

## 19

THE FIRST LAW  
OF THERMODYNAMICS

## LEARNING GOALS

By studying this chapter, you will learn:

- How to represent heat transfer and work done in a thermodynamic process.
- How to calculate the work done by a thermodynamic system when its volume changes.
- What is meant by a path between thermodynamic states.
- How to use the first law of thermodynamics to relate heat transfer, work done, and internal energy change.
- How to distinguish among adiabatic, isochoric, isobaric, and isothermal processes.
- How we know that the internal energy of an ideal gas depends only on its temperature.
- The difference between molar heat capacities at constant volume and at constant pressure, and how to use these quantities in calculations.
- How to analyze adiabatic processes in an ideal gas.

**19.1** The popcorn in the pot is a thermodynamic system. In the thermodynamic process shown here, heat is added to the system, and the system does work on its surroundings to lift the lid of the pot.



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? A steam locomotive operates using the first law of thermodynamics: Water is heated and boils, and the expanding steam does work to propel the locomotive. Would it be possible for the steam to propel the locomotive by doing work as it *condenses*?



Every time you drive a car, turn on an air conditioner, or cook a meal, you reap the practical benefits of *thermodynamics*, the study of relationships involving heat, mechanical work, and other aspects of energy and energy transfer. For example, in a car engine heat is generated by the chemical reaction of oxygen and vaporized gasoline in the engine's cylinders. The heated gas pushes on the pistons within the cylinders, doing mechanical work that is used to propel the car. This is an example of a *thermodynamic process*.

The first law of thermodynamics, central to the understanding of such processes, is an extension of the principle of conservation of energy. It broadens this principle to include energy exchange by both heat transfer and mechanical work and introduces the concept of the *internal energy* of a system. Conservation of energy plays a vital role in every area of physical science, and the first law has extremely broad usefulness. To state energy relationships precisely, we need the concept of a *thermodynamic system*. We'll discuss *heat* and *work* as two means of transferring energy into or out of such a system.

## 19.1 Thermodynamic Systems

We have studied energy transfer through mechanical work (Chapter 6) and through heat transfer (Chapters 17 and 18). Now we are ready to combine and generalize these principles.

We always talk about energy transfer to or from some specific *system*. The system might be a mechanical device, a biological organism, or a specified quantity of material, such as the refrigerant in an air conditioner or steam expanding in a turbine. In general, a **thermodynamic system** is any collection of objects that is convenient to regard as a unit, and that may have the potential to exchange energy with its surroundings. A familiar example is a quantity of popcorn kernels in a pot with a lid. When the pot is placed on a stove, energy is added to the popcorn by conduction of heat. As the popcorn pops and expands, it does work as it

exerts an upward force on the lid and moves it through a displacement (Fig. 19.1). The *state* of the popcorn changes in this process, since the volume, temperature, and pressure of the popcorn all change as it pops. A process such as this one, in which there are changes in the state of a thermodynamic system, is called a **thermodynamic process**.

In mechanics we used the concept of *system* on a regular basis in connection with free-body diagrams and conservation of energy and momentum. With *thermodynamic* systems, as with all others, it is essential to define clearly at the start exactly what is and is not included in the system. Only then can we describe unambiguously the energy transfers into and out of that system. For instance, in our popcorn example we defined the system to include the popcorn but not the pot, lid, or stove.

Thermodynamics has its roots in many practical problems other than popping popcorn (Fig. 19.2). The gasoline engine in an automobile, the jet engines in an airplane, and the rocket engines in a launch vehicle use the heat of combustion of their fuel to perform mechanical work in propelling the vehicle. Muscle tissue in living organisms metabolizes chemical energy in food and performs mechanical work on the organism's surroundings. A steam engine or steam turbine uses the heat of combustion of coal or other fuel to perform mechanical work such as driving an electric generator or pulling a train.

## Signs for Heat and Work in Thermodynamics

We describe the energy relationships in any thermodynamic process in terms of the quantity of heat  $Q$  added to the system and the work  $W$  done by the system. Both  $Q$  and  $W$  may be positive, negative, or zero (Fig. 19.3). A positive value of  $Q$  represents heat flow *into* the system, with a corresponding input of energy to it; negative  $Q$  represents heat flow *out of* the system. A positive value of  $W$  represents work done *by* the system against its surroundings, such as work done by an expanding gas, and hence corresponds to energy *leaving* the system. Negative  $W$ , such as work done during compression of a gas in which work is done *on the gas* by its surroundings, represents energy *entering* the system. We will use these conventions consistently in the examples in this chapter and the next.

**CAUTION** Be careful with the sign of work  $W$  Note that our sign rule for work is *opposite* to the one we used in mechanics, in which we always spoke of the work done by the forces acting *on* a body. In thermodynamics it is usually more convenient to call  $W$  the work done *by* the system so that when a system expands, the pressure, volume change, and work are all positive. Take care to use the sign rules for work and heat consistently!

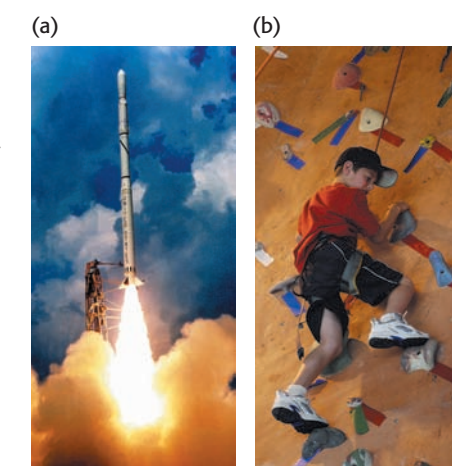
**Test Your Understanding of Section 19.1** In Example 17.8 (Section 17.6), what is the sign of  $Q$  for the coffee? For the aluminum cup? If a block slides along a horizontal surface with friction, what is the sign of  $W$  for the block?

## 19.2 Work Done During Volume Changes

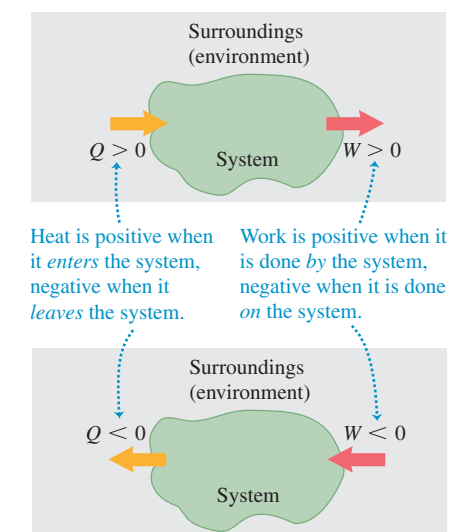
A simple but common example of a thermodynamic system is a quantity of gas enclosed in a cylinder with a movable piston. Internal-combustion engines, steam engines, and compressors in refrigerators and air conditioners all use some version of such a system. In the next several sections we will use the gas-in-cylinder system to explore several kinds of processes involving energy transformations.

We'll use a microscopic viewpoint, based on the kinetic and potential energies of individual molecules in a material, to develop intuition about thermodynamic quantities. But it is important to understand that the central principles of thermodynamics can be treated in a completely *macroscopic* way, without reference to microscopic models. Indeed, part of the great power and generality of thermodynamics is that it does *not* depend on details of the structure of matter.

**19.2** (a) A rocket engine uses the heat of combustion of its fuel to do work propelling the launch vehicle. (b) Humans and other biological organisms are more complicated systems than we can analyze fully in this book, but the same basic principles of thermodynamics apply to them.

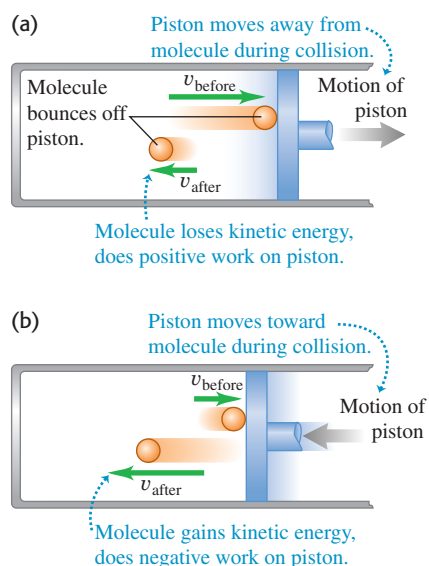


**19.3** A thermodynamic system may exchange energy with its surroundings (environment) by means of heat, work, or both. Note the sign conventions for  $Q$  and  $W$ .





**19.4** A molecule striking a piston (a) does positive work if the piston is moving away from the molecule and (b) does negative work if the piston is moving toward the molecule. Hence a gas does positive work when it expands as in (a) but does negative work when it compresses as in (b).



First we consider the *work* done by the system during a volume change. When a gas expands, it pushes outward on its boundary surfaces as they move outward. Hence an expanding gas always does positive work. The same thing is true of any solid or fluid material that expands under pressure, such as the popcorn in Fig. 19.1.

We can understand the work done by a gas in a volume change by considering the molecules that make up the gas. When one such molecule collides with a stationary surface, it exerts a momentary force on the wall but does no work because the wall does not move. But if the surface is moving, like a piston in a gasoline engine, the molecule *does* do work on the surface during the collision. If the piston in Fig. 19.4a moves to the right, so that the volume of the gas increases, the molecules that strike the piston exert a force through a distance and do *positive* work on the piston. If the piston moves toward the left as in Fig. 19.4b, so the volume of the gas decreases, then positive work is done *on* the molecule during the collision. Hence the gas molecules do *negative* work on the piston.

Figure 19.5 shows a system whose volume can change (a gas, liquid, or solid) in a cylinder with a movable piston. Suppose that the cylinder has cross-sectional area  $A$  and that the pressure exerted by the system at the piston face is  $p$ . The total force  $F$  exerted by the system on the piston is  $F = pA$ . When the piston moves out an infinitesimal distance  $dx$ , the work  $dW$  done by this force is

$$dW = F dx = pA dx$$

But

$$A dx = dV$$

where  $dV$  is the infinitesimal change of volume of the system. Thus we can express the work done by the system in this infinitesimal volume change as

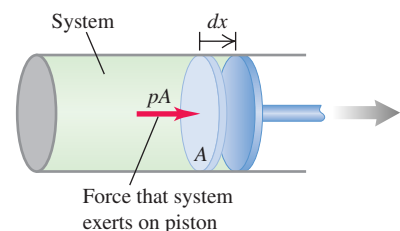
$$dW = p dV \quad (19.1)$$

In a finite change of volume from  $V_1$  to  $V_2$ ,

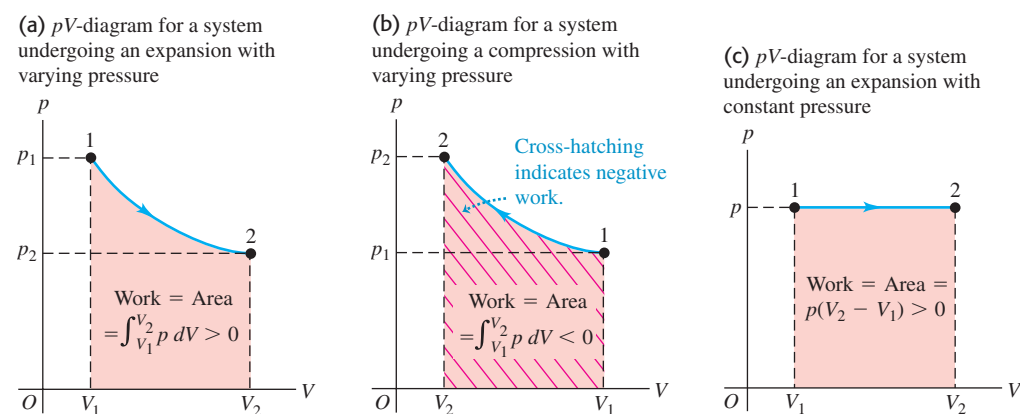
$$W = \int_{V_1}^{V_2} p dV \quad (\text{work done in a volume change}) \quad (19.2)$$

In general, the pressure of the system may vary during the volume change. For example, this is the case in the cylinders of an automobile engine as the pistons move back and forth. To evaluate the integral in Eq. (19.2), we have to know how the pressure varies as a function of volume. We can represent this relationship as a graph of  $p$  as a function of  $V$  (a  $pV$ -diagram, described at the end of Section 18.1). Figure 19.6 a shows a simple example. In this figure, Eq. (19.2) is repre-

**19.5** The infinitesimal work done by the system during the small expansion  $dx$  is  $dW = pA dx$ .



**19.6** The work done equals the area under the curve on a  $pV$ -diagram.



sented graphically as the *area* under the curve of  $p$  versus  $V$  between the limits  $V_1$  and  $V_2$ . (In Section 6.3 we used a similar interpretation of the work done by a force  $F$  as the area under the curve of  $F$  versus  $x$  between the limits  $x_1$  and  $x_2$ .)

According to the rule we stated in Section 19.1, work is *positive* when a system *expands*. In an expansion from state 1 to state 2 in Fig. 19.6a the area under the curve and the work are positive. A *compression* from 1 to 2 in Fig. 19.6b gives a *negative* area; when a system is compressed, its volume decreases and it does *negative* work on its surroundings (see also Fig. 19.4b).

**CAUTION** Be careful with subscripts 1 and 2 When using Eq. (19.2), always remember that  $V_1$  is the *initial* volume and  $V_2$  is the *final* volume. That's why the labels 1 and 2 are reversed in Fig. 19.6b compared to Fig. 19.6a, even though both processes move between the same two thermodynamic states.

If the pressure  $p$  remains constant while the volume changes from  $V_1$  to  $V_2$  (Fig. 19.6c), the work done by the system is

$$W = p(V_2 - V_1) \quad (\text{work done in a volume change at constant pressure}) \quad (19.3)$$

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8.5 Work Done By a Gas

In any process in which the volume is *constant*, the system does no work because there is no displacement.

### Example 19.1 Isothermal expansion of an ideal gas

An ideal gas undergoes an *isothermal* (constant-temperature) *expansion* at temperature  $T$ , during which its volume changes from  $V_1$  to  $V_2$ . How much work does the gas do?

#### SOLUTION

**IDENTIFY:** The ideal-gas law tells us that if the temperature of an ideal gas remains constant, the quantity  $pV = nRT$  also remains constant. If the volume  $V$  changes, the pressure  $p$  must change as well. Hence this problem asks for the work done by a gas that changes volume with varying pressure.

**SET UP:** Although it may be tempting to do so, we *cannot* use Eq. (19.3) to calculate the work done because the temperature, not the pressure, is constant. Instead we must use Eq. (19.2). To evaluate the integral in this equation we need to know the pressure as a function of volume; for this we use the ideal-gas law, Eq. (18.3).

**EXECUTE:** From Eq. (19.2),

$$W = \int_{V_1}^{V_2} p dV$$

From Eq. (18.3) the pressure  $p$  of  $n$  moles of ideal gas occupying volume  $V$  at absolute temperature  $T$  is

$$p = \frac{nRT}{V}$$

where  $R$  is the gas constant. We substitute this into the integral, take the constants  $n$ ,  $R$ , and  $T$  outside, and evaluate the integral:

$$W = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \frac{V_2}{V_1} \quad (\text{ideal gas, isothermal process})$$

Also, when  $T$  is constant,

$$p_1 V_1 = p_2 V_2 \quad \text{or} \quad \frac{V_2}{V_1} = \frac{p_1}{p_2}$$

so the isothermal work may also be expressed as

$$W = nRT \ln \frac{p_1}{p_2} \quad (\text{ideal gas, isothermal process})$$

**EVALUATE:** We check our result by noting that in an expansion  $V_2 > V_1$  and the ratio  $V_2/V_1$  is greater than 1. The logarithm of a number greater than 1 is positive, so  $W > 0$ , as it should be. As an additional check, look at our second expression for  $W$ : In an isothermal expansion the volume increases and the pressure drops, so  $p_2 < p_1$ , the ratio  $p_1/p_2 > 1$ , and  $W = nRT \ln(p_1/p_2)$  is again positive.

These results also apply to an isothermal *compression* of a gas, for which  $V_2 < V_1$  and  $p_2 > p_1$ .

**Test Your Understanding of Section 19.2** A quantity of ideal gas undergoes an expansion that increases its volume from  $V_1$  to  $V_2 = 2V_1$ . The final pressure of the gas is  $p_2$ . Does the gas do more work on its surroundings if the expansion is at constant *pressure* or at constant *temperature*? (i) constant pressure; (ii) constant temperature; (iii) the same amount of work is done in both cases; (iv) not enough information is given to decide.



### 19.3 Paths Between Thermodynamic States

We've seen that if a thermodynamic process involves a change in volume, the system undergoing the process does work (either positive or negative) on its surroundings. Heat also flows into or out of the system during the process if there is a temperature difference between the system and its surroundings. Let's now examine how the work done by and the heat added to the system during a thermodynamic process depend on the details of how the process takes place.

