD in Fig. 23-14):

$$W = 0 \qquad \text{(constant } V\text{)}. \qquad (23\text{-}16)$$

We deduce directly from Eq. 23-15 that $W = 0$ if V is constant. Note that it is not sufficient that the process start and end with the same volume; the volume must be constant throughout the process for the work to vanish. For example, consider process $ACDB$ in Fig. 23-14. The volume starts and ends at V_i, but the work is certainly not zero. The work is zero only for vertical paths such as AB, representing a process at constant volume.

Work Done at Constant Pressure

Here we can easily apply Eq. 23-15, because the constant p comes out of the integral:

$$W = -p \int dV = -p(V_f - V_i) \qquad \text{(constant } p\text{)}. \qquad (23\text{-}17)$$

Examples are the segments *AC* and *BD* in Fig. 23-14. Note that the work done on the gas is negative for both of these segments, because the volume increases in both processes.

Work Done at Constant Temperature

In the gas expands or contracts at constant temperature, the relationship between p and V, given by the ideal gas law ($pV = nRT$), is

$$pV = \text{constant}.$$

On a pV diagram, the plot of the equation $pV =$ constant is exactly like a plot of the equation $xy =$ constant on an xy coordinate system: it is a hyperbola, as shown in Fig. 23-15.

A process done at constant temperature is called an *isothermal* process, and the corresponding hyperbolic curve on the pV diagram is called an *isotherm.* To find the work done on a gas during an isothermal process, we use Eq. 23-15, but we must find a way of carrying out the integral when p varies. To do this we use the ideal gas equation of state to write $p = nRT/V$, and thus

$$W = -\int_{V_i}^{V_f} p\,dV = -\int_{V_i}^{V_f} \frac{nRT}{V}\,dV = -nRT\int_{V_i}^{V_f} \frac{dV}{V},$$

where the last step can be made because we are taking T to be a constant. Carrying out the integral, we find

$$W = -nRT \ln \frac{V_f}{V_i} \qquad \text{(constant } T\text{)}. \qquad (23\text{-}18)$$

Note that this is also negative whenever $V_f > V_i$ ($\ln x$ is positive for $x > 1$) and positive whenever $V_f < V_i$.

Work Done in Thermal Isolation

Let us remove the gas cylinder in Fig. 21-13 from contact with the thermal reservoir and rest it on a slab of insulating material. The gas will then be in complete thermal isolation from its surroundings; if we do work on it, its temperature will change, in contrast to its behavior when it was in contact with the thermal reservoir. A process carried out in thermal isolation is called an *adiabatic* process.

If we allow the gas to change its volume with no other constraints, we state—and we will derive it in Section 23-8—that the path it will follow is represented on a pV diagram by the parabola-like curve

$$pV^\gamma = \text{constant}, \qquad (23\text{-}19)$$

as shown in Fig. 23-16. The dimensionless parameter γ, called the *ratio of specific heats,* must be determined by experiment for any particular gas. Its values are typically in the range 1.1–1.8. Because γ is greater than 1, the curve $pV^\gamma =$ constant is a bit steeper than the curve $pV =$ constant at any point at which they intersect. As Fig. 23-16 shows, this means that the work done by the gas in expanding adiabatically from V_i to V_f will be somewhat smaller in magnitude than the work done in expanding isothermally between these same two volumes.

We can find the "constant" in Eq. 23-19 if we know γ and also the pressure and volume at any particular point on the curve. If we choose the initial point p_i, V_i in Fig. 23-16, the "constant" has the value $p_i V_i^\gamma$ and we can write Eq. 23-19 as

$$pV^\gamma = p_i V_i^\gamma$$

or

$$p = \frac{p_i V_i^\gamma}{V^\gamma}. \qquad (23\text{-}20)$$

We can now find the adiabatic work:

$$W = -\int_{V_i}^{V_f} p\,dV$$

$$= -\int_{V_i}^{V_f} \frac{p_i V_i^\gamma}{V^\gamma}\,dV = -p_i V_i^\gamma \int_{V_i}^{V_f} \frac{dV}{V^\gamma}$$

$$= -\frac{p_i V_i^\gamma}{\gamma - 1}\left(V_i^{1-\gamma} - V_f^{1-\gamma}\right).$$

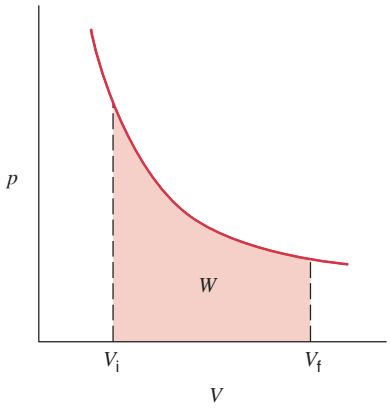

FIGURE 23-15. A process done at constant temperature (isothermal process) is represented by a hyperbola on a pV diagram. The work done in changing the volume is equal to the area under the curve between V_i and V_f.

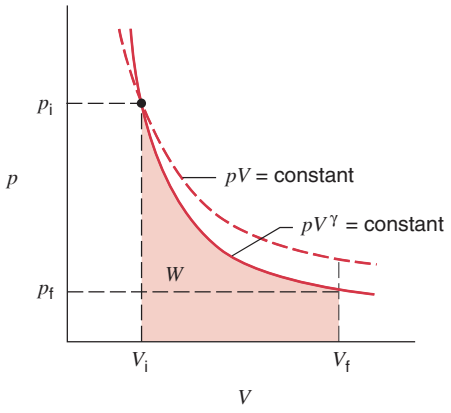

FIGURE 23-16. An adiabatic process is represented on a pV diagram by the hyperbola-like curve $pV^\gamma =$ constant. The work done in changing the volume is equal to the area under the curve between V_i and V_f. Because $\gamma > 1$, the adiabatic curve has a steeper negative slope than the isothermal curve $pV =$ constant.

