

## The First Law of Thermodynamics

You have just seen that when a system changes from a given initial state to a given final state, both the work  $W$  and the heat  $Q$  depend on the nature of the process. Experimentally, however, we find a surprising thing. *The quantity  $Q - W$  is the same for all processes.* It depends only on the initial and final states and does not depend at all on how the system gets from one to the other. All other combinations of  $Q$  and  $W$ , including  $Q$  alone,  $W$  alone,  $Q + W$ , and  $Q - 2W$ , are *path dependent*; only the quantity  $Q - W$  is not.

The quantity  $Q - W$  must represent a change in some intrinsic property of the system. We call this property the *internal energy*  $E_{\text{int}}$  and we write

$$\Delta E_{\text{int}} = E_{\text{int},f} - E_{\text{int},i} = Q - W \quad (\text{first law}). \quad (18-26)$$

Equation 18-26 is the **first law of thermodynamics**. If the thermodynamic system undergoes only a differential change, we can write the first law as\*

$$dE_{\text{int}} = dQ - dW \quad (\text{first law}). \quad (18-27)$$



The internal energy  $E_{\text{int}}$  of a system tends to increase if energy is added as heat  $Q$  and tends to decrease if energy is lost as work  $W$  done by the system.

In Chapter 8, we discussed the principle of energy conservation as it applies to isolated systems—that is, to systems in which no energy enters or leaves the system. The first law of thermodynamics is an extension of that principle to systems that are *not* isolated. In such cases, energy may be transferred into or out of the system as either work  $W$  or heat  $Q$ . In our statement of the first law of thermodynamics above, we assume that there are no changes in the kinetic energy or the potential energy of the system as a whole; that is,  $\Delta K = \Delta U = 0$ .

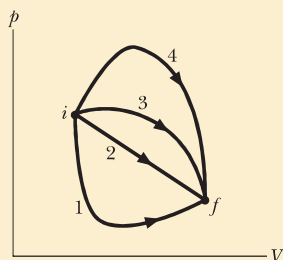
**Rules.** Before this chapter, the term *work* and the symbol  $W$  always meant the work done *on* a system. However, starting with Eq. 18-24 and continuing through the next two chapters about thermodynamics, we focus on the work done *by* a system, such as the gas in Fig. 18-13.

The work done *on* a system is always the negative of the work done *by* the system, so if we rewrite Eq. 18-26 in terms of the work  $W_{\text{on}}$  done *on* the system, we have  $\Delta E_{\text{int}} = Q + W_{\text{on}}$ . This tells us the following: The internal energy of a system tends to increase if heat is absorbed by the system or if positive work is done *on* the system. Conversely, the internal energy tends to decrease if heat is lost by the system or if negative work is done *on* the system.



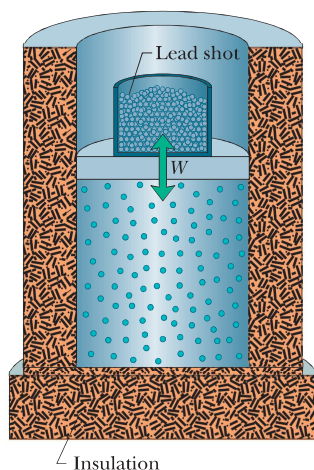
### Checkpoint 5

The figure here shows four paths on a  $p$ - $V$  diagram along which a gas can be taken from state  $i$  to state  $f$ . Rank the paths according to (a) the change  $\Delta E_{\text{int}}$  in the internal energy of the gas, (b) the work  $W$  done by the gas, and (c) the magnitude of the energy transferred as heat  $Q$  between the gas and its environment, greatest first.

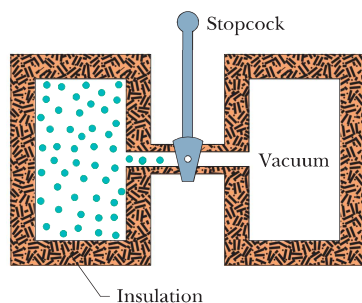


\*Here  $dQ$  and  $dW$ , unlike  $dE_{\text{int}}$ , are not true differentials; that is, there are no such functions as  $Q(p, V)$  and  $W(p, V)$  that depend only on the state of the system. The quantities  $dQ$  and  $dW$  are called *inexact differentials* and are usually represented by the symbols  $dQ$  and  $dW$ . For our purposes, we can treat them simply as infinitesimally small energy transfers.