#### Work Done in a Thermodynamic Process

When a thermodynamic system changes from an initial state to a final state, it passes through a series of intermediate states. We call this series of states a **path**. There are always infinitely many different possibilities for these intermediate states. When they are all equilibrium states, the path can be plotted on a  $pV$ -diagram (Fig. 19.7a). Point 1 represents an initial state with pressure  $p_1$  and volume  $V_1$ , and point 2 represents a final state with pressure  $p_2$  and volume  $V_2$ . To pass from state 1 to state 2, we could keep the pressure constant at  $p_1$  while the system expands to volume  $V_2$  (point 3 in Fig. 19.7b), then reduce the pressure to  $p_2$  (probably by decreasing the temperature) while keeping the volume constant at  $V_2$  (to point 2 on the diagram). The work done by the system during this process is the area under the line  $1 \rightarrow 3$ ; no work is done during the constant-volume process  $3 \rightarrow 2$ . Or the system might traverse the path  $1 \rightarrow 4 \rightarrow 2$  (Fig. 19.7c); in that case the work is the area under the line  $4 \rightarrow 2$ , since no work is done during the constant-volume process  $1 \rightarrow 4$ . The smooth curve from 1 to 2 is another possibility (Fig. 19.7d), and the work for this path is different from that for either of the other paths.

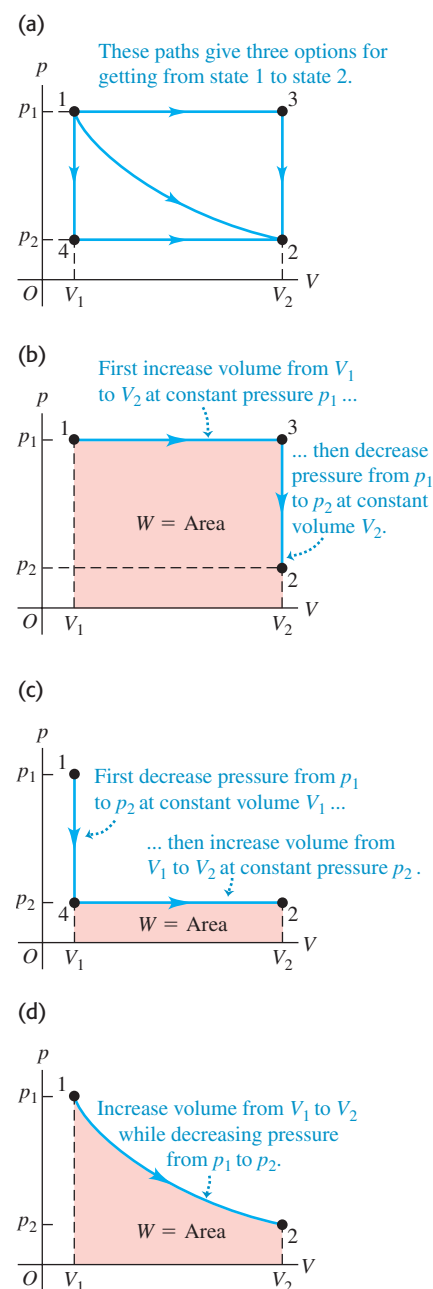
We conclude that the *work done by the system depends not only on the initial and final states, but also on the intermediate states—that is, on the path*. Furthermore, we can take the system through a series of states forming a closed loop, such as  $1 \rightarrow 3 \rightarrow 2 \rightarrow 4 \rightarrow 1$ . In this case the final state is the same as the initial state, but the total work done by the system is *not* zero. (In fact, it is represented on the graph by the area enclosed by the loop; can you prove that? See Exercise 19.7.) It follows that it doesn't make sense to talk about the amount of work contained in a system. In a particular state, a system may have definite values of the state coordinates  $p$ ,  $V$ , and  $T$ , but it wouldn't make sense to say that it has a definite value of  $W$ .

#### Heat Added in a Thermodynamic Process

Like work, the *heat* added to a thermodynamic system when it undergoes a change of state depends on the path from the initial state to the final state. Here's an example. Suppose we want to change the volume of a certain quantity of an ideal gas from 2.0 L to 5.0 L while keeping the temperature constant at  $T = 300$  K. Figure 19.8 shows two different ways in which we can do this. In Fig. 19.8a the gas is contained in a cylinder with a piston, with an initial volume of 2.0 L. We let the gas expand slowly, supplying heat from the electric heater to keep the temperature at 300 K. After expanding in this slow, controlled, isothermal manner, the gas reaches its final volume of 5.0 L; it absorbs a definite amount of heat in the process.

Figure 19.8b shows a different process leading to the same final state. The container is surrounded by insulating walls and is divided by a thin, breakable partition into two compartments. The lower part has volume 2.0 L and the upper part has volume 3.0 L. In the lower compartment we place the same amount of the same gas as in Fig. 19.8a, again at  $T = 300$  K. The initial state is the same as before. Now we break the partition; the gas undergoes a rapid, uncontrolled expansion, with no heat passing through the insulating walls. The final volume is

**19.7** The work done by a system during a transition between two states depends on the path chosen.



5.0 L, the same as in Fig. 19.8a. The gas does no work during this expansion because it doesn't push against anything that moves. This uncontrolled expansion of a gas into vacuum is called a **free expansion**; we will discuss it further in Section 19.6.

Experiments have shown that when an ideal gas undergoes a free expansion, there is no temperature change. Therefore the final state of the gas is the same as in Fig. 19.8a. The intermediate states (pressures and volumes) during the transition from state 1 to state 2 are entirely different in the two cases; Figs. 19.8a and 19.8b represent two different paths connecting the same states 1 and 2. For the path in Fig. 19.8b, no heat is transferred into the system, and the system does no work. Like work, *heat depends not only on the initial and final states but also on the path*.

Because of this path dependence, it would not make sense to say that a system "contains" a certain quantity of heat. To see this, suppose we assign an arbitrary value to the "heat in a body" in some reference state. Then presumably the "heat in the body" in some other state would equal the heat in the reference state plus the heat added when the body goes to the second state. But that's ambiguous, as we have just seen; the heat added depends on the *path* we take from the reference state to the second state. We are forced to conclude that there is *no* consistent way to define "heat in a body"; it is not a useful concept.

While it doesn't make sense to talk about "work in a body" or "heat in a body," it *does* make sense to speak of the amount of *internal energy* in a body. This important concept is our next topic.

**Test Your Understanding of Section 19.3** The system described in Fig. 19.7a undergoes four different thermodynamic processes. Each process is represented in a  $pV$ -diagram as a straight line from the initial state to the final state. (These processes are different from those shown in the  $pV$ -diagrams of Fig. 19.7.) Rank the processes in order of the amount of work done by the system, from the most positive to the most negative. (i)  $1 \rightarrow 2$ ; (ii)  $2 \rightarrow 1$ ; (iii)  $3 \rightarrow 4$ ; (iv)  $4 \rightarrow 3$ .

### 19.4 Internal Energy and the First Law of Thermodynamics

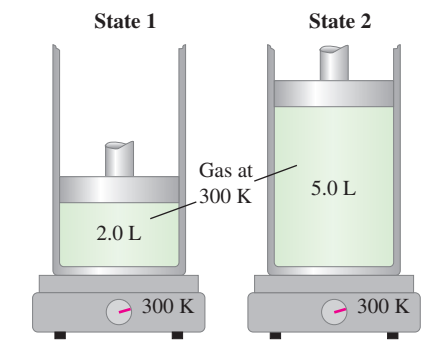
Internal energy is one of the most important concepts in thermodynamics. In Section 7.3, when we discussed energy changes for a body sliding with friction, we stated that warming a body increased its internal energy and that cooling the body decreased its internal energy. But what *is* internal energy? We can look at it in various ways; let's start with one based on the ideas of mechanics. Matter consists of atoms and molecules, and these are made up of particles having kinetic and potential energies. We *tentatively* define the **internal energy** of a system as the sum of the kinetic energies of all of its constituent particles, plus the sum of all the potential energies of interaction among these particles.

**CAUTION Is it internal?** Note that internal energy does *not* include potential energy arising from the interaction between the system and its surroundings. If the system is a glass of water, placing it on a high shelf increases the gravitational potential energy arising from the interaction between the glass and the earth. But this has no effect on the interaction between the molecules of the water, and so the internal energy of the water does not change.

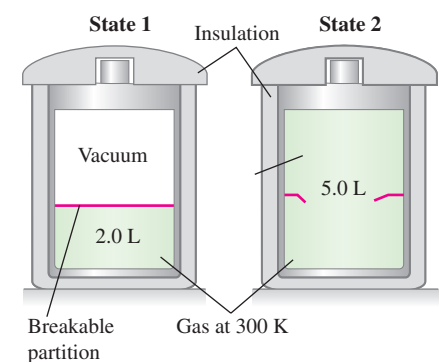
We use the symbol  $U$  for internal energy. (We used this same symbol in our study of mechanics to represent potential energy. You may have to remind yourself occasionally that  $U$  has a different meaning in thermodynamics.) During a change of state of the system the internal energy may change from an initial value  $U_1$  to a final value  $U_2$ . We denote the change in internal energy as  $\Delta U = U_2 - U_1$ .

**19.8** (a) Slow, controlled isothermal expansion of a gas from an initial state 1 to a final state 2 with the same temperature but lower pressure. (b) Rapid, uncontrolled expansion of the same gas starting at the same state 1 and ending at the same state 2.

(a) System does work on piston; hot plate adds heat to system ( $W > 0$  and  $Q > 0$ ).



(b) System does no work; no heat enters or leaves system ( $W = 0$  and  $Q = 0$ ).



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8.6 Heat, Internal Energy, and First Law of Thermodynamics



We know that heat transfer is energy transfer. When we add a quantity of heat  $Q$  to a system and the system does no work during the process, the internal energy increases by an amount equal to  $Q$ ; that is,  $\Delta U = Q$ . When a system does work  $W$  by expanding against its surroundings and no heat is added during the process, energy leaves the system and the internal energy decreases. That is, when  $W$  is positive,  $\Delta U$  is negative, and vice versa. So  $\Delta U = -W$ . When *both* heat transfer and work occur, the *total* change in internal energy is

$$U_2 - U_1 = \Delta U = Q - W \quad (\text{first law of thermodynamics}) \quad (19.4)$$

We can rearrange this to the form

$$Q = \Delta U + W \quad (19.5)$$

The message of Eq. (19.5) is that in general, when heat  $Q$  is added to a system, some of this added energy remains within the system, changing its internal energy by an amount  $\Delta U$ ; the remainder leaves the system again as the system does work  $W$  against its surroundings. Because  $W$  and  $Q$  may be positive, negative, or zero,  $\Delta U$  can be positive, negative, or zero for different processes (Fig. 19.9).

Equation (19.4) or (19.5) is the **first law of thermodynamics**. It is a generalization of the principle of conservation of energy to include energy transfer through heat as well as mechanical work. As you will see in later chapters, this principle can be extended to ever-broader classes of phenomena by identifying additional forms of energy and energy transfer. In every situation in which it seems that the total energy in all known forms is not conserved, it has been possible to identify a new form of energy such that the total energy, including the new form, *is* conserved. There is energy associated with electric fields, with magnetic fields, and, according to the theory of relativity, even with mass itself.

### Understanding the First Law of Thermodynamics

At the beginning of this discussion we tentatively defined internal energy in terms of microscopic kinetic and potential energies. This has drawbacks, however. Actually *calculating* internal energy in this way for any real system would be hopelessly complicated. Furthermore, this definition isn't an *operational* one because it doesn't describe how to determine internal energy from physical quantities that we can measure directly.

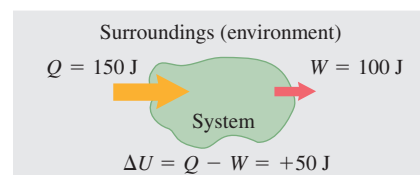
So let's look at internal energy in another way. Starting over, we define the *change* in internal energy  $\Delta U$  during any change of a system as the quantity given by Eq. (19.4),  $\Delta U = Q - W$ . This is an operational definition because we can measure  $Q$  and  $W$ . It does not define  $U$  itself, only  $\Delta U$ . This is not a shortcoming because we can *define* the internal energy of a system to have a specified value in some reference state, and then use Eq. (19.4) to define the internal energy in any other state. This is analogous to our treatment of potential energy in Chapter 7, in which we arbitrarily defined the potential energy of a mechanical system to be zero at a certain position.

This new definition trades one difficulty for another. If we define  $\Delta U$  by Eq. (19.4), then when the system goes from state 1 to state 2 by two different paths, how do we know that  $\Delta U$  is the same for the two paths? We have already seen that  $Q$  and  $W$  are, in general, *not* the same for different paths. If  $\Delta U$ , which equals  $Q - W$ , is also path dependent, then  $\Delta U$  is ambiguous. If so, the concept of internal energy of a system is subject to the same criticism as the erroneous concept of quantity of heat in a system, as we discussed at the end of Section 19.3.

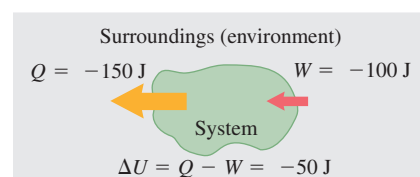
The only way to answer this question is through *experiment*. For various materials we measure  $Q$  and  $W$  for various changes of state and various paths to learn whether  $\Delta U$  is or is not path dependent. The results of many such investigations are clear and unambiguous: While  $Q$  and  $W$  depend on the path,  $\Delta U = Q - W$  is *independent of path*. The change in internal energy of a system

**19.9** In a thermodynamic process, the internal energy  $U$  of a system may (a) increase ( $\Delta U > 0$ ), (b) decrease ( $\Delta U < 0$ ), or (c) remain the same ( $\Delta U = 0$ ).

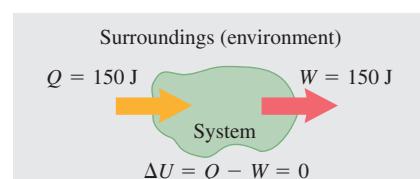
(a) More heat is added to system than system does work: Internal energy of system increases.



(b) More heat flows out of system than work is done: Internal energy of system decreases.



(c) Heat added to system equals work done by system: Internal energy of system unchanged.



during any thermodynamic process depends only on the initial and final states, not on the path leading from one to the other.

Experiment, then, is the ultimate justification for believing that a thermodynamic system in a specific state has a unique internal energy that depends only on that state. An equivalent statement is that the internal energy  $U$  of a system is a function of the state coordinates  $p$ ,  $V$ , and  $T$  (actually, any two of these, since the three variables are related by the equation of state).

To say that the first law of thermodynamics, given by Eq. (19.4) or (19.5), represents conservation of energy for thermodynamic processes is correct, as far as it goes. But an important *additional* aspect of the first law is the fact that internal energy depends only on the state of a system (Fig. 19.10). In changes of state, the change in internal energy is independent of the path.

All this may seem a little abstract if you are satisfied to think of internal energy as microscopic mechanical energy. There's nothing wrong with that view, and we will make use of it at various times during our discussion. But in the interest of precise *operational* definitions, internal energy, like heat, can and must be defined in a way that is independent of the detailed microscopic structure of the material.

### Cyclic Processes and Isolated Systems

Two special cases of the first law of thermodynamics are worth mentioning. A process that eventually returns a system to its initial state is called a *cyclic process*. For such a process, the final state is the same as the initial state, and so the *total* internal energy change must be zero. Then

$$U_2 = U_1 \quad \text{and} \quad Q = W$$

If a net quantity of work  $W$  is done by the system during this process, an equal amount of energy must have flowed into the system as heat  $Q$ . But there is no reason either  $Q$  or  $W$  individually has to be zero (Fig. 19.11).

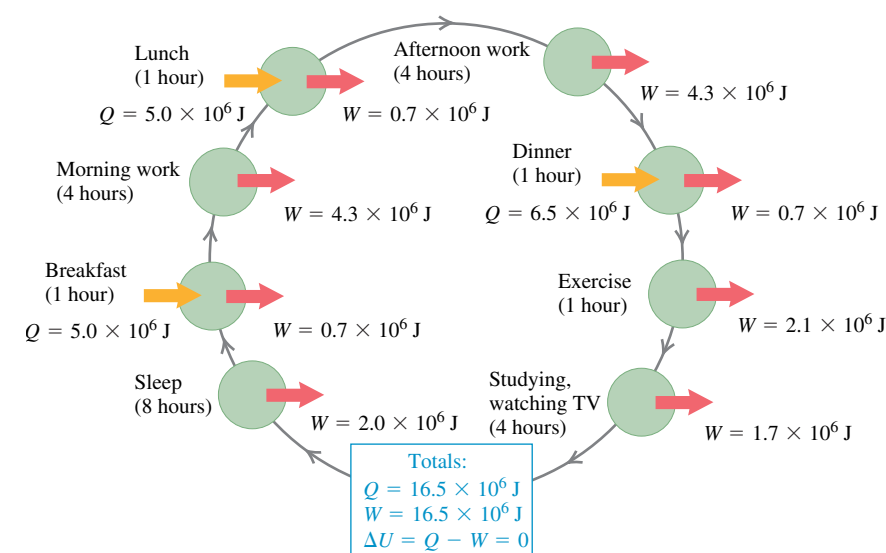
Another special case occurs in an *isolated system*, one that does no work on its surroundings and has no heat flow to or from its surroundings. For any process taking place in an isolated system,

$$W = Q = 0$$

and therefore

$$U_2 = U_1 = \Delta U = 0$$

In other words, *the internal energy of an isolated system is constant*.