By bringing a factor of $V_i^{\gamma-1}$ inside the parentheses, we can write the adiabatic work in the form

$$W = \frac{p_i V_i}{\gamma - 1}\left[\left(\frac{V_i}{V_f}\right)^{\gamma-1} - 1\right]. \qquad (23\text{-}21)$$

If the gas expands, then $V_i/V_f < 1$, and since a number less than 1 raised to any positive power remains less than one, the work is again shown to be negative. By further using $p_i V_i^{\gamma} = p_f V_f^{\gamma}$, we can also write the adiabatic work in equivalent form as

$$W = \frac{1}{\gamma - 1}(p_f V_f - p_i V_i) \qquad \text{(adiabatic)}. \quad (23\text{-}22)$$

SAMPLE PROBLEM 23-4. A sample of gas consisting of 0.11 mol is compressed from a volume of 4.0 m^3 to 1.0 m^3 while its pressure increases from 10 to 40 Pa. Compare the work done along the three different paths shown in Fig. 23-17.

Solution Path 1 consists of two processes, one at constant pressure followed by another at constant volume. The work done at constant pressure is found from Eq. 23-17,

$$W = -p(V_f - V_i) = -(10\text{ Pa})(1.0\text{ m}^3 - 4.0\text{ m}^3) = 30\text{ J}.$$

The work done at constant volume is zero (see Eq. 23-16), so the total work for path 1 is

$$W_1 = 30\text{ J} + 0 = 30\text{ J}.$$

Path 2 represents an isothermal process, along which T = constant. Thus $p_i V_i = p_f V_f = nRT$. The work done during the isothermal process can be found using Eq. 23-18, substituting $p_i V_i$ for nRT, which gives

$$W_2 = -p_i V_i \ln\frac{V_f}{V_i} = -(10\text{ Pa})(4.0\text{ m}^3)\ln\frac{1.0\text{ m}^3}{4.0\text{ m}^3} = 55\text{ J}.$$

Path 3 consists of a process at constant volume, for which the work is again zero, followed by a process at constant pressure, and so the total work for path 3 is

$$W_3 = 0 - p_f(V_f - V_i) = -(40\text{ Pa})(1.0\text{ m}^3 - 4.0\text{ m}^3) = 120\text{ J}.$$

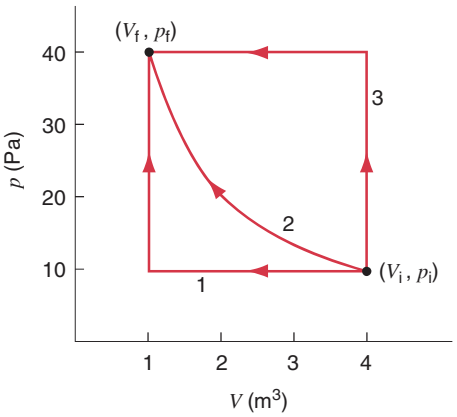

FIGURE 23-17. Sample Problem 23-4. A gas is taken from initial point i to final point f along three different paths. Path 2 is an isotherm.

Note that the work is positive for all three processes, and that the magnitudes increase according to the area under each path on the pV diagram.

SAMPLE PROBLEM 23-5. (*a*) Find the bulk modulus B for an adiabatic process involving an ideal gas. (*b*) Use the adiabatic bulk modulus to find the speed of sound in the gas as a function of temperature. Evaluate for air at room temperature (20°C).

Solution (*a*) In the differential limit, the bulk modulus (see Eq. 15-5) can be written

$$B = -V\frac{dp}{dV}.$$

For an adiabatic process, Eq. 23-19 (pV^{γ} = constant) gives, taking the derivative with respect to V,

$$\frac{d(pV^{\gamma})}{dV} = \left(\frac{dp}{dV}\right)V^{\gamma} + p(\gamma V^{\gamma-1}) = 0,$$

or

$$V\frac{dp}{dV} = -\gamma p.$$

Thus

$$B = \gamma p$$

for an adiabatic process involving an ideal gas.

(*b*) In Section 19-3, we determined that the speed of sound in a gas can be written

$$v = \sqrt{B/\rho},$$

where B is the bulk modulus and ρ is the density of the gas. Using the result of part (*a*) and the ideal gas equation of state ($pV = nRT$), we obtain

$$v = \sqrt{\frac{\gamma p}{\rho}} = \sqrt{\frac{\gamma(nRT/V)}{\rho}} = \sqrt{\frac{\gamma nRT}{\rho V}}.$$

The quantity ρV is the total mass of the gas, which can also be written nM, where n is the number of moles and M is the molar mass. Making this substitution, we have

$$v = \sqrt{\frac{\gamma RT}{M}}.$$

Thus the speed of sound in a gas depends on the square root of the temperature. For air, the average molar mass is about 0.0290 kg/mol, and the parameter γ is about 1.4. Thus for T = 20°C = 293 K,

$$v = \sqrt{\frac{(1.4)(8.31\text{ J/mol}\cdot\text{K})(293\text{ K})}{0.0290\text{ kg/mol}}} = 343\text{ m/s}.$$

23-6 THE INTERNAL ENERGY OF AN IDEAL GAS

In Section 22-4 we showed that the average translational kinetic energy per molecule of an ideal monatomic gas is

$$K_{\text{trans}} = \tfrac{3}{2}kT. \qquad (23\text{-}23)$$

For such a gas this is the entire store of internal energy because there is no other form the internal energy can take. The molecules of an ideal monatomic gas have no potential

energy; they cannot vibrate, nor is any energy associated with their rotation.

The total internal energy of n moles of an ideal monatomic gas is then the number of molecules ($= nN_A$) times the average energy per molecule:

$$E_{int} = (nN_A)(K_{trans}) = (nN_A)(\tfrac{3}{2}kT)$$

or

$$E_{int} = \tfrac{3}{2}nRT. \qquad (23\text{-}24)$$

Here (see Eq. 21-17) we have replaced $N_A k$ with its equal, the molar gas constant R.

Equation 23-24 shows that, if we change the internal energy of the gas—by doing work on it or transferring heat to it—its temperature will change, so that

$$\Delta E_{int} = \tfrac{3}{2}nR\,\Delta T. \qquad (23\text{-}25)$$

Let us now consider, not the monatomic or point molecule that has been the focus of our attention so far, but a molecule consisting of two point particles separated by a given distance. This model gives a better description of diatomic gases, such as O_2, N_2, or CO (carbon monoxide). Such a molecule can acquire kinetic energy by rotating about its center of mass, and we need to consider contributions to the internal energy of the gas from the rotational motions of its molecules as well as from their translational motions.

