

8. Fig. 7 shows the humid air is flowing across a mountain continuously. The pressure detected at observatories  $M_0$  and  $M_3$  are both 100 kPa. The temperature at  $M_0$  is 20 °C. The pressure detected at observatories  $M_1$  and  $M_2$  are 84.5 kPa and 70 kPa respectively. The humid air rises from  $M_0$  and starts to form a cloud at  $M_1$ . After 1500 s, the humid air arrives at  $M_2$ . During the rising process, the water vapor in air condenses and then falls down to the ground. Suppose the mass of the humid air is 2000 kg per meter square, and 2.45 g of water condenses from 1 kg of humid air.

- (1) Find the temperature  $T_1$  at the bottom of the cloud ( $M_1$ ).
- (2) Find the height between  $M_1$  (the bottom of the cloud) and  $M_0$ , if the density of the air decreases linearly with height.
- (3) Find the temperature  $T_2$  detected at  $M_2$ .
- (4) Find the amount of rainfall formed in 3 hours, assuming that the amount of rainfall between  $M_1$  and  $M_2$  is uniform.
- (5) Find the temperature  $T_3$  detected at  $M_3$ . Discuss the state of the air at  $M_3$ , comparing it with that in  $M_0$ .

Hints and data:

1. Consider the air as an ideal gas.
2. Water vapor has negligible effects on the heat capacity and the air.
3. Neglect the change of latent heat of vaporization with temperature.
4. Correct the temperature, the height and the amount of rainfall to the nearest 1 K, 10 m and 1 mm respectively.

The specific heat of air at constant pressure  $C_p = 1005 \text{ J kg}^{-1} \text{ K}^{-1}$ . At  $M_0$ , the density of the air is  $\rho_0 = 1.18 \text{ kg m}^{-3}$ . In the cloud, the latent heat of vaporization at constant volume is  $L_V = 2500 \text{ kJ kg}^{-1}$ . Also,  $C_p / C_V = \gamma$ ,  $\gamma = 1.4$  and  $g = 9.81 \text{ m s}^{-2}$ .

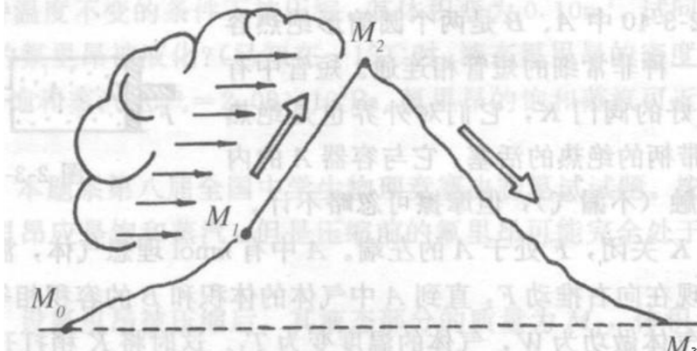


Fig. 7

7. The compression ratio of a four-cycle internal combustion engine is  $\varepsilon = 9.5$ . The temperatures of the gaseous fuel and the exhausted gas are both  $27^\circ\text{C}$ . The volume under atmospheric pressure ( $1\text{ atm} = 100\text{ kPa}$ ) is  $V_0$ . As shown in Fig. 6,  $1 \rightarrow 2$  is an adiabatic compression process;  $2 \rightarrow 3$  is the combustion of the mixture of the gases with doubled pressure;  $3 \rightarrow 4$  is an adiabatic expansion process with the volume expanded to  $9.5 V_0$ ;  $4 \rightarrow 1$  is the process of opening the exhaust valve and the pressure returns to the initial value of  $1\text{ atm}$ . (The compression ratio is the ratio of the largest volume to the smallest volume of the cylinder in the engine.  $\gamma$  is the specific heat ratio, and since the mixture of air and fuel is mainly air, you can effectively consider it as a diatomic gas.)