**19.10** The internal energy of a cup of coffee depends on just its thermodynamic state—how much water and ground coffee it contains, and what its temperature is. It does not depend on the history of how the coffee was prepared—that is, the thermodynamic path that led to its current state.



**19.11** Every day, your body (a thermodynamic system) goes through a cyclic thermodynamic process like this one. Heat  $Q$  is added by metabolizing food, and your body does work  $W$  in breathing, walking, and other activities. If you return to the same state at the end of the day,  $Q = W$  and the net change in your internal energy is zero.

### Problem-Solving Strategy 19.1 The First Law of Thermodynamics



**IDENTIFY** *the relevant concepts:* The first law of thermodynamics is the statement of the law of conservation of energy in its most general form. You can apply it to *any* situation in which you are concerned with changes in the internal energy of a system, with heat flow into or out of a system, and/or with work done by or on a system.

**SET UP** *the problem* using the following steps:

- Carefully define what the thermodynamic system is.
- The first law of thermodynamics focuses on systems that go through thermodynamic processes. Some problems involve processes with more than one step, so make sure that you identify the initial and final states for each step.
- Identify the known quantities and the target variables.
- Check whether you have enough equations. The first law,  $\Delta U = Q - W$ , can be applied just once to each step in a thermodynamic process, so you will often need additional equations. These often include Eq. (19.2) for the work done in a volume change and the equation of state of the material that makes up the thermodynamic system (for an ideal gas,  $pV = nRT$ ).

**EXECUTE** *the solution* as follows:

- You shouldn't be surprised to be told that consistent units are essential. If  $p$  is in Pa and  $V$  in  $\text{m}^3$ , then  $W$  is in joules. Otherwise, you may want to convert the pressure and volume units into units of Pa and  $\text{m}^3$ . If a heat capacity is given in terms of calories, usually the simplest procedure is to convert it to joules. Be especially careful with moles. When you use  $n = m_{\text{total}}/M$  to

convert between total mass and number of moles, remember that if  $m_{\text{total}}$  is in kilograms,  $M$  must be in *kilograms* per mole. The usual units for  $M$  are *grams* per mole; be careful!

- The internal energy change  $\Delta U$  in any thermodynamic process or series of processes is independent of the path, whether the substance is an ideal gas or not. This point is of the utmost importance in the problems in this chapter and the next. Sometimes you will be given enough information about one path between the given initial and final states to calculate  $\Delta U$  for that path. Since  $\Delta U$  is the same for every possible path between the same two states, you can then relate the various energy quantities for other paths.
- When a process consists of several distinct steps, it often helps to make a table showing  $Q$ ,  $W$ , and  $\Delta U$  for each step. Put these quantities for each step on a different line, and arrange them so the  $Q$ 's,  $W$ 's, and  $\Delta U$ 's form columns. Then you can apply the first law to each line; in addition, you can add each column and apply the first law to the sums. Do you see why?
- Using steps 1–3, solve for the target variables.

**EVALUATE** *your answer:* Check your results for reasonableness. In particular, make sure that each of your answers has the correct algebraic sign. Remember that a positive  $Q$  means that heat flows *into* the system, and a negative  $Q$  means that heat flows *out of* the system. A positive  $W$  means that work is done *by* the system on its environment, while a negative  $W$  means that work is done *on* the system by its environment.

### Example 19.2 Working off your dessert

You propose to eat a 900-calorie hot fudge sundae (with whipped cream) and then run up several flights of stairs to work off the energy you have taken in. How high do you have to climb? Assume that your mass is 60.0 kg.

#### SOLUTION

**IDENTIFY:** Eating the hot fudge sundae corresponds to a heat flow into your body, and running up stairs means that you do work. We can relate these quantities using the first law of thermodynamics.

**SET UP:** The system consists of your body. We are given that 900 food calories of heat flow into your body. The purpose of running up the stairs is to make sure that the final state of the system is the same as the initial state (no fatter, no leaner), so there is no net change in internal energy:  $\Delta U = 0$ . The work you must do to raise your mass  $m$  a height  $h$  is  $W = mgh$ ; our target variable is  $h$ .

**EXECUTE:** Using the first law of thermodynamics,  $\Delta U = 0 = Q - W$ , so  $W = Q$ : The work that you do running up the stairs

must just equal the heat input from the sundae. From  $W = mgh$ , the height that you climb is  $h = Q/mg$ . Before substituting values into this equation, we first convert units: One food-value calorie is 1 kcal = 1000 cal = 4190 J (to three significant figures), so

$$Q = 900 \text{ kcal} (4190 \text{ J/1 kcal}) = 3.77 \times 10^6 \text{ J}$$

Then

$$h = \frac{Q}{mg} = \frac{3.77 \times 10^6 \text{ J}}{(60.0 \text{ kg})(9.80 \text{ m/s}^2)} = 6410 \text{ m} \quad (\text{about } 21,000 \text{ ft})$$

**EVALUATE:** Good luck! We have assumed 100% efficiency in the conversion of food energy into mechanical work; this isn't very realistic. As a result, the actual distance you would have to climb is quite a bit less than we have calculated. We'll talk more about efficiency later.

### Example 19.3 A cyclic process

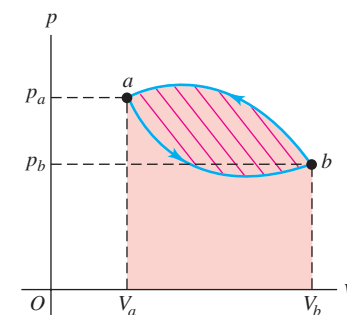
Figure 19.12 shows a  $pV$ -diagram for a *cyclic* process, one in which the initial and final states are the same. It starts at point  $a$  and proceeds counterclockwise in the  $pV$ -diagram to point  $b$ , then back to  $a$ , and the total work is  $W = -500 \text{ J}$ . (a) Why is the work negative? (b) Find the change in internal energy and the heat added during this process.

#### SOLUTION

**IDENTIFY:** This problem asks us to relate the change in internal energy, the heat added, and the work done in a thermodynamic process. Hence we can apply the first law of thermodynamics.

$a \rightarrow b$

**19.12** The net work done by the system in the process  $aba$  is  $-500 \text{ J}$ . What would it have been if the process had proceeded clockwise in this  $pV$ -diagram?



**SET UP:** The thermodynamic process here has two steps: via the lower curve in Fig. 19.12 and  $b \rightarrow a$  via the upper curve. But note that the questions in (a) and (b) are about the *entire* cyclic process  $a \rightarrow b \rightarrow a$  (around the loop in Fig. 19.12).

### Example 19.4 Comparing thermodynamic processes

A series of thermodynamic processes is shown in the  $pV$ -diagram of Fig. 19.13. In process  $ab$ , 150 J of heat is added to the system, and in process  $bd$ , 600 J of heat is added. Find (a) the internal energy change in process  $ab$ ; (b) the internal energy change in process  $abd$  (shown in light blue); and (c) the total heat added in process  $acd$  (shown in dark blue).

#### SOLUTION

**IDENTIFY:** In each process we use  $\Delta U = Q - W$  to determine the desired quantity.

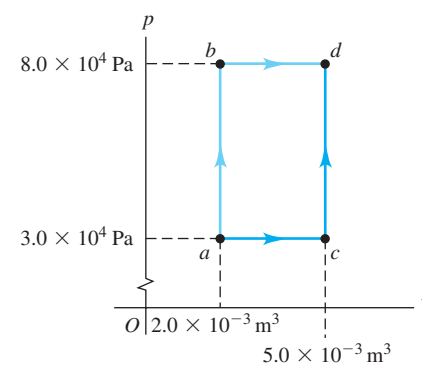
**SET UP:** We are given  $Q_{ab} = +150 \text{ J}$  and  $Q_{bd} = +600 \text{ J}$  (both values are positive because heat is *added* to the system). Our target variables are (a)  $\Delta U_{ab}$ , (b)  $\Delta U_{abd}$ , and (c)  $Q_{acd}$ .

**EXECUTE:** (a) No volume change occurs during process  $ab$ , so  $W_{ab} = 0$  and  $\Delta U_{ab} = Q_{ab} = 150 \text{ J}$ .

(b) Process  $bd$  occurs at constant pressure, so the work done by the system during this expansion is

$$\begin{aligned} W_{bd} &= p(V_2 - V_1) \\ &= (8.0 \times 10^4 \text{ Pa})(5.0 \times 10^{-3} \text{ m}^3 - 2.0 \times 10^{-3} \text{ m}^3) \\ &= 240 \text{ J} \end{aligned}$$

**19.13** A  $pV$ -diagram showing the various thermodynamic processes.



**EXECUTE:** (a) The work done equals the area under the curve, with the area taken as positive for increasing volume and negative for decreasing volume. The area under the lower curve from  $a$  to  $b$  is positive, but it is smaller than the absolute value of the negative area under the upper curve from  $b$  back to  $a$ . Therefore the net area (the area enclosed by the path, shown with red stripes) and the work are negative. In other words, 500 more joules of work is done *on* the system than *by* the system.

(b) For this and any other cyclic process (in which the beginning and end points are the same),  $\Delta U = 0$ , so  $Q = W = -500 \text{ J}$ . That is, 500 joules of heat must come *out of* the system.

**EVALUATE:** This example illustrates a general principle about  $pV$ -diagrams of cyclic processes: The total work is positive if the process goes around the cycle in a clockwise direction, and the total work is negative if the process goes around the cycle in a counterclockwise direction (as in Fig. 19.12).

The total work for process  $abd$  is

$$W_{abd} = W_{ab} + W_{bd} = 0 + 240 \text{ J} = 240 \text{ J}$$

and the total heat is

$$Q_{abd} = Q_{ab} + Q_{bd} = 150 \text{ J} + 600 \text{ J} = 750 \text{ J}$$

Applying Eq. (19.4) to  $abd$ , we find

$$\Delta U_{abd} = Q_{abd} - W_{abd} = 750 \text{ J} - 240 \text{ J} = 510 \text{ J}$$

(c) Because  $\Delta U$  is independent of path, the internal energy change is the same for path  $acd$  as for path  $abd$ ; that is,

$$\Delta U_{acd} = \Delta U_{abd} = 510 \text{ J}$$

The total work for the path  $acd$  is

$$\begin{aligned} W_{acd} &= W_{ac} + W_{cd} = p(V_2 - V_1) + 0 \\ &= (3.0 \times 10^4 \text{ Pa})(5.0 \times 10^{-3} \text{ m}^3 - 2.0 \times 10^{-3} \text{ m}^3) \\ &= 90 \text{ J} \end{aligned}$$

Now we apply Eq. (19.5) to process  $acd$ :

$$Q_{acd} = \Delta U_{acd} + W_{acd} = 510 \text{ J} + 90 \text{ J} = 600 \text{ J}$$

Here is a tabulation of the various quantities:

Step	$Q$	$W$	$\Delta U = Q - W$	Step	$Q$	$W$	$\Delta U = Q - W$
$ab$	150 J	0 J	150 J	$ac$	?	90 J	?
$bd$	600 J	240 J	360 J	$cd$	?	0 J	?
$abd$	750 J	240 J	510 J	$acd$	600 J	90 J	510 J

**EVALUATE:** We see that although  $\Delta U$  is the same (510 J) for  $abd$  and  $acd$ ,  $W$  (240 J versus 90 J) and  $Q$  (750 J versus 600 J) are quite different for the two processes.

Notice that we don't have enough information to find  $Q$  or  $\Delta U$  for the processes  $ac$  and  $cd$ . We were nonetheless able to analyze the composite process  $acd$  by comparing it to the process  $abd$ , which has the same initial and final states and for which we have more complete information.



**Example 19.5 Thermodynamics of boiling water**

One gram of water ( $1 \text{ cm}^3$ ) becomes  $1671 \text{ cm}^3$  of steam when boiled at a constant pressure of  $1 \text{ atm}$  ( $1.013 \times 10^5 \text{ Pa}$ ). The heat of vaporization at this pressure is  $L_v = 2.256 \times 10^6 \text{ J/kg}$ . Compute (a) the work done by the water when it vaporizes and (b) its increase in internal energy.

**SOLUTION**

**IDENTIFY:** The new feature of this problem is that the heat added causes the system (water) to change phase from liquid to vapor. We can nonetheless apply the first law of thermodynamics, which is true for thermodynamic processes of all kinds.

**SET UP:** The water is boiled at a constant pressure, so we can calculate the work  $W$  done by the water using Eq. (19.3). We can calculate the heat  $Q$  added to the water from the mass and the heat of vaporization, and we can then find the internal energy change using  $\Delta U = Q - W$ .

**EXECUTE:** (a) From Eq. (19.3), the work done by the vaporizing water is

$$\begin{aligned} W &= p(V_2 - V_1) \\ &= (1.013 \times 10^5 \text{ Pa})(1671 \times 10^{-6} \text{ m}^3 - 1 \times 10^{-6} \text{ m}^3) \\ &= 169 \text{ J} \end{aligned}$$

(b) From Eq. (17.20), the heat added to the water to vaporize it is

$$Q = mL_v = (10^{-3} \text{ kg})(2.256 \times 10^6 \text{ J/kg}) = 2256 \text{ J}$$

From the first law of thermodynamics, Eq. (19.4), the change in internal energy is

$$\Delta U = Q - W = 2256 \text{ J} - 169 \text{ J} = 2087 \text{ J}$$

**EVALUATE:** To vaporize 1 gram of water, we have to add 2256 J of heat. Most (2087 J) of this added energy remains in the system as an increase in internal energy. The remaining 169 J leaves the system again as it does work against the surroundings while expanding from liquid to vapor. The increase in internal energy is associated mostly with the intermolecular forces that hold the molecules together in the liquid state. These forces are attractive, so the associated potential energies are greater after work has been done to pull the molecules apart, forming the vapor state. It's like increasing gravitational potential energy by pulling an elevator farther from the center of the earth.

**Infinitesimal Changes of State**

In the preceding examples the initial and final states differ by a finite amount. Later we will consider *infinitesimal* changes of state in which a small amount of heat  $dQ$  is added to the system, the system does a small amount of work  $dW$ , and its internal energy changes by an amount  $dU$ . For such a process we state the first law in differential form as

$$dU = dQ - dW \quad \text{(first law of thermodynamics, infinitesimal process)} \quad (19.6)$$

For the systems we will discuss, the work  $dW$  is given by  $dW = p dV$ , so we can also state the first law as

$$dU = dQ - p dV \quad (19.7)$$

**Test Your Understanding of Section 19.4** Rank the following thermodynamic processes according to the change in internal energy in each process, from most positive to most negative. (i) As you do 250 J of work on a system, it transfers 250 J of heat to its surroundings; (ii) as you do 250 J of work on a system, it absorbs 250 J of heat from its surroundings; (iii) as a system does 250 J of work on you, it transfers 250 J of heat to its surroundings; (iv) as a system does 250 J of work on you, it absorbs 250 J of heat from its surroundings.

**19.5 Kinds of Thermodynamic Processes**

In this section we describe four specific kinds of thermodynamic processes that occur often in practical situations. These can be summarized briefly as “no heat transfer” or *adiabatic*, “constant volume” or *isochoric*, “constant pressure” or *isobaric*, and “constant temperature” or *isothermal*. For some of these processes we can use a simplified form of the first law of thermodynamics.

**Adiabatic Process**

An **adiabatic process** (pronounced “ay-dee-ah-bat-ic”) is defined as one with no heat transfer into or out of a system;  $Q = 0$ . We can prevent heat flow either by surrounding the system with thermally insulating material or by carrying out the process so quickly that there is not enough time for appreciable heat flow. From the first law we find that for every adiabatic process,

$$U_2 - U_1 = \Delta U = -W \quad \text{(adiabatic process)} \quad (19.8)$$

When a system expands adiabatically,  $W$  is positive (the system does work on its surroundings), so  $\Delta U$  is negative and the internal energy decreases. When a system is *compressed* adiabatically,  $W$  is negative (work is done on the system by its surroundings) and  $U$  increases. In many (but not all) systems an increase of internal energy is accompanied by a rise in temperature, and a decrease in internal energy with a drop in temperature (Fig. 19.14).

The compression stroke in an internal-combustion engine is an approximately adiabatic process. The temperature rises as the air–fuel mixture in the cylinder is compressed. The expansion of the burned fuel during the power stroke is also an approximately adiabatic expansion with a drop in temperature. In Section 19.8 we'll consider adiabatic processes in an ideal gas.