The rotational kinetic energy of a diatomic molecule, illustrated in Fig. 23-18, can be written

$$K_{rot} = \tfrac{1}{2}I_x\,\omega_x^2 + \tfrac{1}{2}I_y\,\omega_y^2,$$

where I is the rotational inertia of the molecule for rotation about a particular axis. For point masses, no kinetic energy is associated with rotation about the z axis because $I_z = 0$. The total kinetic energy of a diatomic molecule is the sum of its translational and rotational terms, or

$$K = \tfrac{1}{2}mv_x^2 + \tfrac{1}{2}mv_y^2 + \tfrac{1}{2}mv_z^2 + \tfrac{1}{2}I_x\,\omega_x^2 + \tfrac{1}{2}I_y\,\omega_y^2. \qquad (23\text{-}26)$$

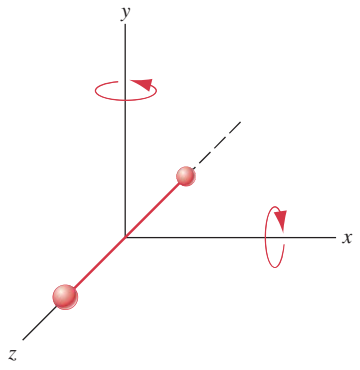

FIGURE 23-18. A diatomic molecule, consisting of two atoms considered to be point particles, is shown with its axis along the z axis of a coordinate system. In this orientation, the rotational inertia for rotations about the z axis is zero, and thus there is no term in the kinetic energy corresponding to such rotations. The rotational inertias for rotations about the x and y axes are not zero, and thus there are kinetic energy terms for such rotations.

To find the total internal energy of the gas, we must find the average energy of a single molecule and then multiply by the number of molecules.

The five terms in Eq. 23-26 represent independent ways in which a molecule can absorb energy and are called *degrees of freedom.* A monatomic gas has three degrees of freedom, since it has only translational kinetic energy ($K = \tfrac{1}{2}mv_x^2 + \tfrac{1}{2}mv_y^2 + \tfrac{1}{2}mv_z^2$.)

As Eq. 23-26 shows, a diatomic molecule has five degrees of freedom, three translational degrees and two rotational degrees. If we increase the internal energy of such a gas by an amount ΔE_{int}, it is clear (because all directions in the gas are equivalent) that the three translational degrees will absorb the same amount of energy. Similarly, the two rotational degrees will absorb the same amount of energy but there seems to be no reason why these two amounts should be the same.

However, James Clerk Maxwell derived a theorem called the *equipartition of energy theorem,* which asserts that the energy of a molecule is shared equally, on average, among *all* independent ways in which the molecule can absorb energy. Specifically,

> *When the number of molecules is large, the average energy per molecule is $\tfrac{1}{2}kT$ for each independent degree of freedom.*

We have already encountered an equipartition of energy situation in our studies of the one-dimensional simple harmonic oscillator. In this case energy can be stored in either kinetic or potential form and, as Fig. 17-8 suggests, on average the available energy is shared equally between these two forms.

Let us use the equipartition of energy theorem to write an expression for the internal energy of a monatomic ideal gas. The average energy per molecule is $\tfrac{3}{2}kT$ (3 degrees of freedom $\times$ $\tfrac{1}{2}kT$ for each degree of freedom). The total energy for N molecules is

$$E_{int} = N(\tfrac{3}{2}kT) = \tfrac{3}{2}nRT \qquad \text{(monatomic gas).} \quad (23\text{-}27)$$

Equation 23-27 is identical with Eq. 23-24. For a diatomic gas, with five degrees of freedom, the result is

$$E_{int} = N(\tfrac{5}{2}kT) = \tfrac{5}{2}nRT \qquad \text{(diatomic gas).} \quad (23\text{-}28)$$

A polyatomic gas (more than two atoms per molecule) generally has three possible axes of rotation (unless the three atoms lie in a straight line, as for CO_2). The kinetic energy of a single molecule would then have a sixth term, $\tfrac{1}{2}I_z\omega_z^2$. For six degrees of freedom, the internal energy is

$$E_{int} = N(\tfrac{6}{2}kT) = 3nRT \qquad \text{(polyatomic gas).} \quad (23\text{-}29)$$

Equations 23-27, 23-28, and 23-29 show us a fact that is inherent in the equipartition of energy theorem—namely, that no matter what the nature of its molecules,

The internal energy of an ideal gas depends only on its temperature.

It does not depend on its pressure or its volume.

So far we have considered only the contributions of the translational or rotational kinetic energy to the internal energy of the gas. Other kinds of energy may also contribute. For example, a diatomic molecule that is free to vibrate (imagine two point atoms connected by a spring) has two additional contributions to the energy: the potential energy of the spring and the kinetic energy of the oscillating atoms. Thus a diatomic molecule free to translate, rotate, and vibrate would have $7(= 3 + 2 + 2)$ degrees of freedom. For polyatomic molecules, the number of vibrational terms can be greater than two. The vibrational modes in the internal energy are usually apparent only at high gas temperatures, where the more violent collisions can cause the molecule to vibrate.

Molar Heat Capacities of Solids

We can also apply the equipartition of energy theorem to the molar heat capacities of solids, a topic that we discussed in Section 23-4. As Fig. 21-9 suggests, an atom in a solid is fixed in a lattice. The atom can oscillate back and forth about its equilibrium position in three independent directions, thus displaying three degrees of freedom associated with its kinetic energy. The atom also has potential energy, associated with the forces between it and its neighboring atoms, again in three independent directions. This gives rise to three more degrees of freedom for a total of six. The average energy per atom is then $6 \times \frac{1}{2}kT = 3kT$. For a sample containing N atoms, the total internal energy is then

$$E_{\text{int}} = N(3kT) = 3nN_{\text{A}}kT = 3nRT,$$

in which n is the number of moles.