We slowly remove lead shot, allowing an expansion without any heat transfer.



**Figure 18-15** An adiabatic expansion can be carried out by slowly removing lead shot from the top of the piston. Adding lead shot reverses the process at any stage.



**Figure 18-16** The initial stage of a free-expansion process. After the stopcock is opened, the gas fills both chambers and eventually reaches an equilibrium state.

## Some Special Cases of the First Law of Thermodynamics

Here are four thermodynamic processes as summarized in Table 18-5.

- 1. Adiabatic processes.** An adiabatic process is one that occurs so rapidly or occurs in a system that is so well insulated that *no transfer of energy as heat* occurs between the system and its environment. Putting  $Q = 0$  in the first law (Eq. 18-26) yields

$$\Delta E_{\text{int}} = -W \quad (\text{adiabatic process}). \quad (18-28)$$

This tells us that if work is done *by* the system (that is, if  $W$  is positive), the internal energy of the system decreases by the amount of work. Conversely, if work is done *on* the system (that is, if  $W$  is negative), the internal energy of the system increases by that amount.

Figure 18-15 shows an idealized adiabatic process. Heat cannot enter or leave the system because of the insulation. Thus, the only way energy can be transferred between the system and its environment is by work. If we remove shot from the piston and allow the gas to expand, the work done by the system (the gas) is positive and the internal energy of the gas decreases. If, instead, we add shot and compress the gas, the work done by the system is negative and the internal energy of the gas increases.

- 2. Constant-volume processes.** If the volume of a system (such as a gas) is held constant, that system can do no work. Putting  $W = 0$  in the first law (Eq. 18-26) yields

$$\Delta E_{\text{int}} = Q \quad (\text{constant-volume process}). \quad (18-29)$$

Thus, if heat is absorbed by a system (that is, if  $Q$  is positive), the internal energy of the system increases. Conversely, if heat is lost during the process (that is, if  $Q$  is negative), the internal energy of the system must decrease.

- 3. Cyclical processes.** There are processes in which, after certain interchanges of heat and work, the system is restored to its initial state. In that case, no intrinsic property of the system—including its internal energy—can possibly change. Putting  $\Delta E_{\text{int}} = 0$  in the first law (Eq. 18-26) yields

$$Q = W \quad (\text{cyclical process}). \quad (18-30)$$

Thus, the net work done during the process must exactly equal the net amount of energy transferred as heat; the store of internal energy of the system remains unchanged. Cyclical processes form a closed loop on a  $p$ - $V$  plot, as shown in Fig. 18-14f. We discuss such processes in detail in Chapter 20.

- 4. Free expansions.** These are adiabatic processes in which no transfer of heat occurs between the system and its environment and no work is done on or by the system. Thus,  $Q = W = 0$ , and the first law requires that

$$\Delta E_{\text{int}} = 0 \quad (\text{free expansion}). \quad (18-31)$$

Figure 18-16 shows how such an expansion can be carried out. A gas, which is in thermal equilibrium within itself, is initially confined by a closed stopcock to one half of an insulated double chamber; the other half is evacuated. The stopcock is opened, and the gas expands freely to fill both halves of the chamber. No heat is

**Table 18-5** The First Law of Thermodynamics: Four Special Cases

<i>The Law: <math>\Delta E_{\text{int}} = Q - W</math> (Eq. 18-26)</i>		
Process	Restriction	Consequence
Adiabatic	$Q = 0$	$\Delta E_{\text{int}} = -W$
Constant volume	$W = 0$	$\Delta E_{\text{int}} = Q$
Closed cycle	$\Delta E_{\text{int}} = 0$	$Q = W$
Free expansion	$Q = W = 0$	$\Delta E_{\text{int}} = 0$

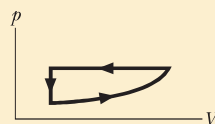
transferred to or from the gas because of the insulation. No work is done by the gas because it rushes into a vacuum and thus does not meet any pressure.