**Isochoric Process**

An **isochoric process** (pronounced “eye-so-kor-ic”) is a *constant-volume* process. When the volume of a thermodynamic system is constant, it does no work on its surroundings. Then  $W = 0$  and

$$U_2 - U_1 = \Delta U = Q \quad \text{(isochoric process)} \quad (19.9)$$

In an isochoric process, all the energy added as heat remains in the system as an increase in internal energy. Heating a gas in a closed constant-volume container is an example of an isochoric process. The processes *ab* and *cd* in Example 19.4 are also examples of isochoric processes. (Note that there are types of work that do not involve a volume change. For example, we can do work on a fluid by stirring it. In some literature, “isochoric” is used to mean that no work of any kind is done.)

**Isobaric Process**

An **isobaric process** (pronounced “eye-so-bear-ic”) is a *constant-pressure* process. In general, none of the three quantities  $\Delta U$ ,  $Q$ , and  $W$  is zero in an isobaric process, but calculating  $W$  is easy nonetheless. From Eq. (19.3),

$$W = p(V_2 - V_1) \quad \text{(isobaric process)} \quad (19.10)$$

Example 19.5 concerns an isobaric process, boiling water at constant pressure (Fig. 19.15).

**Isothermal Process**

An **isothermal process** is a *constant-temperature* process. For a process to be isothermal, any heat flow into or out of the system must occur slowly enough that thermal equilibrium is maintained. In general, none of the quantities  $\Delta U$ ,  $Q$ , or  $W$  is zero in an isothermal process.

In some special cases the internal energy of a system depends *only* on its temperature, not on its pressure or volume. The most familiar system having this special property is an ideal gas, as we'll discuss in the next section. For such systems, if the temperature is constant, the internal energy is also constant;  $\Delta U = 0$  and  $Q = W$ . That is, any energy entering the system as heat  $Q$  must leave it again as work  $W$  done by the system. Example 19.1, involving an ideal gas, is an example of an isothermal process in which  $U$  is also constant. For most systems other than

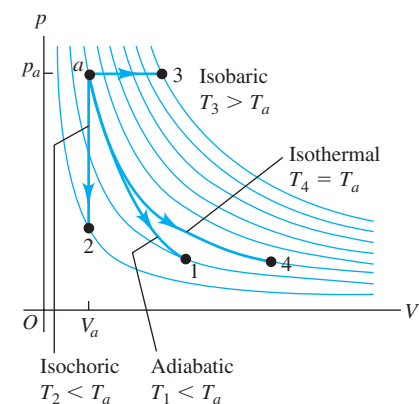
**19.14** When the cork is popped on a bottle of champagne, the pressurized gases inside the bottle expand into the outside air so rapidly that there is no time for them to exchange heat with their surroundings. Hence the expansion is adiabatic. As the expanding gases do work on their surroundings, their internal energy and temperature both drop; the lowered temperature makes water vapor condense and form a miniature cloud.



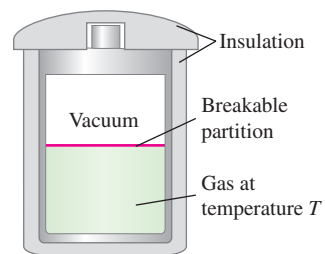
**19.15** Most cooking involves isobaric processes. That's because the air pressure above a saucepan or frying pan, or inside a microwave oven, remains essentially constant while the food is being heated.



**19.16** Four different processes for a constant amount of an ideal gas, all starting at state  $a$ . For the adiabatic process,  $Q = 0$ ; for the isochoric process,  $W = 0$ ; and for the isothermal process,  $\Delta U = 0$ . The temperature increases only during the isobaric expansion.



**19.17** The partition is broken (or removed) to start the free expansion of gas into the vacuum region.



ideal gases, the internal energy depends on pressure as well as temperature, so  $U$  may vary even when  $T$  is constant.

Figure 19.16 shows a  $pV$ -diagram for these four processes for a constant amount of an ideal gas. The path followed in an adiabatic process ( $a$  to 1) is called an **adiabat**. A vertical line (constant volume) is an **isochor**, a horizontal line (constant pressure) is an **isobar**, and a curve of constant temperature (shown as light blue lines in Fig. 19.16) is an **isotherm**.

**Test Your Understanding of Section 19.5** Which of the processes in Fig. 19.7 are isochoric? Which are isobaric? Is it possible to tell if any of the processes are isothermal or adiabatic?

## 19.6 Internal Energy of an Ideal Gas

We now show that for an ideal gas, the internal energy  $U$  depends only on temperature, not on pressure or volume. Let's think again about the free-expansion experiment described in Section 19.3. A thermally insulated container with rigid walls is divided into two compartments by a partition (Fig. 19.17). One compartment has a quantity of an ideal gas and the other is evacuated.

When the partition is removed or broken, the gas expands to fill both parts of the container. The gas does no work on its surroundings because the walls of the container don't move, and there is no heat flow through the insulation. So both  $Q$  and  $W$  are zero and the internal energy  $U$  is constant. This is true of any substance, whether it is an ideal gas or not.

Does the *temperature* change during a free expansion? Suppose it *does* change, while the internal energy stays the same. In that case we have to conclude that the internal energy depends on both the temperature and the volume or on both the temperature and the pressure, but certainly not on the temperature alone. But if  $T$  is constant during a free expansion, for which we know that  $U$  is constant even though both  $p$  and  $V$  change, then we have to conclude that  $U$  depends only on  $T$ , not on  $p$  or  $V$ .

Many experiments have shown that when a low-density gas undergoes a free expansion, its temperature *does not* change. Such a gas is essentially an ideal gas. The conclusion is:

**The internal energy of an ideal gas depends only on its temperature, not on its pressure or volume.**

This property, in addition to the ideal-gas equation of state, is part of the ideal-gas model. Make sure you understand that  $U$  depends only on  $T$  for an ideal gas, for we will make frequent use of this fact.

For nonideal gases, some temperature change occurs during free expansions, even though the internal energy is constant. This shows that the internal energy cannot depend *only* on temperature; it must depend on pressure as well. From the microscopic viewpoint, in which internal energy  $U$  is the sum of the kinetic and potential energies for all the particles that make up the system, this is not surprising. Nonideal gases usually have attractive intermolecular forces, and when molecules move farther apart, the associated potential energies increase. If the total internal energy is constant, the kinetic energies must decrease. Temperature is directly related to molecular *kinetic* energy, and for such a gas a free expansion is usually accompanied by a *drop* in temperature.

**Test Your Understanding of Section 19.6** Is the internal energy of a solid likely to be independent of its volume, as is the case for an ideal gas? Explain your reasoning. (Hint: See Fig. 18.20.)

## 19.7 Heat Capacities of an Ideal Gas

We defined specific heat and molar heat capacity in Section 17.5. We also remarked at the end of that section that the specific heat or molar heat capacity of a substance depends on the conditions under which the heat is added. It is usually easiest to measure the heat capacity of a gas in a closed container under constant-volume conditions. The corresponding heat capacity is the **molar heat capacity at constant volume**, denoted by  $C_V$ . Heat capacity measurements for solids and liquids are usually carried out in the atmosphere under constant atmospheric pressure, and we call the corresponding heat capacity the **molar heat capacity at constant pressure**,  $C_p$ . If neither  $p$  nor  $V$  is constant, we have an infinite number of possible heat capacities.

Let's consider  $C_V$  and  $C_p$  for an ideal gas. To measure  $C_V$ , we raise the temperature of an ideal gas in a rigid container with constant volume, neglecting its thermal expansion (Fig. 19.18a). To measure  $C_p$ , we let the gas expand just enough to keep the pressure constant as the temperature rises (Fig. 19.18b).

Why should these two molar heat capacities be different? The answer lies in the first law of thermodynamics. In a constant-volume temperature increase, the system does no work, and the change in internal energy  $\Delta U$  equals the heat added  $Q$ . In a constant-pressure temperature increase, on the other hand, the volume *must* increase; otherwise, the pressure (given by the ideal-gas equation of state  $p = nRT/V$ ) could not remain constant. As the material expands, it does an amount of work  $W$ . According to the first law,

$$Q = \Delta U + W \quad (19.11)$$

For a given temperature increase, the internal energy change  $\Delta U$  of an ideal gas has the same value no matter what the process (remember that the internal energy of an ideal gas depends only on temperature, not on pressure or volume). Equation (19.11) then shows that the heat input for a constant-pressure process must be *greater* than that for a constant-volume process because additional energy must be supplied to account for the work  $W$  done during the expansion. So  $C_p$  is greater than  $C_V$  for an ideal gas. The  $pV$ -diagram in Fig. 19.19 shows this relationship. For air,  $C_p$  is 40% greater than  $C_V$ .

For a very few substances (one of which is water between  $0^\circ\text{C}$  and  $4^\circ\text{C}$ ) the volume *decreases* during heating. In this case,  $W$  is negative, the heat input is *less* than in the constant-volume case, and  $C_p$  is *less* than  $C_V$ .

### Relating $C_p$ and $C_V$ for an Ideal Gas

We can derive a simple relationship between  $C_p$  and  $C_V$  for an ideal gas. First consider the constant-volume process. We place  $n$  moles of an ideal gas at temperature  $T$  in a constant-volume container. We place it in thermal contact with a hotter body; an infinitesimal quantity of heat  $dQ$  flows into the gas, and its temperature increases by an infinitesimal amount  $dT$ . By the definition of  $C_V$ , the molar heat capacity at constant volume,

$$dQ = nC_V dT \quad (19.12)$$

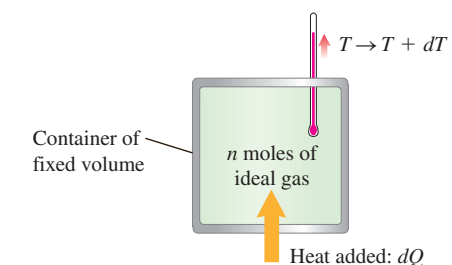
The pressure increases during this process, but the gas does no work ( $dW = 0$ ) because the volume is constant. The first law in differential form, Eq. (19.6), is  $dQ = dU + dW$ . Since  $dW = 0$ ,  $dQ = dU$  and Eq. (19.12) can also be written as

$$dU = nC_V dT \quad (19.13)$$

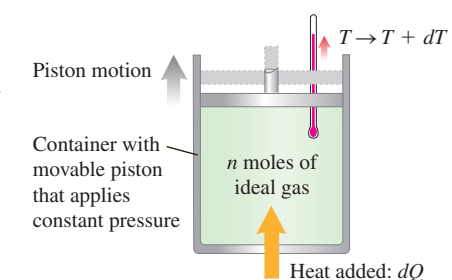
Now consider a constant-pressure process with the same temperature change  $dT$ . We place the same gas in a cylinder with a piston that we can allow to move just enough to maintain constant pressure, as shown in Fig. 19.18b. Again we bring the system into contact with a hotter body. As heat flows into the gas, it

**19.18** Measuring the molar heat capacity of an ideal gas (a) at constant volume and (b) at constant pressure.

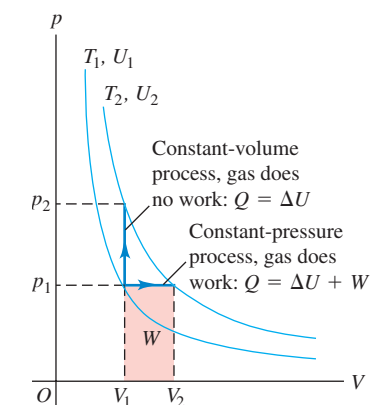
(a) Constant volume:  $dQ = nC_V dT$



(b) Constant pressure:  $dQ = nC_p dT$



**19.19** Raising the temperature of an ideal gas from  $T_1$  to  $T_2$  by a constant-volume or a constant-pressure process. For an ideal gas,  $U$  depends only on  $T$ , so  $\Delta U$  is the same for both processes. But for the constant-pressure process, more heat  $Q$  must be added to both increase  $U$  and do work  $W$ . Hence  $C_p > C_V$ .







- 8.7 Heat Capacity
- 8.8 Isochoric Process
- 8.9 Isobaric Process
- 8.10 Isothermmal Process

expands at constant pressure and does work. By the definition of  $C_p$ , the molar heat capacity at constant pressure, the amount of heat  $dQ$  entering the gas is

$$dQ = nC_p dT \quad (19.14)$$

The work  $dW$  done by the gas in this constant-pressure process is

$$dW = p dV$$

We can also express  $dW$  in terms of the temperature change  $dT$  by using the ideal-gas equation of state,  $pV = nRT$ . Because  $p$  is constant, the change in  $V$  is proportional to the change in  $T$ :

$$dW = p dV = nR dT \quad (19.15)$$

Now we substitute Eqs. (19.14) and (19.15) into the first law,  $dQ = dU + dW$ . We obtain

$$nC_p dT = dU + nR dT \quad (19.16)$$

Now here comes the crux of the calculation. The internal energy change  $dU$  for the constant-pressure process is again given by Eq. (19.13),  $dU = nC_V dT$ , *even though now the volume is not constant*. Why is this so? Recall the discussion of Section 19.6; one of the special properties of an ideal gas is that its internal energy depends *only* on temperature. Thus the *change* in internal energy during any process must be determined only by the temperature change. If Eq. (19.13) is valid for an ideal gas for one particular kind of process, it must be valid for an ideal gas for *every* kind of process with the same  $dT$ . So we may replace  $dU$  in Eq. (19.16) by  $nC_V dT$ :

$$nC_p dT = nC_V dT + nR dT$$

When we divide each term by the common factor  $n dT$ , we get

$$C_p = C_V + R \quad (\text{molar heat capacities of an ideal gas}) \quad (19.17)$$

As we predicted, the molar heat capacity of an ideal gas at constant pressure is *greater* than the molar heat capacity at constant volume; the difference is the gas constant  $R$ . (Of course,  $R$  must be expressed in the same units as  $C_p$  and  $C_V$ , such as  $\text{J/mol} \cdot \text{K}$ .)

We have used the ideal-gas model to derive Eq. (19.17), but it turns out to be obeyed to within a few percent by many real gases at moderate pressures. Measured values of  $C_p$  and  $C_V$  are given in Table 19.1 for several real gases at low pressures; the difference in most cases is approximately  $R = 8.314 \text{ J/mol} \cdot \text{K}$ .

The table also shows that the molar heat capacity of a gas is related to its molecular structure, as we discussed in Section 18.4. In fact, the first two columns of Table 19.1 are the same as Table 18.1.

**Table 19.1** Molar Heat Capacities of Gases at Low Pressure

Type of Gas	Gas	$C_V$ (J/mol · K)	$C_p$ (J/mol · K)	$C_p - C_V$ (J/mol · K)	$\gamma = C_p/C_V$
Monatomic	He	12.47	20.78	8.31	1.67
	Ar	12.47	20.78	8.31	1.67
Diatomic	H <sub>2</sub>	20.42	28.74	8.32	1.41
	N <sub>2</sub>	20.76	29.07	8.31	1.40
	O <sub>2</sub>	20.85	29.17	8.31	1.40
	CO	20.85	29.16	8.31	1.40
Polyatomic	CO <sub>2</sub>	28.46	36.94	8.48	1.30
	SO <sub>2</sub>	31.39	40.37	8.98	1.29
	H <sub>2</sub> S	25.95	34.60	8.65	1.33

## The Ratio of Heat Capacities

The last column of Table 19.1 lists the values of the dimensionless **ratio of heat capacities**,  $C_p/C_V$ , denoted by  $\gamma$  (the Greek letter gamma):

$$\gamma = \frac{C_p}{C_V} \quad (\text{ratio of heat capacities}) \quad (19.18)$$

(This is sometimes called the “ratio of specific heats.”) For gases,  $C_p$  is always greater than  $C_V$  and  $\gamma$  is always greater than unity. This quantity plays an important role in *adiabatic* processes for an ideal gas, which we will study in the next section.

We can use our kinetic-theory discussion of the molar heat capacity of an ideal gas (see Section 18.4) to predict values of  $\gamma$ . As an example, an ideal monatomic gas has  $C_V = \frac{3}{2}R$ . From Eq. (19.17),

$$C_p = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R$$

so

$$\gamma = \frac{C_p}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67$$

As Table 19.1 shows, this agrees well with values of  $\gamma$  computed from measured heat capacities. For most diatomic gases near room temperature,  $C_V = \frac{5}{2}R$ ,  $C_p = C_V + R = \frac{7}{2}R$ , and

$$\gamma = \frac{C_p}{C_V} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = 1.40$$

also in good agreement with measured values.

Here’s a final reminder: For an ideal gas the internal energy change in *any* process is given by  $\Delta U = nC_V \Delta T$ , *whether the volume is constant or not*. This relationship, which comes in handy in the following example, holds for other substances *only* when the volume is constant.

### Example 19.6 Cooling your room

A typical dorm room or bedroom contains about 2500 moles of air. Find the change in the internal energy of this much air when it is cooled from 23.9°C to 11.6°C at a constant pressure of 1.00 atm. Treat the air as an ideal gas with  $\gamma = 1.400$ .

#### SOLUTION

**IDENTIFY:** Our target variable is the change in the internal energy  $\Delta U$  of an ideal gas in a constant-pressure process. We are given the number of moles and the temperature change.