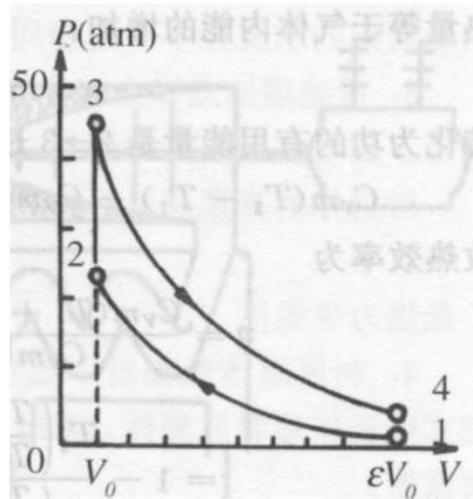
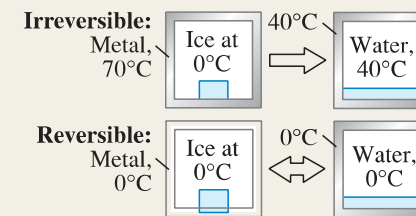


Fig. 6

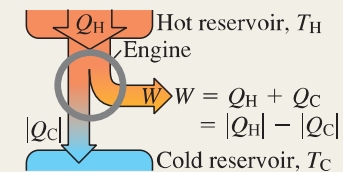
- (a) Find the pressures and temperatures at states 1, 2, 3 and 4.  
 (b) Find the efficiency of this cycle.

**Reversible and irreversible processes:** A reversible process is one whose direction can be reversed by an infinitesimal change in the conditions of the process, and in which the system is always in or very close to thermal equilibrium. All other thermodynamic processes are irreversible.



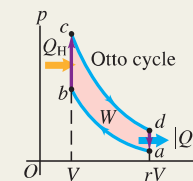
**Heat engines:** A heat engine takes heat  $Q_H$  from a source, converts part of it to work  $W$ , and discards the remainder  $|Q_C|$  at a lower temperature. The thermal efficiency  $e$  of a heat engine measures how much of the absorbed heat is converted to work. (See Example 20.1.)

$$e = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 - \left| \frac{Q_C}{Q_H} \right| \quad (20.4)$$



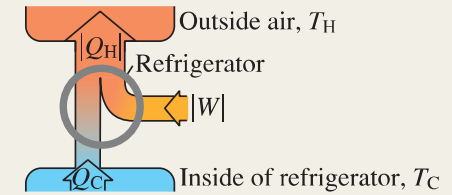
**The Otto cycle:** A gasoline engine operating on the Otto cycle has a theoretical maximum thermal efficiency  $e$  that depends on the compression ratio  $r$  and the ratio of heat capacities  $\gamma$  of the working substance.

$$e = 1 - \frac{1}{r^{\gamma-1}} \quad (20.6)$$

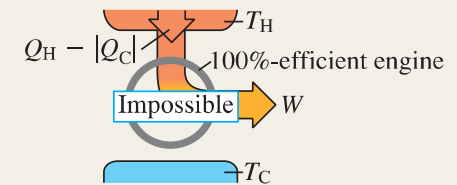


**Refrigerators:** A refrigerator takes heat  $Q_C$  from a colder place, has a work input  $|W|$ , and discards heat  $|Q_H|$  at a warmer place. The effectiveness of the refrigerator is given by its coefficient of performance  $K$ .

$$K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|} \quad (20.9)$$



**The second law of thermodynamics:** The second law of thermodynamics describes the directionality of natural thermodynamic processes. It can be stated in several equivalent forms. The *engine* statement is that no cyclic process can convert heat completely into work. The *refrigerator* statement is that no cyclic process can transfer heat from a colder place to a hotter place with no input of mechanical work.

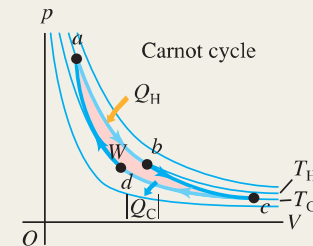


**The Carnot cycle:** The Carnot cycle operates between two heat reservoirs at temperatures  $T_H$  and  $T_C$  and uses only reversible processes. Its thermal efficiency depends only on  $T_H$  and  $T_C$ . An additional equivalent statement of the second law is that no engine operating between the same two temperatures can be more efficient than a Carnot engine. (See Examples 20.2 and 20.3.)