Suppose that energy Q is added to the solid sample as heat, raising its temperature by ΔT. Because no work is done in this process ($W = 0$), the first law of thermodynamics ($Q + W = \Delta E_{\text{int}}$) yields

$$Q = \Delta E_{\text{int}} = 3nR\,\Delta T.$$

The molar heat capacity is then

$$C = \frac{Q}{n\,\Delta T} = \frac{3nR\,\Delta T}{n\,\Delta T} = 3R$$

$$= (3)(8.31\ \text{J/mol}\cdot\text{K}) \approx 25\ \text{J/mol}\cdot\text{K}.$$

As Fig. 23-11 shows, this is simply the experimentally observed high-temperature limit for the molar heat capacities of solids. Note that, although the (classical) equipartition of energy theorem gives the correct value for the molar heat capacity in the limit of sufficiently high temperatures, it fails at lower temperatures. In this region only a treatment based on quantum physics proves to agree with experiment.

23-7 HEAT CAPACITIES OF AN IDEAL GAS

We have used the equipartition of energy theorem to calculate the molar heat capacity of a solid. Let us now use it to calculate the molar heat capacities of an ideal gas. The measured heat capacity of a substance depends on the manner in which the heat is added to it. In the case of a gas, for example, is the volume held constant during the process? Is the pressure held constant? We explore both possibilities.

Molar Heat Capacity at Constant Volume

Let us introduce n moles of a gas into a cylinder fitted with a piston. We fix the position of the piston so that there can be no volume change and thus no work done, and then we add an amount of energy Q to the gas as heat. From the first law of thermodynamics (Eq. 23-6) we have, because $W = 0$,

$$Q = \Delta E_{\text{int}}. \tag{23-30}$$

We let C_{V} represent the molar heat capacity at constant volume, so that

$$C_{\text{V}} = \frac{Q}{n\,\Delta T} = \frac{\Delta E_{\text{int}}}{n\,\Delta T}. \tag{23-31}$$

From Eq. 23-27, for a monatomic ideal gas $\Delta E_{\text{int}} = \frac{3}{2}nR\,\Delta T$, and so

$$C_{\text{V}} = \tfrac{3}{2}R = 12.5\ \text{J/mol}\cdot\text{K} \quad \text{(monatomic gas)}. \tag{23-32}$$

Repeating this derivation using Eqs. 23-28 and 23-29 for diatomic and polyatomic gases, we find

$$C_{\text{V}} = \tfrac{5}{2}R = 20.8\ \text{J/mol}\cdot\text{K} \quad \text{(diatomic gas)}, \tag{23-33}$$

$$C_{\text{V}} = 3R = 24.9\ \text{J/mol}\cdot\text{K} \quad \text{(polyatomic gas)}. \tag{23-34}$$

Molar Heat Capacity at Constant Pressure

Figure 23-19 shows two ideal gas isotherms differing in temperature by ΔT. Path AB is the constant-volume process considered previously. Path AC is a constant-pressure

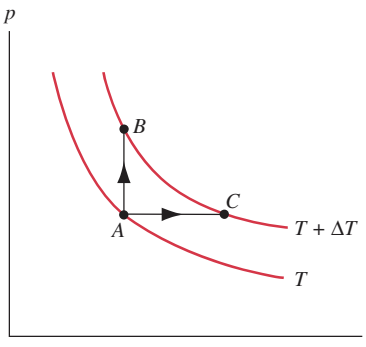

FIGURE 23-19. Two ideal-gas isotherms differing in temperature by ΔT are connected by the constant-volume process AB and the constant-pressure process AC.

process that connects the same two isotherms. In Section 23-6 we established that *the internal energy of an ideal gas depends only on the temperature.* For all paths connecting the two isotherms of Fig. 23-19, the change in internal energy has the same value, because all paths correspond to the same change in temperature. In particular, the change in internal energy is the same for paths AB and AC.

$$\Delta E_{\text{int},AB} = \Delta E_{\text{int},AC}. \tag{23-35}$$

There are two contributions to the change in internal energy along path AC—the heat Q transferred to the gas and the work W done on the gas:

$$\Delta E_{\text{int},AC} = Q + W. \tag{23-36}$$

Note the sign conventions that are implicit in Eq. 23-36. Heat transferred *from* the environment is considered to be positive and tends to increase the internal energy. If the volume decreases, the work done on the gas by the environment is positive, which tends to increase the internal energy. If the volume increases ($W < 0$), we regard the gas as doing work on the environment, which tends to decrease the supply of internal energy of the gas.

The heat transferred in a constant-pressure process can be written

$$Q = nC_p\,\Delta T, \tag{23-37}$$

where C_p is the *molar heat capacity at constant pressure.* Equation 23-15 gives the work along path AC as $W = -p\,\Delta V$, which can be written for this constant-pressure process using the ideal gas law as

$$W = -p\,\Delta V = -nR\,\Delta T. \tag{23-38}$$

Using Eq. 23-31 to obtain the change in internal energy along path AB, we can substitute into Eq. 23-36 to find

$$nC_V\,\Delta T = nC_p\,\Delta T - nR\,\Delta T$$

or

$$C_p = C_V + R. \tag{23-39}$$

From Eqs. 23-32 to 23-34 we then find the molar heat capacities at constant pressure:

$$C_p = \tfrac{5}{2}R = 20.8\ \text{J/mol}\cdot\text{K} \quad \text{(monatomic gas)}, \tag{23-40}$$

$$C_p = \tfrac{7}{2}R = 29.1\ \text{J/mol}\cdot\text{K} \quad \text{(diatomic gas)}, \tag{23-41}$$

$$C_p = 4R = 33.3\ \text{J/mol}\cdot\text{K} \quad \text{(polyatomic gas)}. \tag{23-42}$$

Another parameter of interest, which can be directly measured independently of the values of C_p and C_V, is the *ratio of molar heat capacities* γ, defined as

$$\gamma = \frac{C_p}{C_V}. \tag{23-43}$$

Because the specific heat capacity is related to the molar heat capacity by $c = C/M$, where M is the molar mass of the substance, we can also express γ as c_p/c_V. For this reason γ is often called the *ratio of specific heats* or *specific heat ratio.* We used γ previously in the expression for the speed of sound in a gas (Sample Problem 23-5) and in the relationship between pressure and volume in an adiabatic process (Eq. 23-19).