**SET UP:** Your first impulse may be to find  $C_p$  and then calculate  $Q$  from  $Q = nC_p \Delta T$ ; find the volume change and find the work done by the gas from  $W = p \Delta V$ ; then finally use the first law to find  $\Delta U$ . This would be perfectly correct, but there’s a much easier way. For an ideal gas the internal energy change is  $\Delta U = nC_V \Delta T$  for *every* process, *whether the volume is constant or not*. So all we have to do is find  $C_V$  and use this expression for  $\Delta U$ .

**EXECUTE:** We are given the value of  $\gamma$  for air, so we use Eqs. (19.17) and (19.18) to determine  $C_V$ :

$$\gamma = \frac{C_p}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V}$$

$$C_V = \frac{R}{\gamma - 1} = \frac{8.314 \text{ J/mol} \cdot \text{K}}{1.400 - 1} = 20.79 \text{ J/mol} \cdot \text{K}$$

Then

$$\Delta U = nC_V \Delta T$$

$$= (2500 \text{ mol})(20.79 \text{ J/mol} \cdot \text{K})(11.6^\circ\text{C} - 23.9^\circ\text{C})$$

$$= -6.39 \times 10^5 \text{ J}$$

**EVALUATE:** A room air conditioner must extract this much internal energy from the air in your room and transfer it to the air outside. We’ll discuss how this is done in Chapter 20.

**Test Your Understanding of Section 19.7** You want to cool a storage cylinder containing 10 moles of compressed gas from 30°C to 20°C. For which kind of gas would this be easiest? (i) a monatomic gas; (ii) a diatomic gas; (iii) a polyatomic gas; (iv) it would be equally easy for all of these.

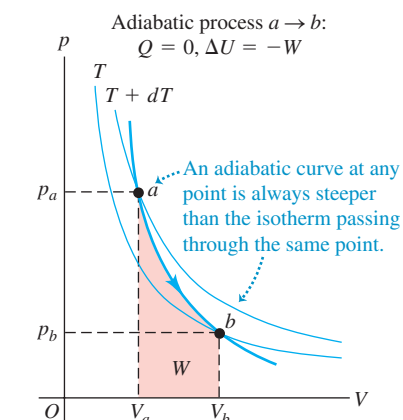


## 19.8 Adiabatic Processes for an Ideal Gas

An adiabatic process, defined in Section 19.5, is a process in which no heat transfer takes place between a system and its surroundings. Zero heat transfer is an idealization, but a process is approximately adiabatic if the system is well insulated or if the process takes place so quickly that there is not enough time for appreciable heat flow to occur.

In an adiabatic process,  $Q = 0$ , so from the first law,  $\Delta U = -W$ . An adiabatic process for an ideal gas is shown in the  $pV$ -diagram of Fig. 19.20. As the gas expands from volume  $V_a$  to  $V_b$ , it does positive work  $W$  on its environment, its internal energy decreases ( $\Delta U = -W < 0$ ), and its temperature drops from  $T + dT$  to  $T$ . (An adiabatic process is also shown in Fig. 19.16.)

**19.20** A  $pV$ -diagram of an adiabatic ( $Q = 0$ ) process for an ideal gas. As the gas expands from  $V_a$  to  $V_b$ , it does positive work  $W$  on its environment, its internal energy decreases ( $\Delta U = -W < 0$ ), and its temperature drops from  $T + dT$  to  $T$ . (An adiabatic process is also shown in Fig. 19.16.)



The air in the output hoses of air compressors used in gasoline stations, in paint-spraying equipment, and to fill scuba tanks is always warmer than the air entering the compressor; this is because the compression is rapid and hence approximately adiabatic. Adiabatic cooling occurs when you open a bottle of your favorite carbonated beverage. The gas just above the beverage surface expands rapidly in a nearly adiabatic process; the temperature of the gas drops so much that water vapor in the gas condenses, forming a miniature cloud (see Fig. 19.14).

**CAUTION** "Heating" and "cooling" without heat Keep in mind that when we talk about "adiabatic heating" and "adiabatic cooling," we really mean "raising the temperature" and "lowering the temperature," respectively. In an adiabatic process, the temperature change is due to work done by or on the system; there is *no* heat flow at all. ■

### Adiabatic Ideal Gas: Relating $V$ , $T$ , and $p$

We can derive a relationship between volume and temperature changes for an infinitesimal adiabatic process in an ideal gas. Equation (19.13) gives the internal energy change  $dU$  for any process for an ideal gas, adiabatic or not, so we have  $dU = nC_V dT$ . Also, the work done by the gas during the process is given by  $dW = p dV$ . Then, since  $dU = -dW$  for an adiabatic process, we have

$$nC_V dT = -p dV \quad (19.19)$$

To obtain a relationship containing only the volume  $V$  and temperature  $T$ , we eliminate  $p$  using the ideal-gas equation in the form  $p = nRT/V$ . Substituting this into Eq.(19.19) and rearranging, we get

$$nC_V dT = -\frac{nRT}{V} dV$$

$$\frac{dT}{T} + \frac{R}{C_V} \frac{dV}{V} = 0$$

The coefficient  $R/C_V$  can be expressed in terms of  $\gamma = C_p/C_V$ . We have

$$\frac{R}{C_V} = \frac{C_p - C_V}{C_V} = \frac{C_p}{C_V} - 1 = \gamma - 1$$

$$\frac{dT}{T} + (\gamma - 1) \frac{dV}{V} = 0 \quad (19.20)$$

Because  $\gamma$  is always greater than unity for a gas,  $(\gamma - 1)$  is always positive. This means that in Eq. (19.20),  $dV$  and  $dT$  always have opposite signs. An adiabatic expansion of an ideal gas ( $dV > 0$ ) always occurs with a drop in temperature ( $dT < 0$ ), and an adiabatic compression ( $dV < 0$ ) always occurs with a rise in temperature ( $dT > 0$ ); this confirms our earlier prediction.

For finite changes in temperature and volume we integrate Eq. (19.20), obtaining

$$\ln T + (\gamma - 1) \ln V = \text{constant}$$

$$\ln T + \ln V^{\gamma-1} = \text{constant}$$

$$\ln(TV^{\gamma-1}) = \text{constant}$$

and finally,

$$TV^{\gamma-1} = \text{constant} \quad (19.21)$$

Thus for an initial state  $(T_1, V_1)$  and a final state  $(T_2, V_2)$ ,

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \quad (\text{adiabatic process, ideal gas}) \quad (19.22)$$

Because we have used the ideal-gas equation in our derivation of Eqs. (19.21) and (19.22), the  $T$ 's must always be absolute (Kelvin) temperatures.

We can also convert Eq. (19.21) into a relationship between pressure and volume by eliminating  $T$ , using the ideal-gas equation in the form  $T = pV/nR$ . Substituting this into Eq. (19.21), we find

$$\frac{pV}{nR} V^{\gamma-1} = \text{constant}$$

or, because  $n$  and  $R$  are constant,

$$pV^\gamma = \text{constant} \quad (19.23)$$

For an initial state  $(p_1, V_1)$  and a final state  $(p_2, V_2)$ , Eq. (19.23) becomes

$$p_1 V_1^\gamma = p_2 V_2^\gamma \quad (\text{adiabatic process, ideal gas}) \quad (19.24)$$

We can also calculate the work done by an ideal gas during an adiabatic process. We know that  $Q = 0$  and  $W = -\Delta U$  for any adiabatic process. For an ideal gas,  $\Delta U = nC_V(T_2 - T_1)$ . If the number of moles  $n$  and the initial and final temperatures  $T_1$  and  $T_2$  are known, we have simply

$$W = nC_V(T_1 - T_2) \quad (\text{adiabatic process, ideal gas}) \quad (19.25)$$

We may also use  $pV = nRT$  in this equation to obtain

$$W = \frac{C_V}{R}(p_1 V_1 - p_2 V_2) = \frac{1}{\gamma - 1}(p_1 V_1 - p_2 V_2) \quad (\text{adiabatic process, ideal gas}) \quad (19.26)$$

(We used the result  $C_V = R/(\gamma - 1)$  from Example 19.6.) If the process is an expansion, the temperature drops,  $T_1$  is greater than  $T_2$ ,  $p_1 V_1$  is greater than  $p_2 V_2$ , and the work is positive, as we should expect. If the process is a compression, the work is negative.

Throughout this analysis of adiabatic processes we have used the ideal-gas equation of state, which is valid only for equilibrium states. Strictly speaking, our results are valid only for a process that is fast enough to prevent appreciable heat exchange with the surroundings (so that  $Q = 0$  and the process is adiabatic), yet slow enough that the system does not depart very much from thermal and mechanical equilibrium. Even when these conditions are not strictly satisfied, though, Eqs. (19.22), (19.24), and (19.26) give useful approximate results.

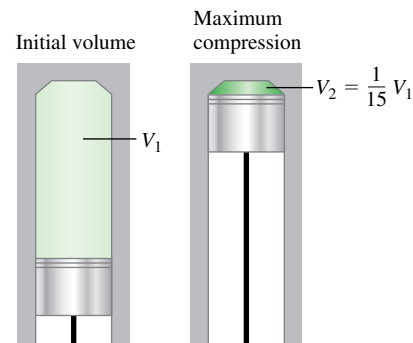
**Example 19.7** Adiabatic compression in a diesel engine

The compression ratio of a diesel engine is 15 to 1; this means that air in the cylinders is compressed to  $\frac{1}{15}$  of its initial volume (Fig. 19.21). If the initial pressure is  $1.01 \times 10^5$  Pa and the initial temperature is  $27^\circ\text{C}$  (300 K), find the final pressure and the temperature after compression. Air is mostly a mixture of diatomic oxygen and nitrogen; treat it as an ideal gas with  $\gamma = 1.40$ .

**SOLUTION**

**IDENTIFY:** Since this problem involves the adiabatic compression of an ideal gas, we can use the ideas of this section.

**19.21** Adiabatic compression of air in a cylinder of a diesel engine.



**SET UP:** We are given the initial pressure  $p_1 = 1.01 \times 10^5$  Pa and the initial temperature  $T_1 = 300$  K, and we are told that the ratio of initial and final volumes is  $V_1/V_2 = 15$ . We can find the final temperature  $T_2$  using Eq. (19.22) and the final pressure  $p_2$  using Eq. (19.24).

**EXECUTE:** From Eq. (19.22),

$$T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1} = (300 \text{ K})(15)^{0.40} = 886 \text{ K} = 613^\circ\text{C}$$

From Eq. (19.24),

$$p_2 = p_1 \left( \frac{V_1}{V_2} \right)^\gamma = (1.01 \times 10^5 \text{ Pa})(15)^{1.40} = 44.8 \times 10^5 \text{ Pa} = 44 \text{ atm}$$

**EVALUATE:** If the compression had been isothermal, the final pressure would have been 15 atm, but because the temperature also increases during an adiabatic compression, the final pressure is much greater. When fuel is injected into the cylinders near the end of the compression stroke, the high temperature of the air attained during compression causes the fuel to ignite spontaneously without the need for spark plugs.

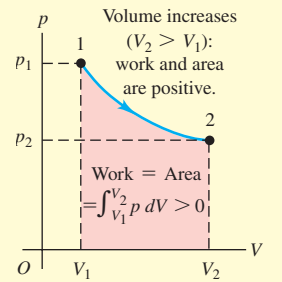
**Heat and work in thermodynamic processes:** A thermodynamic system has the potential to exchange energy with its surroundings by heat transfer or by mechanical work. When a system at pressure  $p$  changes volume from  $V_1$  to  $V_2$ , it does an amount of work  $W$  given by the integral of  $p$  with respect to volume. If the pressure is constant, the work done is equal to  $p$  times the change in volume. A negative value of  $W$  means that work is done on the system. (See Example 19.1.)

In any thermodynamic process, the heat added to the system and the work done by the system depend not only on the initial and final states, but also on the path (the series of intermediate states through which the system passes).

$$W = \int_{V_1}^{V_2} p \, dV \quad (19.2)$$

$$W = p(V_2 - V_1) \quad (19.3)$$

(constant pressure only)



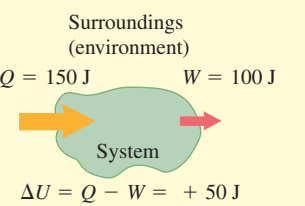
**The first law of thermodynamics:** The first law of thermodynamics states that when heat  $Q$  is added to a system while the system does work  $W$ , the internal energy  $U$  changes by an amount equal to  $Q - W$ . This law can also be expressed for an infinitesimal process. (See Examples 19.2, 19.3, and 19.5.)

The internal energy of any thermodynamic system depends only on its state. The change in internal energy in any process depends only on the initial and final states, not on the path. The internal energy of an isolated system is constant. (See Example 19.4.)

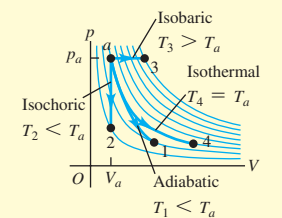
$$\Delta U = Q - W \quad (19.4)$$

$$dU = dQ - dW \quad (19.6)$$

(infinitesimal process)

**Important types of thermodynamic processes:**

- Adiabatic process: No heat transfer into or out of a system;  $Q = 0$ .
- Isochoric process: Constant volume;  $W = 0$ .
- Isobaric process: Constant pressure;  $W = p(V_2 - V_1)$ .
- Isothermal process: Constant temperature.

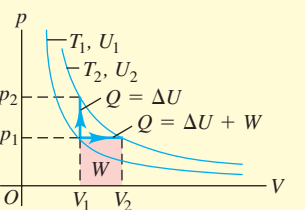


**Thermodynamics of ideal gases:** The internal energy of an ideal gas depends only on its temperature, not its pressure or volume. For other substances the internal energy generally depends on both pressure and temperature.

The molar heat capacities  $C_V$  and  $C_p$  of an ideal gas differ by  $R$ , the ideal gas constant. The dimensionless ratio of heat capacities,  $C_p/C_V$ , is denoted by  $\gamma$ . (See Example 19.6.)

$$C_p = C_V + R \quad (19.17)$$

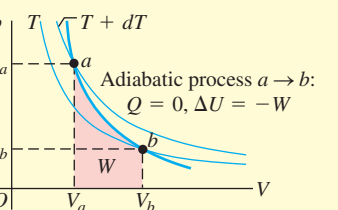
$$\gamma = \frac{C_p}{C_V} \quad (19.18)$$



**Adiabatic processes in ideal gases:** For an adiabatic process for an ideal gas, the quantities  $TV^{\gamma-1}$  and  $pV^\gamma$  are constant. The work done by an ideal gas during an adiabatic expansion can be expressed in terms of the initial and final values of temperature, or in terms of the initial and final values of pressure and volume. (See Examples 19.7 and 19.8.)

$$W = nC_V(T_1 - T_2) = \frac{C_V}{R}(p_1V_1 - p_2V_2) \quad (19.25)$$

$$= \frac{1}{\gamma - 1}(p_1V_1 - p_2V_2) \quad (19.26)$$

**Example 19.8** Work done in an adiabatic process

In Example 19.7, how much work does the gas do during the compression if the initial volume of the cylinder is  $1.00 \text{ L} = 1.00 \times 10^{-3} \text{ m}^3$ ? Assume that  $C_V$  for air is  $20.8 \text{ J/mol} \cdot \text{K}$  and  $\gamma = 1.40$ .

**SOLUTION**

**IDENTIFY:** Our target variable is the work done by the gas during the adiabatic compression. We are given the initial volume of the gas, and we know (from Example 19.7) the initial and final values of temperature and pressure.

**SET UP:** We use Eq. (19.25) to determine the work done. We are not given the number of moles  $n$ , but we can calculate it from the given information using the ideal-gas law  $pV = nRT$ .

**EXECUTE:** The number of moles is

$$n = \frac{p_1V_1}{RT_1} = \frac{(1.01 \times 10^5 \text{ Pa})(1.00 \times 10^{-3} \text{ m}^3)}{(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})} = 0.0405 \text{ mol}$$

and Eq. (19.25) gives

$$W = nC_V(T_1 - T_2) = (0.0405 \text{ mol})(20.8 \text{ J/mol} \cdot \text{K})(300 \text{ K} - 886 \text{ K}) = -494 \text{ J}$$

**EVALUATE:** We can check our result using Eq. (19.26), the alternative expression for work done by an ideal gas in an adiabatic process:

$$W = \frac{1}{\gamma - 1}(p_1V_1 - p_2V_2) = \frac{1}{1.40 - 1} \left[ (1.01 \times 10^5 \text{ Pa})(1.00 \times 10^{-3} \text{ m}^3) - (44.8 \times 10^5 \text{ Pa}) \left( \frac{1.00 \times 10^{-3} \text{ m}^3}{15} \right) \right] = -494 \text{ J}$$

The work is negative because the gas is compressed.

**Test Your Understanding of Section 19.8** You have four samples of ideal gas, each of which contains the same number of moles of gas and has the same initial temperature, volume, and pressure. You compress each sample to one-half of its initial volume. Rank the four samples in order from highest to lowest value of the final pressure. (i) a monatomic gas compressed isothermally; (ii) a monatomic gas compressed adiabatically; (iii) a diatomic gas compressed isothermally; (iv) a diatomic gas compressed adiabatically.