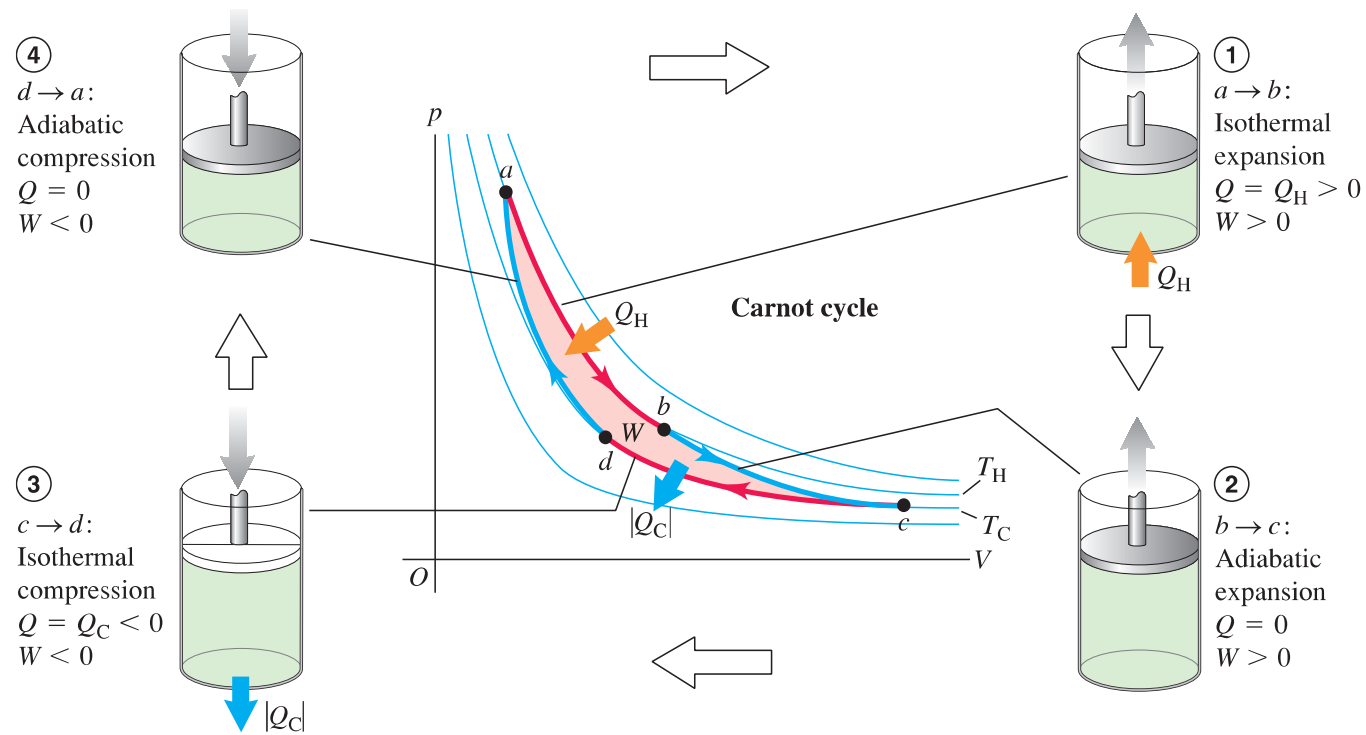
$$e_{\text{Carnot}} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H} \quad (20.14)$$

A Carnot engine run backward is a Carnot refrigerator. Its coefficient of performance depends only on  $T_H$  and  $T_C$ . Another form of the second law states that no refrigerator operating between the same two temperatures can have a larger coefficient of performance than a Carnot refrigerator. (See Example 20.4.)

$$K_{\text{Carnot}} = \frac{T_C}{T_H - T_C} \quad (20.15)$$



**20.13** The Carnot cycle for an ideal gas. The light blue lines in the  $pV$ -diagram are isotherms (curves of constant temperature) and the dark blue lines are adiabats (curves of zero heat flow).



### Example 20.2 Analyzing a Carnot engine I

A Carnot engine takes 2000 J of heat from a reservoir at 500 K, does some work, and discards some heat to a reservoir at 350 K. How much work does it do, how much heat is discarded, and what is its efficiency?

#### SOLUTION

**IDENTIFY and SET UP:** This problem involves a Carnot engine, so we can use the ideas of this section and those of Section 20.2 (which apply to heat engines of all kinds). Figure 20.14 shows the energy-flow diagram. We have  $Q_H = 2000$  J,  $T_H = 500$  K, and  $T_C = 350$  K. We use Eq. (20.13) to find  $Q_C$ , and then use the first law of thermodynamics as given by Eq. (20.2) to find  $W$ . We find the efficiency  $e$  from  $T_C$  and  $T_H$  using Eq. (20.14).