TABLE 23-4 Molar Heat Capacities of Gases

Gas	C_p (J/mol·K)	C_V (J/mol·K)	$C_p - C_V$ (J/mol·K)	γ
Monatomic				
Ideal	20.8	12.5	8.3	1.67
He	20.8	12.5	8.3	1.66
Ar	20.8	12.5	8.3	1.67
Diatomic				
Ideal	29.1	20.8	8.3	1.40
H_2	28.8	20.4	8.4	1.41
N_2	29.1	20.8	8.3	1.40
O_2	29.4	21.1	8.3	1.40
Polyatomic				
Ideal	33.3	24.9	8.3	1.33
CO_2	37.0	28.5	8.5	1.30
NH_3	36.8	27.8	9.0	1.31

Using Eqs. 23-40 to 23-42 for C_p and Eqs. 23-32 to 23-34 for C_V, we obtain

$$\gamma = \tfrac{5}{3} = 1.67 \quad \text{(monatomic gas)}, \tag{23-44}$$

$$\gamma = \tfrac{7}{5} = 1.40 \quad \text{(diatomic gas)}, \tag{23-45}$$

$$\gamma = \tfrac{4}{3} = 1.33 \quad \text{(polyatomic gas)}. \tag{23-46}$$

Table 23-4 shows a comparison of observed values with the predictions of the ideal gas model. The agreement is excellent.

SAMPLE PROBLEM 23-6. A family enters a winter vacation cabin that has been unheated for such a long time that the interior temperature is the same as the outside temperature (0°C). The cabin consists of a single room of floor area 6 m by 4 m and height 3 m. The room contains one 2-kW electric heater. Assuming that the room is perfectly airtight and that all the heat from the electric heater is absorbed by the air, none escaping through the walls or being absorbed by the furnishings, how long after the heater is turned on will the air temperature reach the comfort level of 21°C (= 70°F)?

Solution Let us assume that the air in the room (which is mostly nitrogen and oxygen) behaves like an ideal diatomic gas, so that (according to Table 23-4) $C_V = 20.8$ J/mol·K. The volume of the room is

$$V = (6\ \text{m})(4\ \text{m})(3\ \text{m}) = 72\ \text{m}^3 = 72{,}000\ \text{L}.$$

Since 1 mole of an ideal gas occupies 22.4 L at 0°C and 1 atm, the number of moles is

$$n = (72{,}000\ \text{L})/(22.4\ \text{L/mol}) = 3.2 \times 10^3\ \text{mol}.$$

If the room is airtight (see the discussion below), we can regard the absorption of heat to take place at constant volume, for which

$$Q = nC_V\,\Delta T = (3.2 \times 10^3\ \text{mol})(20.8\ \text{J/mol}\cdot\text{K})(21\ \text{K})$$
$$= 1.4 \times 10^6\ \text{J}.$$

The heater delivers a power P of 2 kW and can provide this energy in a time of

$$t = \frac{Q}{P} = \frac{1.4 \times 10^6 \text{ J}}{2 \times 10^3 \text{ W}} = 700 \text{ s},$$

or about 12 min.

This problem contained some very unphysical assumptions about the absorption of heat in this room. Try to estimate the heat capacity of some pieces of furniture to see whether neglecting their effect on the heat absorption (and thus on the time to bring the room to comfort level) was reasonable. The heat loss through the walls of the room, which we considered in Section 23-2, also will have a considerable effect on this problem.

Is the assumption about the room being airtight reasonable? If the air in the cabin were originally at a pressure of 1 atm when the temperature was 0°C, what will be the interior pressure at 21°C? What will be the resulting outward force on the roof and walls? A more reasonable assumption might be that the room is not quite airtight, but that as the temperature rises some air will escape, thereby keeping the pressure constant. See Problem 16 for a calculation based on this assumption.

SAMPLE PROBLEM 23-7. Consider once again the situation of Sample Problem 23-4, in which 0.11 mole of an ideal gas begins at the initial point with volume $V_i = 4.0 \text{ m}^3$ and pressure $p_i = 10$ Pa. Let the cylinder be removed from the thermal reservoir, and let us compress the gas adiabatically until its volume is $V_f = 1.0 \text{ m}^3$. Find the change in internal energy of the gas, assuming it to be helium (a monatomic gas with $\gamma = 1.66$).

Solution To find the change in internal energy, we can use Eq. 23-27 if we know the change in temperature. We can find the initial temperature using the ideal gas law (since p_i and V_i are known), and we can find the final temperature if we know the pressure and volume of the final point. The final pressure can be found using the adiabatic relationship of Eq. 23-19:

$$p_f = \frac{p_i V_i^\gamma}{V_f^\gamma} = \frac{(10 \text{ Pa})(4.0 \text{ m}^3)^{1.66}}{(1.0 \text{ m}^3)^{1.66}} = 100 \text{ Pa}.$$

On the pV diagram of Fig. 23-17, the final point reached in the adiabatic process lies vertically far above the final point reached in the isothermal process (40 Pa). This is consistent with the adiabatic curves being steeper than the isothermal curves, as shown in Fig. 23-16.

We can now proceed to find the initial and final temperatures and then the change in internal energy:

$$T_i = \frac{p_i V_i}{nR} = \frac{(10 \text{ Pa})(4.0 \text{ m}^3)}{(0.11 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K})} = 44 \text{ K}.$$

$$T_f = \frac{p_f V_f}{nR} = \frac{(100 \text{ Pa})(1.0 \text{ m}^3)}{(0.11 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K})} = 109 \text{ K}.$$

$$\Delta E_{int} = \tfrac{3}{2} nR\Delta T$$
$$= \tfrac{3}{2}(0.11 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K})(109 \text{ K} - 44 \text{ K}) = 89 \text{ J}.$$

The change in internal energy is positive. This is consistent with the first law of thermodynamics ($Q + W = \Delta E_{int}$) because $Q = 0$ for this adiabatic process and the work done in compressing the gas is positive.

23-8 APPLICATIONS OF THE FIRST LAW OF THERMODYNAMICS

Now that we have examined many of the properties of the ideal gas, including its internal energy (Section 23-6) and its heat capacities (Section 23-7), we are ready to study the various processes that a system consisting of an ideal gas can undergo.