## Key Terms

thermodynamic system, 646  
 thermodynamic process, 647  
 path, 650  
 free expansion, 651  
 internal energy, 651  
 first law of thermodynamics, 652  
 adiabatic process, 657

isochoric process, 657  
 isobaric process, 657  
 isothermal process, 657  
 adiabat, 658  
 isochor, 658  
 isobar, 658  
 isotherm, 658

molar heat capacity at constant volume, 659  
 molar heat capacity at constant pressure, 659  
 ratio of heat capacities, 661

## Answer to Chapter Opening Question ?

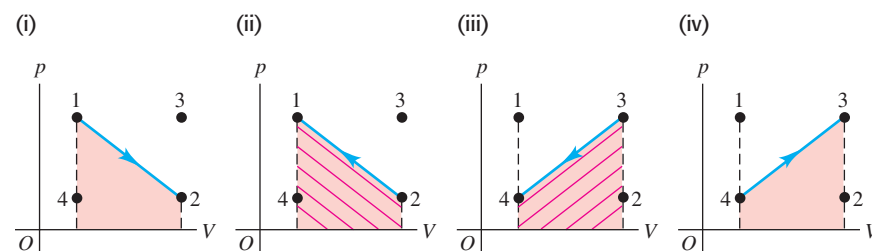
No. The work done by a gas as its volume changes from  $V_1$  to  $V_2$  is equal to the integral  $\int p dV$  between those two volume limits. If the volume of the gas contracts, the final volume  $V_2$  is less than the initial volume  $V_1$  and the gas does negative work. Propelling the locomotive requires that the gas do positive work, so the gas doesn't contribute to propulsion while contracting.

## Answers to Test Your Understanding Questions

**19.1** Answers: negative, positive, positive Heat flows out of the coffee, so  $Q_{\text{coffee}} < 0$ ; heat flows into the aluminum cup, so  $Q_{\text{aluminum}} > 0$ . In mechanics, we would say that negative work is done on the block, since the surface exerts a force on the block that opposes the block's motion. But in thermodynamics we use the opposite convention and say that  $W > 0$ , which means that positive work is done by the block on the surface.

**19.2** Answer: (ii) The work done in an expansion is represented by the area under the curve of pressure  $p$  versus volume  $V$ . In an isothermal expansion the pressure decreases as the volume increases, so the  $pV$ -diagram looks like Fig. 19.6a and the work done equals the shaded area under the blue curve from point 1 to point 2. If, however, the expansion is at constant pressure, the curve of  $p$  versus  $V$  would be the same as the dashed horizontal line at pressure  $p_2$  in Fig. 19.6a. The area under this dashed line is smaller than the area under the blue curve for an isothermal expansion, so less work is done in the constant-pressure expansion than in the isothermal expansion.

**19.3** Answer: (i) and (iv) (tie), (ii) and (iii) (tie) The accompanying figure shows the  $pV$ -diagrams for each of the four processes. The trapezoidal area under the curve, and hence the absolute value of the work, is the same in all four cases. In cases (i) and (iv) the volume increases, so the system does positive work as it expands against its surroundings. In cases (ii) and (iii) the volume decreases, so the system does negative work (shown by cross-hatching) as the surroundings push inward on it.



**19.4** Answer: (ii), (i) and (iv) (tie), (iii) In the expression  $\Delta U = Q - W$ ,  $Q$  is the heat added to the system and  $W$  is the work done by the system. If heat is transferred from the system to its surroundings,  $Q$  is negative; if work is done on the system,  $W$  is negative. Hence we have (i)  $Q = -250 \text{ J}$ ,  $W = -250 \text{ J}$ ,  $\Delta U = -250 \text{ J} - (-250 \text{ J}) = 0$ ; (ii)  $Q = 250 \text{ J}$ ,  $W = -250 \text{ J}$ ,  $\Delta U = 250 \text{ J} - (-250 \text{ J}) = 500 \text{ J}$ ; (iii)  $Q = -250 \text{ J}$ ,  $W = 250 \text{ J}$ ,  $\Delta U = -250 \text{ J} - 250 \text{ J} = -500 \text{ J}$ ; and (iv)  $Q = 250 \text{ J}$ ,  $W = 250 \text{ J}$ ,  $\Delta U = 250 \text{ J} - 250 \text{ J} = 0$ .

**19.5** Answers: 1  $\rightarrow$  4 and 3  $\rightarrow$  2 are isochoric; 1  $\rightarrow$  3 and 4  $\rightarrow$  2 are isobaric; no In a  $pV$ -diagram like those shown in Fig. 19.7, isochoric processes are represented by vertical lines (lines of constant volume) and isobaric processes are represented by horizontal lines (lines of constant pressure). The process 1  $\rightarrow$  2 in Fig. 19.7 is shown as a curved line, which superficially resembles the adiabatic and isothermal processes for an ideal gas in Fig. 19.16. Without more information we can't tell whether process 1  $\rightarrow$  2 is isothermal, adiabatic, or neither.

**19.6** Answer: no Using the model of a solid in Fig. 18.20, we can see that the internal energy of a solid does depend on its volume. Compressing the solid means compressing the "springs" between the atoms, thereby increasing their stored potential energy and hence the internal energy of the solid.

**19.7** Answer: (i) For a given number of moles  $n$  and a given temperature change  $\Delta T$ , the amount of heat that must be transferred out of a fixed volume of air is  $Q = nC_V\Delta T$ . Hence the amount of heat transfer required is least for the gas with the smallest value of  $C_V$ . From Table 19.1, the value of  $C_V$  is smallest for monatomic gases.

**19.8** Answer: (ii), (iv), (i) and (iii) (tie) Samples (i) and (iii) are compressed isothermally, so  $pV = \text{constant}$ . The volume of each sample decreases to one-half of its initial value, so the final pressure is twice the initial pressure. By contrast, samples (ii) and (iv) are compressed adiabatically, so  $pV^\gamma = \text{constant}$  and the pressure increases by a factor of  $2^\gamma$ . Sample (ii) is a monatomic gas for which  $\gamma = \frac{5}{3}$ , so its final pressure is  $2^{\frac{5}{3}} = 3.17$  times greater than the initial pressure. Sample (iv) is a diatomic gas for which  $\gamma = \frac{7}{5}$ , so its final pressure is greater than the initial pressure by a factor of  $2^{\frac{7}{5}} = 2.64$ .

## PROBLEMS

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## Discussion Questions

**Q19.1.** For the following processes, is the work done by the system (defined as the expanding or contracting gas) on the environment positive or negative? (a) expansion of the burned gasoline-air mixture in the cylinder of an automobile engine; (b) opening a bottle of champagne; (c) filling a scuba tank with compressed air; (d) partial crumpling of a sealed, empty water bottle, as you drive from the mountains down to sea level.

**Q19.2.** It is not correct to say that a body contains a certain amount of heat, yet a body can transfer heat to another body. How can a body give away something it does not have in the first place?

**Q19.3.** In which situation must you do more work: inflating a balloon at sea level or inflating the same balloon to the same volume at the summit of Mt. McKinley? Explain in terms of pressure and volume change.

**Q19.4.** If you are told the initial and final states of a system and the associated change in internal energy, can you determine whether the internal energy change was due to work or to heat transfer? Explain.

**Q19.5.** Discuss the application of the first law of thermodynamics to a mountaineer who eats food, gets warm and perspires a lot during a climb, and does a lot of mechanical work in raising herself to the summit. The mountaineer also gets warm during the descent. Is the source of this energy the same as the source during the ascent?

**Q19.6.** When ice melts at  $0^\circ\text{C}$ , its volume decreases. Is the internal energy change greater than, less than, or equal to the heat added? How can you tell?

**Q19.7.** You hold an inflated balloon over a hot air vent in your house and watch it slowly expand. You then remove it and let it cool back to room temperature. During the expansion, which was larger: the heat added to the balloon or the work done by the air inside it? Explain. (Assume that air is an ideal gas.) Once the balloon has returned to room temperature, how does the net heat gained or lost by the air inside it compare to the net work done on or by the surrounding air?

**Q19.8.** You bake chocolate chip cookies and put them, still warm, in a container with a loose (not airtight) lid. What kind of process does the air inside the container undergo as the cookies gradually cool to room temperature (isothermal, isochoric, adiabatic, isobaric, or some combination)? Explain your answer.

**Q19.9.** Imagine a gas made up entirely of negatively charged electrons. Like charges repel, so the electrons exert repulsive forces on each other. Would you expect that the temperature of such a gas would rise, fall, or stay the same in a free expansion? Why?

**Q19.10.** There are a few materials that contract when their temperature is increased, such as water between  $0^\circ\text{C}$  and  $4^\circ\text{C}$ . Would you expect  $C_p$  for such materials to be greater or less than  $C_V$ ? Explain?

**Q19.11.** When you blow on the back of your hand with your mouth wide open, your breath feels warm. But if you partially close your mouth to form an "o" and then blow on your hand, your breath feels cool. Why?

**Q19.12.** In hot-air balloons, the air in the balloon envelope is heated through a hole in the bottom by a propane burner. The hot air inside the envelope stays at atmospheric pressure because of the hole in the bottom, and the volume of the envelope is essentially constant. Thus, when the pilot fires up the burner to heat the air, the volume of the envelope and the pressure inside it are constant, but the temperature rises. The ideal-gas law seems to forbid this. What's going on?

**Q19.13.** On a warm summer day, a large cylinder of compressed gas (propane or butane) is used to supply several large gas burners at a cookout. After a while, frost forms on the outside of the tank. Why?

**Q19.14.** When you use a hand pump to inflate the tires of your bicycle, the pump gets warm after a while. Why? What happens to the temperature of the air in the pump as you compress it? Why does this happen? When you raise the pump handle to draw outside air into the pump, what happens to the temperature of the air taken in? Again, why does this happen?

**Q19.15.** In the carburetor of an aircraft or automobile engine, air flows through a relatively small aperture and then expands. In cool, foggy weather, ice sometimes forms in this aperture even though the outside air temperature is above freezing. Why?

**Q19.16.** On a sunny day, large "bubbles" of air form on the sun-warmed earth, gradually expand, and finally break free to rise through the atmosphere. Soaring birds and glider pilots are fond of using these "thermals" to gain altitude easily. This expansion is essentially an adiabatic process. Why?

**Q19.17.** The prevailing winds on the Hawaiian island of Kauai blow from the northeast. The winds cool as they go up the slope of Mt. Waialeale (elevation 1523 m), causing water vapor to condense and rain to fall. There is much more precipitation at the summit than at the base of the mountain. In fact, Mt. Waialeale is the rainiest spot on earth, averaging 11.7 m of rainfall a year. But what makes the winds cool?

**Q19.18.** Applying the same considerations as in Question 19.17, explain why the island of Niihau, a few kilometers to the southwest of Kauai, is almost a desert and farms there need to be irrigated.

**Q19.19.** In a constant-volume process,  $dU = nC_VdT$ . But in a constant-pressure process, it is *not* true that  $dU = nC_pdT$ . Why not?

**Q19.20.** When a gas surrounded by air is compressed adiabatically, its temperature rises even though there is no heat input to the gas. Where does the energy come from to raise the temperature?

**Q19.21.** When a gas expands adiabatically, it does work on its surroundings. But if there is no heat input to the gas, where does the energy come from to do the work?

**Q19.22.** The gas used in separating the two uranium isotopes  $^{235}\text{U}$  and  $^{238}\text{U}$  has the formula  $\text{UF}_6$ . If you added heat at equal rates to a mole of  $\text{UF}_6$  gas and a mole of  $\text{H}_2$  gas, which one's temperature would you expect to rise faster? Explain.

## Exercises

## Section 19.2 Work Done During Volume Changes and Section 19.3 Paths Between Thermodynamic States

**19.1.** Two moles of an ideal gas are heated at constant pressure from  $T = 27^\circ\text{C}$  to  $T = 107^\circ\text{C}$ . (a) Draw a  $pV$ -diagram for this process. (b) Calculate the work done by the gas.

**19.2.** Six moles of an ideal gas are in a cylinder fitted at one end with a movable piston. The initial temperature of the gas is  $27.0^\circ\text{C}$  and the pressure is constant. As part of a machine design project, calculate the final temperature of the gas after it has done  $1.75 \times 10^3 \text{ J}$  of work.

**19.3.** Two moles of an ideal gas are compressed in a cylinder at a constant temperature of  $85.0^\circ\text{C}$  until the original pressure has tripled. (a) Sketch a  $pV$ -diagram for this process. (b) Calculate the amount of work done.

**19.4.** A metal cylinder with rigid walls contains 2.50 mol of oxygen gas. The gas is cooled until the pressure decreases to 30.0% of its original value. You can ignore the thermal contraction of the cylinder. (a) Draw a  $pV$ -diagram for this process. (b) Calculate the work done by the gas.

**19.5.** During the time 0.305 mol of an ideal gas undergoes an isothermal compression at 22.0°C, 518 J of work is done on it by the surroundings. (a) If the final pressure is 1.76 atm, what was the initial pressure? (b) Sketch a  $pV$ -diagram for the process.

**19.6.** A gas undergoes two processes. In the first, the volume remains constant at 0.200 m<sup>3</sup> and the pressure increases from  $2.00 \times 10^5$  Pa to  $5.00 \times 10^5$  Pa. The second process is a compression to a volume of 0.120 m<sup>3</sup> at a constant pressure of  $5.00 \times 10^5$  Pa. (a) In a  $pV$ -diagram, show both processes. (b) Find the total work done by the gas during both processes.

**19.7. Work Done in a Cyclic Process.** (a) In Fig. 19.7a, consider the closed loop  $1 \rightarrow 3 \rightarrow 2 \rightarrow 4 \rightarrow 1$ . This is a *cyclic* process in which the initial and final states are the same. Find the total work done by the system in this cyclic process, and show that it is equal to the area enclosed by the loop. (b) How is the work done for the process in part (a) related to the work done if the loop is traversed in the opposite direction,  $1 \rightarrow 4 \rightarrow 2 \rightarrow 3 \rightarrow 1$ ? Explain.

### Section 19.4 Internal Energy and the First Law of Thermodynamics

**19.8.** You close off the nozzle of a bicycle tire pump and very slowly depress the plunger so that the air inside is compressed to half its original volume. Assume the air behaves like an ideal gas. If you do this so slowly that the temperature of the air inside the pump never changes: (a) Is the work done by the air in the pump positive or negative? (b) Is the heat flow to the air positive or negative? (c) What can you say about the relative *magnitudes* of the heat flow and the work? Explain.

**19.9.** A gas in a cylinder expands from a volume of 0.110 m<sup>3</sup> to 0.320 m<sup>3</sup>. Heat flows into the gas just rapidly enough to keep the pressure constant at  $1.80 \times 10^5$  Pa during the expansion. The total heat added is  $1.15 \times 10^5$  J. (a) Find the work done by the gas. (b) Find the change in internal energy of the gas. (c) Does it matter whether the gas is ideal? Why or why not?

**19.10.** Five moles of an ideal monatomic gas with an initial temperature of 127°C expand and, in the process, absorb 1200 J of heat and do 2100 J of work. What is the final temperature of the gas?

**19.11.** You kick a soccer ball, compressing it suddenly to  $\frac{2}{3}$  of its original volume. In the process, you do 410 J of work on the air (assumed to be an ideal gas) inside the ball. (a) What is the change in internal energy of the air inside the ball due to being compressed? (b) Does the temperature of the air inside the ball rise or fall due to being compressed? Explain.

**19.12.** A gas in a cylinder is held at a constant pressure of  $2.30 \times 10^5$  Pa and is cooled and compressed from 1.70 m<sup>3</sup> to 1.20 m<sup>3</sup>. The internal energy of the gas decreases by  $1.40 \times 10^5$  J. (a) Find the work done by the gas. (b) Find the absolute value  $|Q|$  of the heat flow into or out of the gas, and state the direction of the heat flow. (c) Does it matter whether the gas is ideal? Why or why not?

**19.13. Doughnuts: Breakfast of Champions!** A typical doughnut contains 2.0 g of protein, 17.0 g of carbohydrates, and 7.0 g of fat. The average food energy values of these substances are 4.0 kcal/g for protein and carbohydrates and 9.0 kcal/g for fat. (a) During heavy exercise, an average person uses energy at a rate of 510 kcal/h. How long would you have to exercise to “work off”

one doughnut? (b) If the energy in the doughnut could somehow be converted into the kinetic energy of your body as a whole, how fast could you move after eating the doughnut? Take your mass to be 60 kg, and express your answer in m/s and km/h.

**19.14.** A liquid is irregularly stirred in a well-insulated container and thereby undergoes a rise in temperature. Regard the liquid as the system. (a) Has heat been transferred? How can you tell? (b) Has work been done? How can you tell? Why is it important that the stirring is irregular? (c) What is the sign of  $\Delta U$ ? How can you tell?