**EXECUTE:** From Eq. (20.13),

$$Q_C = -Q_H \frac{T_C}{T_H} = -(2000 \text{ J}) \frac{350 \text{ K}}{500 \text{ K}} = -1400 \text{ J}$$

Then from Eq. (20.2), the work done is

$$W = Q_H + Q_C = 2000 \text{ J} + (-1400 \text{ J}) = 600 \text{ J}$$

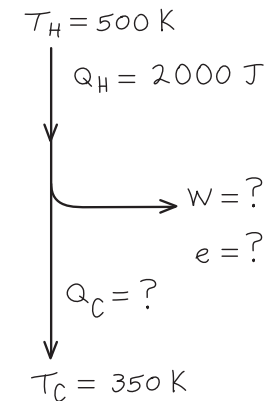
From Eq. (20.14), the thermal efficiency is

$$e = 1 - \frac{T_C}{T_H} = 1 - \frac{350 \text{ K}}{500 \text{ K}} = 0.30 = 30\%$$

**EVALUATE:** The negative sign of  $Q_C$  is correct: It shows that 1400 J of heat flows *out* of the engine and into the cold reservoir. We can check our result for  $e$  by using the basic definition of thermal efficiency, Eq. (20.3):

$$e = \frac{W}{Q_H} = \frac{600 \text{ J}}{2000 \text{ J}} = 0.30 = 30\%$$

**20.14** Our sketch for this problem.



### Example 20.3 Analyzing a Carnot engine II

Suppose 0.200 mol of an ideal diatomic gas ( $\gamma = 1.40$ ) undergoes a Carnot cycle between  $227^\circ\text{C}$  and  $27^\circ\text{C}$ , starting at  $p_a = 10.0 \times 10^5$  Pa at point  $a$  in the  $pV$ -diagram of Fig. 20.13. The volume doubles during the isothermal expansion step  $a \rightarrow b$ . (a) Find the pressure and volume at points  $a$ ,  $b$ ,  $c$ , and  $d$ . (b) Find  $Q$ ,  $W$ , and  $\Delta U$  for each step and for the entire cycle. (c) Find the efficiency directly from the results of part (b), and compare with the value calculated from Eq. (20.14).

**IDENTIFY and SET UP:** This problem involves the properties of the Carnot cycle and those of an ideal gas. We are given the number of moles  $n$  and the pressure and temperature at point  $a$  (which is at the higher of the two reservoir temperatures); we can find the volume at  $a$  using the ideal-gas equation  $pV = nRT$ . We then find the pressure and volume at points  $b$ ,  $c$ , and  $d$  from the known doubling of volume in step  $a \rightarrow b$ , from equations given in this section, and from  $pV = nRT$ . In each step we use Eqs. (20.10) and (20.11) to find the heat flow and work done and Eq. (19.13) to find the internal energy change.

**EXECUTE:** (a) With  $T_H = (227 + 273.15)$  K = 500 K and  $T_C = (27 + 273.15)$  K = 300 K,  $pV = nRT$  yields

$$\begin{aligned} V_a &= \frac{nRT_H}{p_a} = \frac{(0.200 \text{ mol})(8.314 \text{ J/mol}\cdot\text{K})(500 \text{ K})}{10.0 \times 10^5 \text{ Pa}} \\ &= 8.31 \times 10^{-4} \text{ m}^3 \end{aligned}$$

The volume doubles during the isothermal expansion  $a \rightarrow b$ :

$$V_b = 2V_a = 2(8.31 \times 10^{-4} \text{ m}^3) = 16.6 \times 10^{-4} \text{ m}^3$$

Because the expansion  $a \rightarrow b$  is isothermal,  $p_a V_a = p_b V_b$ , so

$$p_b = \frac{p_a V_a}{V_b} = 5.00 \times 10^5 \text{ Pa}$$

For the adiabatic expansion  $b \rightarrow c$ , we use the equation  $T_H V_b^{\gamma-1} = T_C V_c^{\gamma-1}$  that follows Eq. (20.12) as well as the ideal-gas equation:

$$\begin{aligned} V_c &= V_b \left( \frac{T_H}{T_C} \right)^{1/(\gamma-1)} = (16.6 \times 10^{-4} \text{ m}^3) \left( \frac{500 \text{ K}}{300 \text{ K}} \right)^{2.5} \\ &= 59.6 \times 10^{-4} \text{ m}^3 \\ p_c &= \frac{nRT_C}{V_c} = \frac{(0.200 \text{ mol})(8.314 \text{ J/mol}\cdot\text{K})(300 \text{ K})}{59.6 \times 10^{-4} \text{ m}^3} \\ &= 0.837 \times 10^5 \text{ Pa} \end{aligned}$$