Adiabatic Processes

In an adiabatic process the system is well insulated so that no heat enters or leaves, in which case $Q = 0$. The first law becomes, in this case,

$$\Delta E_{int} = W \qquad \text{(adiabatic process)}. \qquad (23\text{-}47)$$

Let us derive the relationship between p and V for an adiabatic process carried out on an ideal gas, which we used in Section 23-5. We assume the process to be carried out slowly, so that the pressure is always well defined. For an ideal gas, we can write Eq. 23-31 as

$$dE_{int} = nC_V\, dT.$$

Thus

$$p\, dV = -dW = -dE_{int} = -nC_V\, dT. \qquad (23\text{-}48)$$

The equation of state of the gas can be written in differential form as

$$d(pV) = d(nRT)$$

$$p\, dV + V\, dp = nR\, dT. \qquad (23\text{-}49)$$

However, $p\, dV$ is simply $-dW$, which is equal to $-dE_{int}$ (since Eq. 23-47 can be written in differential form as $dE_{int} = dW$). Solving Eq. 23-49 for $V\, dp$ and substituting Eq. 23-48, we have

$$V\, dp = nC_V\, dT + nR\, dT = nC_p\, dT, \qquad (23\text{-}50)$$

where the last result has been obtained using Eq. 23-39, $C_p = C_V + R$. We now take the ratio between Eqs. 23-50 and 23-48, which gives

$$\frac{V\, dp}{p\, dV} = \frac{nC_p\, dT}{-nC_V\, dT} = -\frac{C_p}{C_V} = -\gamma,$$

using Eq. 23-43 for the ratio of molar heat capacities γ. Rewriting, we find

$$\frac{dp}{p} = -\gamma \frac{dV}{V},$$

which we can integrate between initial state i and final state f

$$\int_{p_i}^{p_f} \frac{dp}{p} = -\gamma \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\ln \frac{p_f}{p_i} = -\gamma \ln \frac{V_f}{V_i},$$

which can be written

$$p_i V_i^\gamma = p_f V_f^\gamma. \qquad (23\text{-}51)$$

Since i and f are arbitrary points, we can write this equation as

$$pV^{\gamma} = \text{constant}. \qquad (23\text{-}52)$$

Equations 23-51 and 23-52 give the relationship between the pressure and volume of an ideal gas that undergoes an adiabatic process. Given the values of the pressure and volume at the initial point, the adiabatic process will proceed through final points whose pressure and volume can be calculated from Eq. 23-51. Equivalently, Eq. 23-52 defines a family of curves on a pV diagram. Every adiabatic process can be represented by a segment of one of these curves (Fig. 23-20).

We can rewrite these results in terms of temperature, using the ideal gas equation of state:

$$(pV)V^{\gamma-1} = \text{constant}$$

$$TV^{\gamma-1} = \text{constant}. \qquad (23\text{-}53)$$

The constant in Eq. 23-53 is not the same as that in Eq. 23-52. Equivalently, we can write Eq. 23-53 as

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

$$T_f = T_i \left(\frac{V_i}{V_f}\right)^{\gamma-1} \qquad (23\text{-}54)$$

Suppose we compress a gas in an adiabatic process. Then $V_i > V_f$, and Eq. 23-54 requires that $T_f > T_i$. The temperature of the gas rises as it is compressed, as we frequently observe from the warming of a bicycle pump. Conversely, the temperature falls when a gas expands, which is often used as a means to achieve low temperatures in the laboratory (see Fig. 23-20).

Sound waves in air can be represented in terms of adiabatic processes. At audio frequencies, air is a poor conductor of heat. There is an increase in temperature in the compression zones of a sound wave, but due to the poor conduction there is no appreciable heat transfer to the neighboring cooler rarefactions; the process is thus adiabatic. The compressions and expansions of steam in a steam engine, or of the hot gases in the cylinders of an internal combustion engine, are also essentially adiabatic, because there is insufficient time for heat to be transferred.

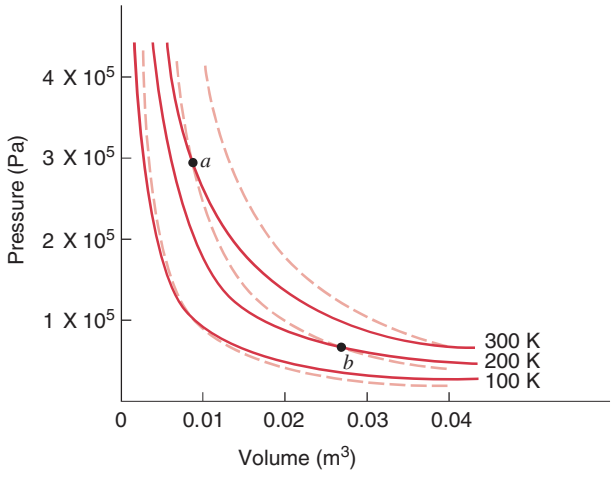

FIGURE 23-20. Isothermal processes (solid lines) and adiabatic processes (dashed lines) carried out on 1 mole of a diatomic ideal gas. Note that an adiabatic *increase* in volume (for example, the segment *ab*) is always accompanied by a *decrease* in temperature.

Isothermal Processes

In an isothermal process, the temperature remains constant. If the system is an ideal gas, then the internal energy must therefore also remain constant. With $\Delta E_{int} = 0$, the first law gives

$$Q + W = 0 \qquad \text{(isothermal process; ideal gas).} \qquad (23\text{-}55)$$

If an amount of (positive) work W is done on the gas, an equivalent amount of heat $Q = -W$ is released by the gas to the environment. None of the work done on the gas remains with the gas as stored internal energy.

Figure 23-20 compares isothermal and adiabatic processes for 1 mole of a monatomic ideal gas.

Constant-Volume Processes

If the volume of a gas remains constant, it can do no work. Thus $W = 0$, and the first law gives

$$\Delta E_{int} = Q \qquad \text{(constant-volume process).} \qquad (23\text{-}56)$$

In this case all the heat that enters the gas ($Q > 0$) is stored as internal energy ($\Delta E_{int} > 0$).