**19.15.** An ideal gas is taken from a state  $a$  to state  $b$  on the  $pV$ -diagram shown in Fig. 19.22. During this process, 400 J of heat is added and the pressure doubles. (a) How much work is done by or on the gas? Explain. (b) How does the temperature of the gas at  $a$  compare to its temperature at  $b$ ? Be specific. (c) How does the internal energy of the gas at  $a$  compare to the internal energy at  $b$ ? Again, be specific and explain.

**19.16.** A system is taken from state  $a$  to state  $b$  along the three paths shown in Fig. 19.23. (a) Along which path is the work done by the system the greatest? The least? (b) If  $U_b > U_a$ , along which path is the absolute value  $|Q|$  of the heat transfer the greatest? For this path, is heat absorbed or liberated by the system?

**19.17.** A thermodynamic system undergoes a cyclic process as shown in Fig. 19.24. The cycle consists of two closed loops: I and II. (a) Over one complete cycle, does the system do positive or negative work? (b) In each of loops I and II, is the net work done by the system positive or negative? (c) Over one complete cycle, does heat flow into or out of the system? (d) In each of loops I and II, does heat flow into or out of the system?

**19.18.** A student performs a combustion experiment by burning a mixture of fuel and oxygen in a constant-volume metal can surrounded by a water bath. During the experiment the temperature of the water is observed to rise. Regard the mixture of fuel and oxygen as the system. (a) Has heat been transferred? How can you tell? (b) Has work been done? How can you tell? (c) What is the sign of  $\Delta U$ ? How can you tell?

**19.19. Boiling Water at High Pressure.** When water is boiled at a pressure of 2.00 atm, the heat of vaporization is  $2.20 \times 10^6$  J/kg and the boiling point is 120°C. At this pressure, 1.00 kg of water has a volume of  $1.00 \times 10^{-3}$  m<sup>3</sup>, and 1.00 kg of steam has a volume of 0.824 m<sup>3</sup>. (a) Compute the work done when 1.00 kg of steam is formed at this temperature. (b) Compute the increase in internal energy of the water.

Figure 19.22 Exercise 19.15.

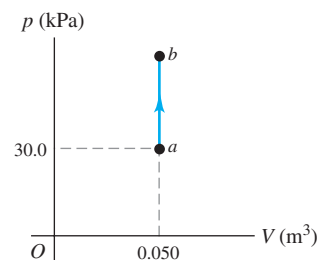


Figure 19.23 Exercise 19.16.

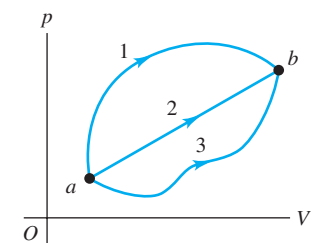
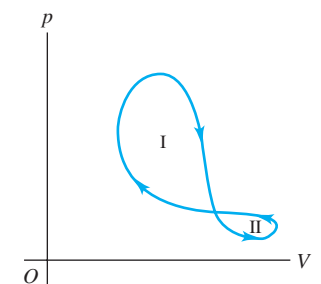


Figure 19.24 Exercise 19.17.



### Section 19.5 Kinds of Thermodynamic Processes, Section 19.6 Internal Energy of an Ideal Gas, and Section 19.7 Heat Capacities of an Ideal Gas

**19.20.** During an isothermal compression of an ideal gas, 335 J of heat must be removed from the gas to maintain constant temperature. How much work is done by the gas during the process?

**19.21.** A cylinder contains 0.250 mol of carbon dioxide ( $\text{CO}_2$ ) gas at a temperature of 27.0°C. The cylinder is provided with a frictionless piston, which maintains a constant pressure of 1.00 atm on the gas. The gas is heated until its temperature increases to 127.0°C. Assume that the  $\text{CO}_2$  may be treated as an ideal gas. (a) Draw a  $pV$ -diagram for this process. (b) How much work is done by the gas in this process? (c) On what is this work done? (d) What is the change in internal energy of the gas? (e) How much heat was supplied to the gas? (f) How much work would have been done if the pressure had been 0.50 atm?

**19.22.** A cylinder contains 0.0100 mol of helium at  $T = 27.0^\circ\text{C}$ . (a) How much heat is needed to raise the temperature to 67.0°C while keeping the volume constant? Draw a  $pV$ -diagram for this process. (b) If instead the pressure of the helium is kept constant, how much heat is needed to raise the temperature from 27.0°C to 67.0°C? Draw a  $pV$ -diagram for this process. (c) What accounts for the difference between your answers to parts (a) and (b)? In which case is more heat required? What becomes of the additional heat? (d) If the gas is ideal, what is the change in its internal energy in part (a)? In part (b)? How do the two answers compare? Why?

**19.23.** In an experiment to simulate conditions inside an automobile engine, 0.185 mol of air at a temperature of 780 K and a pressure of  $3.00 \times 10^6$  Pa is contained in a cylinder of volume 40.0 cm<sup>3</sup>. Then 645 J of heat is transferred to the cylinder. (a) If the volume of the cylinder is constant while the heat is added, what is the final temperature of the air? Assume that the air is essentially nitrogen gas, and use the data in Table 19.1 even though the pressure is not low. Draw a  $pV$ -diagram for this process. (b) If instead the volume of the cylinder is allowed to increase while the pressure remains constant, find the final temperature of the air. Draw a  $pV$ -diagram for this process.

**19.24.** An ideal gas expands while the pressure is kept constant. During this process, does heat flow into the gas or out of the gas? Justify your answer.

**19.25.** Heat  $Q$  flows into a monatomic ideal gas, and the volume increases while the pressure is kept constant. What fraction of the heat energy is used to do the expansion work of the gas?

**19.26.** When a quantity of monatomic ideal gas expands at a constant pressure of  $4.00 \times 10^4$  Pa, the volume of the gas increases from  $2.00 \times 10^{-3}$  m<sup>3</sup> to  $8.00 \times 10^{-3}$  m<sup>3</sup>. What is the change in the internal energy of the gas?

**19.27.** A cylinder with a movable piston contains 3.00 mol of  $\text{N}_2$  gas (assumed to behave like an ideal gas). (a) The  $\text{N}_2$  is heated at constant volume until 1557 J of heat have been added. Calculate the change in temperature. (b) Suppose the same amount of heat is added to the  $\text{N}_2$ , but this time the gas is allowed to expand while remaining at constant pressure. Calculate the temperature change. (c) In which case, (a) or (b), is the final internal energy of the  $\text{N}_2$  higher? How do you know? What accounts for the difference between the two cases?

**19.28.** Three moles of an ideal monatomic gas expands at a constant pressure of 2.50 atm; the volume of the gas changes from  $3.20 \times 10^{-2}$  m<sup>3</sup> to  $4.50 \times 10^{-2}$  m<sup>3</sup>. (a) Calculate the initial and final temperatures of the gas. (b) Calculate the amount of work the gas does in expanding. (c) Calculate the amount of heat added to the gas. (d) Calculate the change in internal energy of the gas.

**19.29.** The temperature of 0.150 mol of an ideal gas is held constant at 77.0°C while its volume is reduced to 25.0% of its initial volume. The initial pressure of the gas is 1.25 atm. (a) Determine the work done by the gas. (b) What is the change in its internal energy? (c) Does the gas exchange heat with its surroundings? If so, how much? Does the gas absorb or liberate heat?

**19.30.** Propane gas ( $\text{C}_3\text{H}_8$ ) behaves like an ideal gas with  $\gamma = 1.127$ . Determine the molar heat capacity at constant volume and the molar heat capacity at constant pressure.

**19.31.** An experimenter adds 970 J of heat to 1.75 mol of an ideal gas to heat it from 10.0°C to 25.0°C at constant pressure. The gas does +223 J of work during the expansion. (a) Calculate the change in internal energy of the gas. (b) Calculate  $\gamma$  for the gas.

### Section 19.8 Adiabatic Processes for an Ideal Gas

**19.32.** In an adiabatic process for an ideal gas, the pressure decreases. In this process does the internal energy of the gas increase or decrease? Explain your reasoning.

**19.33.** A monatomic ideal gas that is initially at a pressure of  $1.50 \times 10^5$  Pa and has a volume of 0.0800 m<sup>3</sup> is compressed adiabatically to a volume of 0.0400 m<sup>3</sup>. (a) What is the final pressure? (b) How much work is done by the gas? (c) What is the ratio of the final temperature of the gas to its initial temperature? Is the gas heated or cooled by this compression?

**19.34.** The engine of a Ferrari F355 F1 sports car takes in air at 20.0°C and 1.00 atm and compresses it adiabatically to 0.0900 times the original volume. The air may be treated as an ideal gas with  $\gamma = 1.40$ . (a) Draw a  $pV$ -diagram for this process. (b) Find the final temperature and pressure.

**19.35.** Two moles of carbon monoxide ( $\text{CO}$ ) start at a pressure of 1.2 atm and a volume of 30 liters. The gas is then compressed adiabatically to  $\frac{1}{3}$  this volume. Assume that the gas may be treated as ideal. What is the change in the internal energy of the gas? Does the internal energy increase or decrease? Does the temperature of the gas increase or decrease during this process? Explain.

**19.36.** A player bounces a basketball on the floor, compressing it to 80.0% of its original volume. The air (assume it is essentially  $\text{N}_2$  gas) inside the ball is originally at a temperature of 20.0°C and a pressure of 2.00 atm. The ball's diameter is 23.9 cm. (a) What temperature does the air in the ball reach at its maximum compression? (b) By how much does the internal energy of the air change between the ball's original state and its maximum compression?

**19.37.** During an adiabatic expansion the temperature of 0.450 mol of argon ( $\text{Ar}$ ) drops from 50.0°C to 10.0°C. The argon may be treated as an ideal gas. (a) Draw a  $pV$ -diagram for this process. (b) How much work does the gas do? (c) What is the change in internal energy of the gas?

**19.38.** A cylinder contains 0.100 mol of an ideal monatomic gas. Initially the gas is at a pressure of  $1.00 \times 10^5$  Pa and occupies a volume of  $2.50 \times 10^{-3}$  m<sup>3</sup>. (a) Find the initial temperature of the gas in kelvins. (b) If the gas is allowed to expand to twice the initial volume, find the final temperature (in kelvins) and pressure of the gas if the expansion is (i) isothermal; (ii) isobaric; (iii) adiabatic.

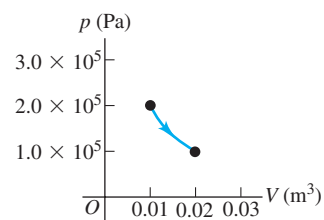
**19.39.** On a warm summer day, a large mass of air (atmospheric pressure  $1.01 \times 10^5$  Pa) is heated by the ground to a temperature of 26.0°C and then begins to rise through the cooler surrounding air. (This can be treated approximately as an adiabatic process; why?) Calculate the temperature of the air mass when it has risen to a level at which atmospheric pressure is only  $0.850 \times 10^5$  Pa. Assume that air is an ideal gas, with  $\gamma = 1.40$ . (This rate of cooling for dry, rising air, corresponding to roughly 1°C per 100 m of altitude, is called the *dry adiabatic lapse rate*.)



## Problems

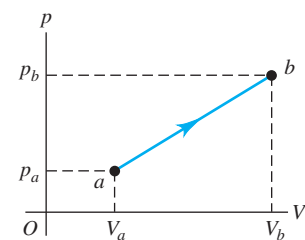
**19.40.** Figure 19.25 shows the  $pV$ -diagram for an isothermal expansion of 1.50 mol of an ideal gas, at a temperature of  $15.0^\circ\text{C}$ . (a) What is the change in internal energy of the gas? Explain. (b) Calculate the work done by (or on) the gas and the heat absorbed (or released) by the gas during the expansion.

Figure 19.25 Problem 19.40.



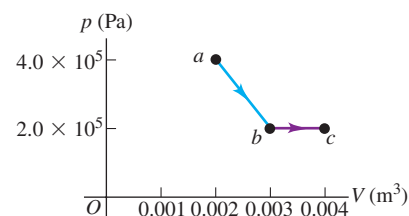
**19.41.** A quantity of air is taken from state  $a$  to state  $b$  along a path that is a straight line in the  $pV$ -diagram (Fig. 19.26). (a) In this process, does the temperature of the gas increase, decrease, or stay the same? Explain. (b) If  $V_a = 0.0700\text{ m}^3$ ,  $V_b = 0.1100\text{ m}^3$ ,  $p_a = 1.00 \times 10^5\text{ Pa}$ , and  $p_b = 1.40 \times 10^5\text{ Pa}$ , what is the work  $W$  done by the gas in this process? Assume that the gas may be treated as ideal.

Figure 19.26 Problem 19.41.



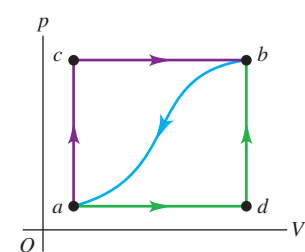
**19.42.** One-half mole of an ideal gas is taken from state  $a$  to state  $c$ , as shown in Fig. 19.27. (a) Calculate the final temperature of the gas. (b) Calculate the work done on (or by) the gas as it moves from state  $a$  to state  $c$ . (c) Does heat leave the system or enter the system during this process? How much heat? Explain.

Figure 19.27 Problem 19.42.



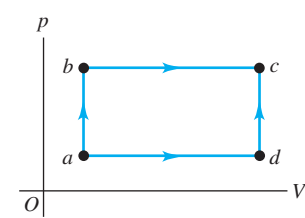
**19.43.** When a system is taken from state  $a$  to state  $b$  in Fig. 19.28 along the path  $acb$ ,  $90.0\text{ J}$  of heat flows into the system and  $60.0\text{ J}$  of work is done by the system. (a) How much heat flows into the system along path  $adb$  if the work done by the system is  $15.0\text{ J}$ ? (b) When the system is returned from  $b$  to  $a$  along the curved path, the absolute value of the work done by the system is  $35.0\text{ J}$ . Does the system absorb or liberate heat? How much heat? (c) If  $U_a = 0$  and  $U_d = 8.0\text{ J}$ , find the heat absorbed in the processes  $ad$  and  $db$ .

Figure 19.28 Problem 19.43.



**19.44.** A thermodynamic system is taken from state  $a$  to state  $c$  in Fig. 19.29 along either path  $abc$  or path  $adc$ . Along path  $abc$ , the work  $W$  done by the system is  $450\text{ J}$ . Along path  $adc$ ,  $W$  is  $120\text{ J}$ . The internal energies of each of the four states shown in the figure are  $U_a = 150\text{ J}$ ,

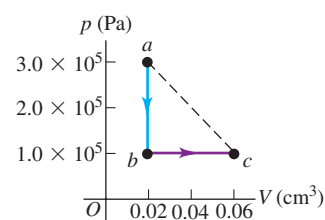
Figure 19.29 Problem 19.44.



$U_b = 240\text{ J}$ ,  $U_c = 680\text{ J}$ , and  $U_d = 330\text{ J}$ . Calculate the heat flow  $Q$  for each of the four processes  $ab$ ,  $bc$ ,  $ad$ , and  $dc$ . In each process, does the system absorb or liberate heat?

**19.45.** A volume of air (assumed to be an ideal gas) is first cooled without changing its volume and then expanded without changing its pressure, as shown by the path  $abc$  in Fig. 19.30.

Figure 19.30 Problem 19.45.



(a) How does the final temperature of the gas compare with its initial temperature? (b) How much heat does the air exchange with its surroundings during the process  $abc$ ? Does the air absorb heat or release heat during this process? Explain. (c) If the air instead expands from state  $a$  to state  $c$  by the straight-line path shown, how much heat does it exchange with its surroundings?

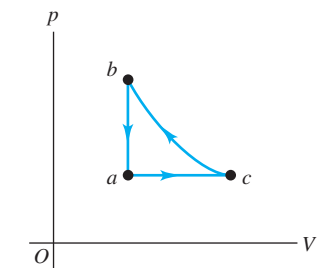
**19.46.** Three moles of argon gas (assumed to be an ideal gas) originally at a pressure of  $1.50 \times 10^4\text{ Pa}$  and a volume of  $0.0280\text{ m}^3$  are first heated and expanded at constant pressure to a volume of  $0.0435\text{ m}^3$ , then heated at constant volume until the pressure reaches  $3.50 \times 10^4\text{ Pa}$ , then cooled and compressed at constant pressure until the volume is again  $0.0280\text{ m}^3$ , and finally cooled at constant volume until the pressure drops to its original value of  $1.50 \times 10^4\text{ Pa}$ .

(a) Draw the  $pV$ -diagram for this cycle. (b) Calculate the total work done by (or on) the gas during the cycle. (c) Calculate the net heat exchanged with the surroundings. Does the gas gain or lose heat overall?

**19.47.** Two moles of an ideal monatomic gas go through the cycle  $abc$ . For the complete cycle,  $800\text{ J}$  of heat flows out of the gas. Process  $ab$  is at constant pressure, and process  $bc$  is at constant volume. States  $a$  and  $b$  have temperatures  $T_a = 200\text{ K}$  and  $T_b = 300\text{ K}$ . (a) Sketch the  $pV$ -diagram for the cycle. (b) What is the work  $W$  for the process  $ca$ ?