For the adiabatic compression  $d \rightarrow a$  we have  $T_C V_d^{\gamma-1} = T_H V_a^{\gamma-1}$  and so

$$\begin{aligned} V_d &= V_a \left( \frac{T_H}{T_C} \right)^{1/(\gamma-1)} = (8.31 \times 10^{-4} \text{ m}^3) \left( \frac{500 \text{ K}}{300 \text{ K}} \right)^{2.5} \\ &= 29.8 \times 10^{-4} \text{ m}^3 \\ p_d &= \frac{nRT_C}{V_d} = \frac{(0.200 \text{ mol})(8.314 \text{ J/mol}\cdot\text{K})(300 \text{ K})}{29.8 \times 10^{-4} \text{ m}^3} \\ &= 1.67 \times 10^5 \text{ Pa} \end{aligned}$$

(b) For the isothermal expansion  $a \rightarrow b$ ,  $\Delta U_{ab} = 0$ . From Eq. (20.10),

$$\begin{aligned} W_{ab} &= Q_H = nRT_H \ln \frac{V_b}{V_a} \\ &= (0.200 \text{ mol})(8.314 \text{ J/mol}\cdot\text{K})(500 \text{ K})(\ln 2) = 576 \text{ J} \end{aligned}$$

For the adiabatic expansion  $b \rightarrow c$ ,  $Q_{bc} = 0$ . From the first law of thermodynamics,  $\Delta U_{bc} = Q_{bc} - W_{bc} = -W_{bc}$ ; the work  $W_{bc}$  done by the gas in this adiabatic expansion equals the negative of the change in internal energy of the gas. From Eq. (19.13) we have  $\Delta U = nC_V\Delta T$ , where  $\Delta T = T_C - T_H$ . Using  $C_V = 20.8 \text{ J/mol} \cdot \text{K}$  for an ideal diatomic gas, we find

$$\begin{aligned} W_{bc} &= -\Delta U_{bc} = -nC_V(T_C - T_H) = nC_V(T_H - T_C) \\ &= (0.200 \text{ mol})(20.8 \text{ J/mol} \cdot \text{K})(500 \text{ K} - 300 \text{ K}) = 832 \text{ J} \end{aligned}$$

For the isothermal compression  $c \rightarrow d$ ,  $\Delta U_{cd} = 0$ ; Eq. (20.11) gives

$$\begin{aligned} W_{cd} &= Q_C = nRT_C \ln \frac{V_d}{V_c} \\ &= (0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K}) \left( \ln \frac{29.8 \times 10^{-4} \text{ m}^3}{59.6 \times 10^{-4} \text{ m}^3} \right) \\ &= -346 \text{ J} \end{aligned}$$

For the adiabatic compression  $d \rightarrow a$ ,  $Q_{da} = 0$  and

$$\begin{aligned} W_{da} &= -\Delta U_{da} = -nC_V(T_H - T_C) = nC_V(T_C - T_H) \\ &= (0.200 \text{ mol})(20.8 \text{ J/mol} \cdot \text{K})(300 \text{ K} - 500 \text{ K}) = -832 \text{ J} \end{aligned}$$

We can tabulate these results as follows:

Process	$Q$	$W$	$\Delta U$
$a \rightarrow b$	576 J	576 J	0
$b \rightarrow c$	0	832 J	-832 J
$c \rightarrow d$	-346 J	-346 J	0
$d \rightarrow a$	0	-832 J	832 J
Total	230 J	230 J	0

(c) From the above table,  $Q_H = 576 \text{ J}$  and the total work is 230 J. Thus

$$e = \frac{W}{Q_H} = \frac{230 \text{ J}}{576 \text{ J}} = 0.40 = 40\%$$

We can compare this to the result from Eq. (20.14),

$$e = \frac{T_H - T_C}{T_H} = \frac{500 \text{ K} - 300 \text{ K}}{500 \text{ K}} = 0.40 = 40\%$$

**EVALUATE:** The table in part (b) shows that for the entire cycle  $Q = W$  and  $\Delta U = 0$ , just as we would expect: In a complete cycle, the *net* heat input is used to do work, and there is zero net change in the internal energy of the system. Note also that the quantities of work in the two adiabatic processes are negatives of each other. Can you show from the analysis leading to Eq. (20.13) that this must *always* be the case in a Carnot cycle?