Cyclical Processes

In a cyclical process we carry out a sequence of operations that eventually restores the system to its initial state, as, for example, the three-step process illustrated in Fig. 23-21. Because the process starts and finishes at the point A, the internal energy change for the cycle is zero. Thus, according to the first law,

$$Q + W = 0 \qquad \text{(cyclical process),} \qquad (23\text{-}57)$$

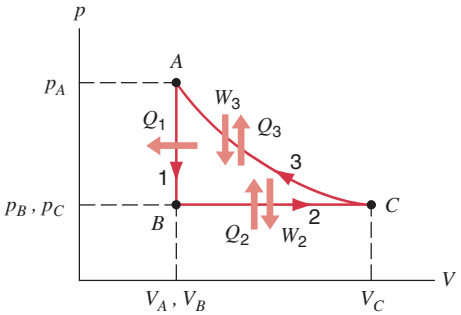

FIGURE 23-21. A gas undergoes a cyclical process starting at point A and consisting of (1) a constant-volume process AB, (2) a constant-pressure process BC, and (3) an isothermal process CA.

TABLE 23-5 Applications of the First Law

Process	*Restriction*	*First Law*	*Other Results*
All	None	$\Delta E_{int} = Q + W$	$\Delta E_{int} = nC_V \Delta T$, $W = -\int p\, dV$
Adiabatic	$Q = 0$	$\Delta E_{int} = W$	$W = (p_f V_f - p_i V_i)/(\gamma - 1)$
Constant volume	$W = 0$	$\Delta E_{int} = Q$	$Q = nC_V \Delta T$
Constant pressure	$\Delta p = 0$	$\Delta E_{int} = Q + W$	$W = -p\Delta V$, $Q = nC_p \Delta T$
Isothermal	$\Delta E_{int} = 0$	$Q = -W$	$W = -nRT \ln(V_f/V_i)$
Cycle	$\Delta E_{int} = 0$	$Q = -W$	
Free expansion	$Q = W = 0$	$\Delta E_{int} = 0$	$\Delta T = 0$

Items underlined apply only to ideal gases; all other items apply in general.

where Q and W represent the totals for the cycle. In Fig. 23-21, the total work is positive, because there is more positive area under the curve representing step 3 than there is negative area under the line representing step 2. Thus $W > 0$ and it follows from Eq. 23-57 that $Q < 0$. In fact, for any cycle that is done in a counterclockwise direction, we must have $W > 0$ (and thus $Q < 0$), whereas cycles performed in the clockwise direction have $W < 0$ and $Q > 0$.

Free Expansion

Figure 23-22 represents the process known as *free expansion.* The gas is initially in one side of the container, and when the stopcock is opened, the gas expands into the previously evacuated half. No weights can be raised in this process, so no work is done. The container is insulated, so the process is adiabatic. Hence, with $W = 0$ and $Q = 0$, the first law gives

$$\Delta E_{int} = 0 \qquad \text{(free expansion)}. \qquad (23\text{-}58)$$

Thus the internal energy of an ideal gas undergoing a free expansion remains constant, and because the internal energy of an ideal gas depends only on the temperature, its temperature must similarly remain constant.

The free expansion is a good example of a *nonequilibrium* process. If a gas has a well-defined pressure and volume (and therefore temperature), we can show the state of the gas as a point on a pV diagram. The assignment of a temperature to the gas means that it must be in thermal equilibrium; each point on a pV diagram therefore represents a system in equilibrium. In the case of a free expansion, the initial state (all gas on one side) is an equilibrium state, as is the final state; but at intermediate times, as the gas rushes from one side to the other, the temperature and the pressure do not have unique values, and we cannot plot this process on a pV diagram. Only the initial and final points appear on the graph. Nevertheless, we can still use the first law to analyze this process, because the change in internal energy depends only on the initial and final points.

Table 23-5 summarizes the processes we have considered and their energy transfers.

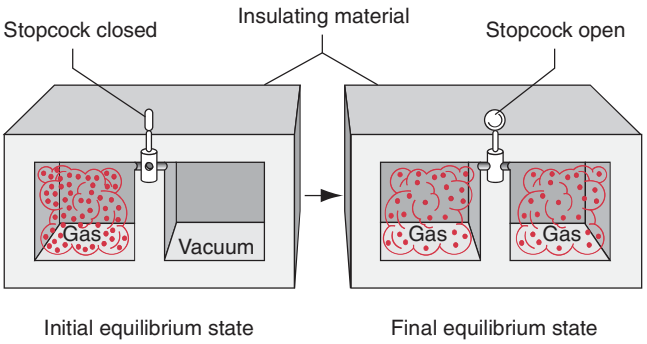

FIGURE 23-22. Free expansion. Opening the stopcock allows gas to flow from one side of the insulated container to the other. No work is done, and no heat is transferred to the environment.

SAMPLE PROBLEM 23-8. Let 1.00 kg of liquid water be converted to steam by boiling at standard atmospheric pressure; see Fig. 23-23. The volume changes from an initial value of 1.00×10^{-3} m^3 as a liquid to 1.671 m^3 as steam. For this process, find (*a*) the work done on the system, (*b*) the heat added to the system, and (*c*) the change in the internal energy of the system.

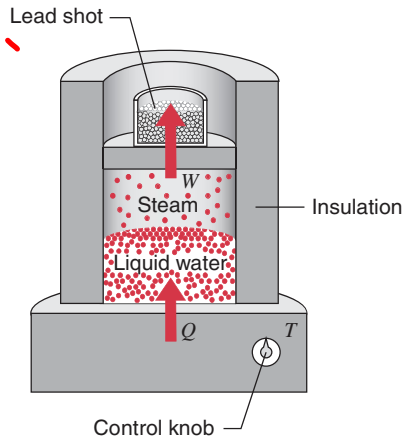

FIGURE 23-23. Sample Problem 23-8. Water is boiling at constant pressure. Heat flows from the reservoir until the water has changed completely into steam. Work is done by the expanding gas as it lifts the piston.