A free expansion differs from all other processes we have considered because it cannot be done slowly and in a controlled way. As a result, at any given instant during the sudden expansion, the gas is not in thermal equilibrium and its pressure is not uniform. Thus, although we can plot the initial and final states on a  $p$ - $V$  diagram, we cannot plot the expansion itself.



### Checkpoint 6

For one complete cycle as shown in the  $p$ - $V$  diagram here, are (a)  $\Delta E_{\text{int}}$  for the gas and (b) the net energy transferred as heat  $Q$  positive, negative, or zero?



### Sample Problem 18.05 First law of thermodynamics: work, heat, internal energy change

Let 1.00 kg of liquid water at  $100^\circ\text{C}$  be converted to steam at  $100^\circ\text{C}$  by boiling at standard atmospheric pressure (which is 1.00 atm or  $1.01 \times 10^5$  Pa) in the arrangement of Fig. 18-17. The volume of that water changes from an initial value of  $1.00 \times 10^{-3}$  m<sup>3</sup> as a liquid to 1.671 m<sup>3</sup> as steam.

(a) How much work is done by the system during this process?

#### KEY IDEAS

(1) The system must do positive work because the volume increases. (2) We calculate the work  $W$  done by integrating the pressure with respect to the volume (Eq. 18-25).

**Calculation:** Because here the pressure is constant at  $1.01 \times 10^5$  Pa, we can take  $p$  outside the integral. Thus,

$$\begin{aligned} W &= \int_{V_i}^{V_f} p \, dV = p \int_{V_i}^{V_f} dV = p(V_f - V_i) \\ &= (1.01 \times 10^5 \text{ Pa})(1.671 \text{ m}^3 - 1.00 \times 10^{-3} \text{ m}^3) \\ &= 1.69 \times 10^5 \text{ J} = 169 \text{ kJ.} \end{aligned} \quad (\text{Answer})$$

(b) How much energy is transferred as heat during the process?

#### KEY IDEA

Because the heat causes only a phase change and not a change in temperature, it is given fully by Eq. 18-16 ( $Q = Lm$ ).

**Calculation:** Because the change is from liquid to gaseous phase,  $L$  is the heat of vaporization  $L_V$ , with the value given in Eq. 18-17 and Table 18-4. We find

$$\begin{aligned} Q &= L_V m = (2256 \text{ kJ/kg})(1.00 \text{ kg}) \\ &= 2256 \text{ kJ} \approx 2260 \text{ kJ.} \end{aligned} \quad (\text{Answer})$$

(c) What is the change in the system's internal energy during the process?

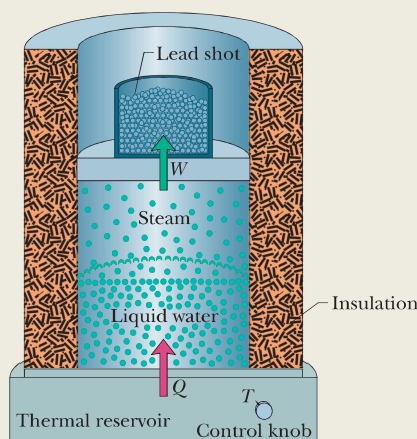
#### KEY IDEA

The change in the system's internal energy is related to the heat (here, this is energy transferred into the system) and the work (here, this is energy transferred out of the system) by the first law of thermodynamics (Eq. 18-26).

**Calculation:** We write the first law as

$$\begin{aligned} \Delta E_{\text{int}} &= Q - W = 2256 \text{ kJ} - 169 \text{ kJ} \\ &\approx 2090 \text{ kJ} = 2.09 \text{ MJ.} \end{aligned} \quad (\text{Answer})$$

This quantity is positive, indicating that the internal energy of the system has increased during the boiling process. The added energy goes into separating the H<sub>2</sub>O molecules, which strongly attract one another in the liquid state. We see that, when water is boiled, about 7.5% (= 169 kJ/2260 kJ) of the heat goes into the work of pushing back the atmosphere. The rest of the heat goes into the internal energy of the system.



**Figure 18-17** Water boiling at constant pressure. Energy is transferred from the thermal reservoir as heat until the liquid water has changed completely into steam. Work is done by the expanding gas as it lifts the loaded piston.



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