### Example 20.4 Analyzing a Carnot refrigerator

If the cycle described in Example 20.3 is run backward as a refrigerator, what is its coefficient of performance?

#### SOLUTION

**IDENTIFY and SET UP:** This problem uses the ideas of Section 20.3 (for refrigerators in general) and the above discussion of Carnot refrigerators. Equation (20.9) gives the coefficient of performance  $K$  of *any* refrigerator in terms of the heat  $Q_C$  extracted from the cold reservoir per cycle and the work  $W$  that must be done per cycle.

**EXECUTE:** In Example 20.3 we found that in one cycle the Carnot engine rejects heat  $Q_C = -346$  J to the cold reservoir and does work  $W = 230$  J. When run in reverse as a refrigerator, the system

extracts heat  $Q_C = +346$  J from the cold reservoir while requiring a work input of  $W = -230$  J. From Eq. (20.9),

$$K = \frac{|Q_C|}{|W|} = \frac{346 \text{ J}}{230 \text{ J}} = 1.50$$

Because this is a Carnot cycle, we can also use Eq. (20.15):

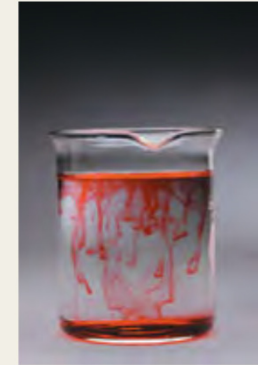
$$K = \frac{T_C}{T_H - T_C} = \frac{300 \text{ K}}{500 \text{ K} - 300 \text{ K}} = 1.50$$

**EVALUATE:** Equations (20.14) and (20.15) show that  $e$  and  $K$  for a Carnot cycle depend only on  $T_H$  and  $T_C$ , and we don't need to calculate  $Q$  and  $W$ . For cycles containing irreversible processes, however, these two equations are not valid, and more detailed calculations are necessary.

**Entropy:** Entropy is a quantitative measure of the disorder of a system. The entropy change in any reversible process depends on the amount of heat flow and the absolute temperature  $T$ . Entropy depends only on the state of the system, and the change in entropy between given initial and final states is the same for all processes leading from one state to the other. This fact can be used to find the entropy change in an irreversible process. (See Examples 20.5–20.10.)

$$\Delta S = \int_1^2 \frac{dQ}{T} \quad (20.19)$$

(reversible process)

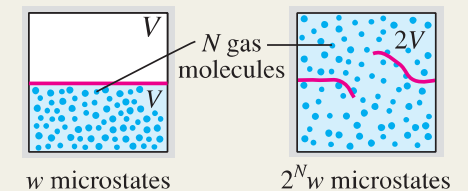


**(path-independent!)**

An important statement of the second law of thermodynamics is that the entropy of an isolated system may increase but can never decrease. When a system interacts with its surroundings, the total entropy change of system and surroundings can never decrease. When the interaction involves only reversible processes, the total entropy is constant and  $\Delta S = 0$ ; when there is any irreversible process, the total entropy increases and  $\Delta S > 0$ .

**Entropy and microscopic states:** When a system is in a particular macroscopic state, the particles that make up the system may be in any of  $w$  possible microscopic states. The greater the number  $w$ , the greater the entropy. (See Example 20.11.)

$$S = k \ln w \quad (20.22)$$



## Example 20.6 Entropy change in a temperature change

One kilogram of water at 0°C is heated to 100°C. Compute its change in entropy. Assume that the specific heat of water is constant at 4190 J/kg · K over this temperature range.

### SOLUTION

**IDENTIFY and SET UP:** The entropy change of the water depends only on the initial and final states of the system, no matter whether the process is reversible or irreversible. We can imagine a reversible process in which the water temperature is increased in a sequence of infinitesimal steps  $dT$ . We can use Eq. (20.19) to integrate over all these steps and calculate the entropy change for such a reversible process. (Heating the water on a stove whose cooking surface is maintained at 100°C would be an irreversible process. The entropy change would be the same, however.)