Solution (*a*) The work done on the gas during this constant-pressure process is given by Eq. 23-17:

$$W = -p(V_f - V_i)$$
$$= -(1.01 \times 10^5 \text{ Pa})(1.671 \text{ m}^3 - 1.00 \times 10^{-3} \text{ m}^3)$$
$$= -1.69 \times 10^5 \text{ J} = -169 \text{ kJ}.$$

The work done on the system is negative; equivalently, positive work is done *by* the system on its environment in lifting the weighted piston of Fig. 23-23.
(*b*) From Eq. 23-13 we have

$$Q = Lm = (2256 \text{ kJ/kg})(1.00 \text{ kg}) = 2260 \text{ kJ}.$$

This quantity is positive, as is appropriate for a process in which heat is transferred to the system.
(*c*) We find the change in internal energy from the first law:

$$\Delta E_{int} = Q + W = 2260 \text{ kJ} + (-169 \text{ kJ}) = 2090 \text{ kJ}.$$

This quantity is positive, indicating that the internal energy of the system has increased during the boiling process. This energy represents the internal work done in overcoming the strong attraction that the H_2O molecules have for each other in the liquid state.

We see that, when water boils, about 7.5% (169 kJ/2260 kJ = 0.075) of the added heat goes into external work in pushing back the atmosphere. The rest goes into internal energy that is added to the system.

SAMPLE PROBLEM 23-9. The cycle shown in Fig. 23-21 consists of three processes, starting at point *A*: a reduction in pressure at constant volume from point *A* to point *B*; an increase in volume at constant pressure from point *B* to point *C*; an isothermal compression (decrease in volume) from point *C* back to point *A*. Let the cycle be carried out on 0.75 mol of a diatomic ideal gas, with $p_A = 3.2 \times 10^3$ Pa, $V_A = 0.21$ m^3, and $p_B = 1.2 \times 10^3$ Pa. For each of the three processes and for the cycle, find Q, W, and ΔE_{int}.

Solution The first step is to find the values of p, V, and T at each point. At point *A*, we are given p_A and V_A, and we can solve for T_A from the ideal gas law:

$$T_A = \frac{p_A V_A}{nR} = \frac{(3.2 \times 10^3 \text{ Pa})(0.21 \text{ m}^3)}{(0.75 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})} = 108 \text{ K}.$$

At point *B*, we are given p_B and V_B ($= V_A$), and we can similarly find T_B:

$$T_B = \frac{p_B V_B}{nR} = \frac{(1.2 \times 10^3 \text{ Pa})(0.21 \text{ m}^3)}{(0.75 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})} = 40 \text{ K}.$$

At point *C*, we know p_C ($= p_B$) and T_C ($= T_A$, because process *CA* is an isotherm). We can then find V_C:

$$V_C = \frac{nRT_C}{p_C} = \frac{(0.75 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(108 \text{ K})}{1.2 \times 10^3 \text{ Pa}} = 0.56 \text{ m}^3.$$

With this information, we can now calculate the heat transfer, work done, and change in internal energy for each process. For process 1 (*AB*), we have

$$Q_1 = nC_V(T_B - T_A)$$
$$= (0.75 \text{ mol})(20.8 \text{ J/mol} \cdot \text{K})(40 \text{ K} - 108 \text{ K}) = -1060 \text{ J},$$
$$W_1 = 0 \qquad \text{(constant-volume process)},$$
$$\Delta E_{int,1} = Q_1 + W_1 = -1060 \text{ J} + 0 = -1060 \text{ J}.$$

The system transfers energy to the environment as heat during process 1, and its temperature falls, corresponding to a negative change in internal energy.

For the constant-pressure process 2 (*BC*), we obtain

$$Q_2 = nC_p(T_C - T_B)$$
$$= (0.75 \text{ mol})(29.1 \text{ J/mol} \cdot \text{K})(108 \text{ K} - 40 \text{ K}) = 1480 \text{ J},$$
$$W_2 = -p(V_C - V_B)$$
$$= -(1.2 \times 10^3 \text{ Pa})(0.56 \text{ m}^3 - 0.21 \text{ m}^3) = -420 \text{ J},$$
$$\Delta E_{int,2} = Q_2 + W_2 = 1480 \text{ J} + (-420 \text{ J}) = 1060 \text{ J}.$$

Energy is transferred to the gas as heat during process 2, and in expanding the gas does work on its environment (the environment does negative work on the gas.)

Along the isotherm (*CA*), the work is given by Eq. 23-18;

$$W_3 = -nRT_C \ln \frac{V_A}{V_C}$$
$$= -(0.75 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(108 \text{ K}) \ln \frac{0.21 \text{ m}^3}{0.56 \text{ m}^3}$$
$$= 660 \text{ J},$$
$$\Delta E_{int,3} = 0 \text{ (isothermal process)},$$
$$Q_3 = \Delta E_{int,3} - W_3 = 0 - 660 \text{ J} = -660 \text{ J}.$$

For the cycle, we have

$$Q = Q_1 + Q_2 + Q_3 = -1060 \text{ J} + 1480 \text{ J} + (-660 \text{ J})$$
$$= -240 \text{ J},$$
$$W = W_1 + W_2 + W_3 = 0 + (-420 \text{ J}) + 660 \text{ J} = 240 \text{ J},$$
$$\Delta E_{int} = \Delta E_{int,1} + \Delta E_{int,2} + \Delta E_{int,3} = -1060 \text{ J} + 1060 \text{ J} + 0 = 0.$$

Note that, as expected for the cycle, $\Delta E_{int} = 0$ and $Q = -W$. The total work for the cycle is positive, as we expect for a cycle that is done in the counterclockwise direction.

In solving problems of this type, we can use expressions that give directly the heat transfer in adiabatic ($Q = 0$), constant-pressure, and constant-volume processes. For other processes, such as the isothermal step in this problem, we can find Q only by first finding ΔE_{int} and W and then using the first law.

MULTIPLE CHOICE

23-1 Heat: Energy in Transit

23-2 The Transfer of Heat

1. Two identical long, thin, solid cylinders are used to conduct heat from a reservoir at temperature T_{hot} to a reservoir at temperature T_{cold}. Originally the cylinders are connected in series as shown in Fig. 23-24*a*, and the rate of heat transfer is H_0. If the cylinders are connected in parallel instead as shown in Fig. 23-24*b*, then what would be the rate of heat transfer?
(A) $16H_0$ (B) $4H_0$ (C) $2H_0$ (D) $H_0/2$