**19.48.** Three moles of an ideal gas are taken around the cycle  $abc$  shown in Fig. 19.31. For this gas,  $C_p = 29.1\text{ J/mol}\cdot\text{K}$ . Process  $ac$  is at constant pressure, process  $ba$  is at constant volume, and process  $cb$  is adiabatic. The temperatures of the gas in states  $a$ ,  $c$ , and  $b$  are  $T_a = 300\text{ K}$ ,  $T_c = 492\text{ K}$ , and  $T_b = 600\text{ K}$ . Calculate the total work  $W$  for the cycle.

Figure 19.31 Problem 19.48.



**19.49.** Starting with  $2.50\text{ mol}$  of  $\text{N}_2$  gas (assumed to be ideal) in a cylinder at  $1.00\text{ atm}$  and  $20.0^\circ\text{C}$ , a chemist first heats the gas at constant volume, adding  $1.52 \times 10^4\text{ J}$  of heat, then continues heating and allows the gas to expand at constant pressure to twice its original volume. (a) Calculate the final temperature of the gas. (b) Calculate the amount of work done by the gas. (c) Calculate the amount of heat added to the gas while it was expanding. (d) Calculate the change in internal energy of the gas for the whole process.

**19.50.** Nitrogen gas in an expandable container is cooled from  $50.0^\circ\text{C}$  to  $10.0^\circ\text{C}$  with the pressure held constant at  $3.00 \times 10^5\text{ Pa}$ . The total heat liberated by the gas is  $2.50 \times 10^4\text{ J}$ . Assume that the gas may be treated as ideal. (a) Find the number of moles of gas. (b) Find the change in internal energy of the gas. (c) Find the work done by the gas. (d) How much heat would be liberated by the gas for the same temperature change if the volume were constant?

**19.51.** In a certain process,  $2.15 \times 10^5\text{ J}$  of heat is liberated by a system, and at the same time the system contracts under a constant external pressure of  $9.50 \times 10^5\text{ Pa}$ . The internal energy of the system is the same at the beginning and end of the process. Find the change in volume of the system. (The system is *not* an ideal gas.)

**19.52.** A cylinder with a frictionless, movable piston like that shown in Fig. 19.5 contains a quantity of helium gas. Initially the gas is at a pressure of  $1.00 \times 10^5\text{ Pa}$ , has a temperature of  $300\text{ K}$ , and occupies a volume of  $1.50\text{ L}$ . The gas then undergoes two processes. In the first, the gas is heated and the piston is allowed to move to keep the temperature equal to  $300\text{ K}$ . This continues until the pressure reaches  $2.50 \times 10^4\text{ Pa}$ . In the second process, the gas is compressed at constant pressure until it returns to its original volume of  $1.50\text{ L}$ . Assume that the gas may be treated as ideal. (a) In a  $pV$ -diagram, show both processes. (b) Find the volume of the gas at the end of the first process, and find the pressure and temperature at the end of the second process. (c) Find the total work done by the gas during both processes. (d) What would you have to do to the gas to return it to its original pressure and temperature?

**19.53. A Thermodynamic Process in a Liquid.** A chemical engineer is studying the properties of liquid methanol ( $\text{CH}_3\text{OH}$ ). She uses a steel cylinder with a cross-sectional area of  $0.0200\text{ m}^2$  and containing  $1.20 \times 10^{-2}\text{ m}^3$  of methanol. The cylinder is equipped with a tightly fitting piston that supports a load of  $3.00 \times 10^4\text{ N}$ . The temperature of the system is increased from  $20.0^\circ\text{C}$  to  $50.0^\circ\text{C}$ . For methanol, the coefficient of volume expansion is  $1.20 \times 10^{-3}\text{ K}^{-1}$ , the density is  $791\text{ kg/m}^3$ , and the specific heat capacity at constant pressure is  $c_p = 2.51 \times 10^3\text{ J/kg}\cdot\text{K}$ . You can ignore the expansion of the steel cylinder. Find (a) the increase in volume of the methanol; (b) the mechanical work done by the methanol against the  $3.00 \times 10^4\text{ N}$  force; (c) the amount of heat added to the methanol; (d) the change in internal energy of the methanol. (e) Based on your results, explain whether there is any substantial difference between the specific heat capacities  $c_p$  (at constant pressure) and  $c_v$  (at constant volume) for methanol under these conditions.

**19.54. A Thermodynamic Process in a Solid.** A cube of copper  $2.00\text{ cm}$  on a side is suspended by a string. (The physical properties of copper are given in Tables 14.1, 17.2, and 17.3.) The cube is heated with a burner from  $20.0^\circ\text{C}$  to  $90.0^\circ\text{C}$ . The air surrounding the cube is at atmospheric pressure ( $1.01 \times 10^5\text{ Pa}$ ). Find (a) the increase in volume of the cube; (b) the mechanical work done by the cube to expand against the pressure of the surrounding air; (c) the amount of heat added to the cube; (d) the change in internal energy of the cube. (e) Based on your results, explain whether there is any substantial difference between the specific heat capacities  $c_p$  (at constant pressure) and  $c_v$  (at constant volume) for copper under these conditions.

**19.55. A Thermodynamic Process in an Insect.** The African bombardier beetle *Stenaptinus insignis* can emit a jet of defensive spray from the movable tip of its abdomen (Fig. 19.32). The beetle's body has reservoirs of two different chemicals; when the beetle is disturbed, these chemicals are combined in a reaction chamber, producing a compound that is warmed from  $20^\circ\text{C}$  to  $100^\circ\text{C}$  by the heat of reaction. The high pressure produced allows the compound to be sprayed out at speeds up to  $19\text{ m/s}$  ( $68\text{ km/h}$ ), scaring away predators of all kinds.

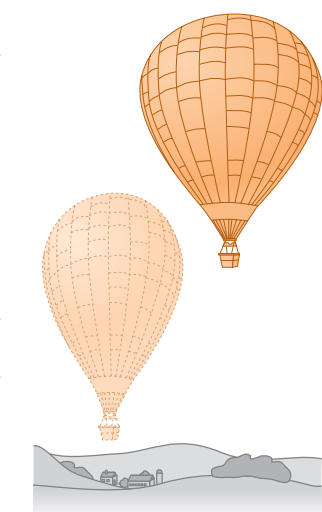
Figure 19.32 Problem 19.55.



Calculate the heat of reaction of the two chemicals (in  $\text{J/kg}$ ). Assume that the specific heat capacity of the two chemicals and the spray is the same as that of water,  $4.19 \times 10^3\text{ J/kg}\cdot\text{K}$ , and that the initial temperature of the chemicals is  $20^\circ\text{C}$ .

**19.56. High-Altitude Research.** A large research balloon containing  $2.00 \times 10^3\text{ m}^3$  of helium gas at  $1.00\text{ atm}$  and a temperature of  $15.0^\circ\text{C}$  rises rapidly from ground level to an altitude at which the atmospheric pressure is only  $0.900\text{ atm}$  (Fig. 19.33). Assume the helium behaves like an ideal gas and the balloon's ascent is too rapid to permit much heat exchange with the surrounding air. (a) Calculate the volume of the gas at the higher altitude. (b) Calculate the temperature of the gas at the higher altitude. (c) What is the change in internal energy of the helium as the balloon rises to the higher altitude?

Figure 19.33 Problem 19.56.



**19.57. Chinook.** During certain seasons strong winds called chinooks blow from the west across the eastern slopes of the Rockies and downhill into Denver and nearby areas. Although the mountains are cool, the wind in Denver is very hot; within a few minutes after the chinook wind arrives, the temperature can climb  $20^\circ\text{C}$  ("chinook" is a Native American word meaning "snow eater"). Similar winds occur in the Alps (called foehns) and in southern California (called Santa Anas). (a) Explain why the temperature of the chinook wind rises as it descends the slopes. Why is it important that the wind be fast moving? (b) Suppose a strong wind is blowing toward Denver (elevation  $1630\text{ m}$ ) from Grays Peak ( $80\text{ km}$  west of Denver, at an elevation of  $4350\text{ m}$ ), where the air pressure is  $5.60 \times 10^4\text{ Pa}$  and the air temperature is  $-15.0^\circ\text{C}$ . The temperature and pressure in Denver before the wind arrives are  $2.0^\circ\text{C}$  and  $8.12 \times 10^4\text{ Pa}$ . By how many Celsius degrees will the temperature in Denver rise when the chinook arrives?

**19.58.** A certain ideal gas has molar heat capacity at constant volume  $C_v$ . A sample of this gas initially occupies a volume  $V_0$  at pressure  $p_0$  and absolute temperature  $T_0$ . The gas expands isobarically to a volume  $2V_0$  and then expands further adiabatically to a final volume of  $4V_0$ . (a) Draw a  $pV$ -diagram for this sequence of processes. (b) Compute the total work done by the gas for this sequence of processes. (c) Find the final temperature of the gas. (d) Find the absolute value  $|Q|$  of the total heat flow into or out of the gas for this sequence of processes, and state the direction of heat flow.

**19.59.** An air pump has a cylinder  $0.250\text{ m}$  long with a movable piston. The pump is used to compress air from the atmosphere (at absolute pressure  $1.01 \times 10^5\text{ Pa}$ ) into a very large tank at  $4.20 \times 10^5\text{ Pa}$  gauge pressure. (For air,  $C_v = 20.8\text{ J/mol}\cdot\text{K}$ .) (a) The piston begins the compression stroke at the open end of the cylinder. How far down the length of the cylinder has the piston moved when air first begins to flow from the cylinder into the tank? Assume that the compression is adiabatic. (b) If the air is taken into the pump at  $27.0^\circ\text{C}$ , what is the temperature of the compressed air? (c) How much work does the pump do in putting  $20.0\text{ mol}$  of air into the tank?

**19.60. Engine Turbochargers and Intercoolers.** The power output of an automobile engine is directly proportional to the mass

of air that can be forced into the volume of the engine's cylinders to react chemically with gasoline. Many cars have a *turbocharger*, which compresses the air before it enters the engine, giving a greater mass of air per volume. This rapid, essentially adiabatic compression also heats the air. To compress it further, the air then passes through an *intercooler* in which the air exchanges heat with its surroundings at essentially constant pressure. The air is then drawn into the cylinders. In a typical installation, air is taken into the turbocharger at atmospheric pressure ( $1.01 \times 10^5 \text{ Pa}$ ), density  $\rho = 1.23 \text{ kg/m}^3$ , and temperature  $15.0^\circ\text{C}$ . It is compressed adiabatically to  $1.45 \times 10^5 \text{ Pa}$ . In the intercooler, the air is cooled to the original temperature of  $15.0^\circ\text{C}$  at a constant pressure of  $1.45 \times 10^5 \text{ Pa}$ . (a) Draw a  $pV$ -diagram for this sequence of processes. (b) If the volume of one of the engine's cylinders is  $575 \text{ cm}^3$ , what mass of air exiting from the intercooler will fill the cylinder at  $1.45 \times 10^5 \text{ Pa}$ ? Compared to the power output of an engine that takes in air at  $1.01 \times 10^5 \text{ Pa}$  at  $15.0^\circ\text{C}$ , what percentage increase in power is obtained by using the turbocharger and intercooler? (c) If the intercooler is not used, what mass of air exiting from the turbocharger will fill the cylinder at  $1.45 \times 10^5 \text{ Pa}$ ? Compared to the power output of an engine that takes in air at  $1.01 \times 10^5 \text{ Pa}$  at  $15.0^\circ\text{C}$ , what percentage increase in power is obtained by using the turbocharger alone?

**19.61.** A monatomic ideal gas expands slowly to twice its original volume, doing  $300 \text{ J}$  of work in the process. Find the heat added to the gas and the change in internal energy of the gas if the process is (a) isothermal; (b) adiabatic; (c) isobaric.

**19.62.** A cylinder with a piston contains  $0.250 \text{ mol}$  of oxygen at  $2.40 \times 10^5 \text{ Pa}$  and  $355 \text{ K}$ . The oxygen may be treated as an ideal gas. The gas first expands isobarically to twice its original volume. It is then compressed isothermally back to its original volume, and finally it is cooled isochorically to its original pressure. (a) Show the series of processes on a  $pV$ -diagram. (b) Compute the temperature during the isothermal compression. (c) Compute the maximum pressure. (d) Compute the total work done by the piston on the gas during the series of processes.

**19.63.** Use the conditions and processes of Problem 19.62 to compute (a) the work done by the gas, the heat added to it, and its internal-energy change during the initial expansion; (b) the work done, the heat added, and the internal-energy change during the final cooling; (c) the internal-energy change during the isothermal compression.

**19.64.** A cylinder with a piston contains  $0.150 \text{ mol}$  of nitrogen at  $1.80 \times 10^5 \text{ Pa}$  and  $300 \text{ K}$ . The nitrogen may be treated as an ideal gas. The gas is first compressed isobarically to half its original volume. It then expands adiabatically back to its original volume, and finally it is heated isochorically to its original pressure. (a) Show the series of processes in a  $pV$ -diagram. (b) Compute the temperatures at the beginning and end of the adiabatic expansion. (c) Compute the minimum pressure.

**19.65.** Use the conditions and processes of Problem 19.64 to compute (a) the work done by the gas, the heat added to it, and its internal-energy change during the initial compression; (b) the work done by the gas, the heat added to it, and its internal-energy change during the adiabatic expansion; (c) the work done, the heat added, and the internal-energy change during the final heating.

**19.66. Comparing Thermodynamic Processes.** In a cylinder,  $1.20 \text{ mol}$  of an ideal monatomic gas, initially at  $3.60 \times 10^5 \text{ Pa}$  and  $300 \text{ K}$ , expands until its volume triples. Compute the work done by the gas if the expansion is (a) isothermal; (b) adiabatic; (c) isobaric. (d) Show each process in a  $pV$ -diagram. In which case is the absolute value of the work done by the gas greatest? Least? (e) In

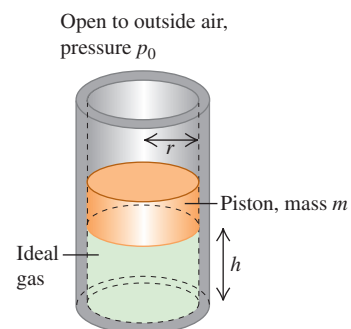
which case is the absolute value of the heat transfer greatest? Least? (f) In which case is the absolute value of the change in internal energy of the gas greatest? Least?

**19.67.** In a cylinder sealed with a piston, you rapidly compress  $3.00 \text{ L}$  of  $\text{N}_2$  gas initially at  $1.00 \text{ atm}$  pressure and  $0.00^\circ\text{C}$  to half its original volume. Assume the  $\text{N}_2$  behaves like an ideal gas. (a) Calculate the final temperature and pressure of the gas. (b) If you now cool the gas back to  $0.00^\circ\text{C}$  without changing the pressure, what is its final volume?

### Challenge Problems

**19.68. Oscillations of a Piston.** A vertical cylinder of radius  $r$  contains a quantity of ideal gas and is fitted with a piston with mass  $m$  that is free to move (Fig. 19.34). The piston and the walls of the cylinder are frictionless and the entire cylinder is placed in a constant-temperature bath. The outside air pressure is  $p_0$ . In equilibrium, the piston sits at a height  $h$  above the bottom of the cylinder. (a) Find the absolute pressure of the gas trapped below the piston when in equilibrium. (b) The piston is pulled up by a small distance and released. Find the net force acting on the piston when its base is a distance  $h + y$  above the bottom of the cylinder, where  $y$  is much less than  $h$ . (c) After the piston is displaced from equilibrium and released, it oscillates up and down. Find the frequency of these small oscillations. If the displacement is not small, are the oscillations simple harmonic? How can you tell?

Figure 19.34 Challenge Problem 19.68.



**19.69.** The van der Waals equation of state, an approximate representation of the behavior of gases at high pressure, is given by Eq. (18.7):

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

where  $a$  and  $b$  are constants having different values for different gases. (In the special case of  $a = b = 0$ , this is the ideal-gas equation.) (a) Calculate the work done by a gas with this equation of state in an isothermal expansion from  $V_1$  to  $V_2$ . Show that your answer agrees with the ideal-gas result found in Example 19.1 (Section 19.2) when you set  $a = b = 0$ . (b) For ethane gas ( $\text{C}_2\text{H}_6$ ),  $a = 0.554 \text{ J} \cdot \text{m}^3/\text{mol}^2$  and  $b = 6.38 \times 10^{-5} \text{ m}^3/\text{mol}$ . Calculate the work  $W$  done by  $1.80 \text{ mol}$  of ethane when it expands from  $2.00 \times 10^{-3} \text{ m}^3$  to  $4.00 \times 10^{-3} \text{ m}^3$  at a constant temperature of  $300 \text{ K}$ . Do the calculation using (i) the van der Waals equation of state and (ii) the ideal-gas equation of state. (c) How large is the difference between the two results for  $W$  in part (b)? For which equation of state is  $W$  larger? Use the interpretation of the terms  $a$  and  $b$  given in Section 18.1 to explain why this should be so. Are the differences between the two equations of state important in this case?