**EXECUTE:** From Eq. (17.14) the heat required to carry out each infinitesimal step is  $dQ = mc dT$ . Substituting this into Eq. (20.19) and integrating, we find

$$\begin{aligned}\Delta S &= S_2 - S_1 = \int_1^2 \frac{dQ}{T} = \int_{T_1}^{T_2} mc \frac{dT}{T} = mc \ln \frac{T_2}{T_1} \\ &= (1.00 \text{ kg})(4190 \text{ J/kg} \cdot \text{K}) \left( \ln \frac{373 \text{ K}}{273 \text{ K}} \right) \\ &= 1.31 \times 10^3 \text{ J/K}\end{aligned}$$

**EVALUATE:** The entropy change is positive, as it must be for a process in which the system absorbs heat. Our assumption about the specific heat is a pretty good one, since  $c$  for water increases by only 1% between 0°C and 100°C.

**CAUTION** When  $\Delta S = Q/T$  can (and cannot) be used In solving this problem you might be tempted to avoid doing an integral by using the simpler expression in Eq. (20.18),  $\Delta S = Q/T$ . This would be incorrect, however, because Eq. (20.18) is applicable only to *isothermal* processes, and the initial and final temperatures in our example are *not* the same. The *only* correct way to find the entropy change in a process with different initial and final temperatures is to use Eq. (20.19). ▮

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### Conceptual Example 20.7 Entropy change in a reversible adiabatic process

A gas expands adiabatically and reversibly. What is its change in entropy?

#### SOLUTION

In an adiabatic process, no heat enters or leaves the system. Hence  $dQ = 0$  and there is *no* change in entropy in this reversible

process:  $\Delta S = 0$ . Every *reversible* adiabatic process is a constant-entropy process. (That's why such processes are also called *isentropic* processes.) The increase in disorder resulting from the gas occupying a greater volume is exactly balanced by the decrease in disorder associated with the lowered temperature and reduced molecular speeds.

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### Example 20.9 Entropy and the Carnot cycle

For the Carnot engine in Example 20.2 (Section 20.6), what is the total entropy change during one cycle?

#### SOLUTION

**IDENTIFY and SET UP:** All four steps in the Carnot cycle (see Fig. 20.13) are reversible, so we can use our expressions for the entropy change  $\Delta S$  in a reversible process. We find  $\Delta S$  for each step and add them to get  $\Delta S$  for the complete cycle.

**EXECUTE:** There is no entropy change during the adiabatic expansion  $b \rightarrow c$  or the adiabatic compression  $d \rightarrow a$ . During the isothermal expansion  $a \rightarrow b$  at  $T_H = 500$  K, the engine takes in 2000 J of heat, and from Eq. (20.18),

$$\Delta S_H = \frac{Q_H}{T_H} = \frac{2000 \text{ J}}{500 \text{ K}} = 4.0 \text{ J/K}$$

During the isothermal compression  $c \rightarrow d$  at  $T_C = 350$  K, the engine gives off 1400 J of heat, and

$$\Delta S_C = \frac{Q_C}{T_C} = \frac{-1400 \text{ J}}{350 \text{ K}} = -4.0 \text{ J/K}$$

The total entropy change in the engine during one cycle is  $\Delta S_{\text{tot}} = \Delta S_H + \Delta S_C = 4.0 \text{ J/K} + (-4.0 \text{ J/K}) = 0$ .

**EVALUATE:** The result  $\Delta S_{\text{total}} = 0$  tells us that when the Carnot engine completes a cycle, it has the same entropy as it did at the beginning of the cycle. We'll explore this result in the next subsection.

What is the total entropy change of the engine's *environment* during this cycle? During the reversible isothermal expansion  $a \rightarrow b$ , the hot (500 K) reservoir gives off 2000 J of heat, so its entropy change is  $(-2000 \text{ J})/(500 \text{ K}) = -4.0 \text{ J/K}$ . During the reversible isothermal compression  $c \rightarrow d$ , the cold (350 K) reservoir absorbs 1400 J of heat, so its entropy change is  $(+1400 \text{ J})/(350 \text{ K}) = +4.0 \text{ J/K}$ . Thus the hot and cold reservoirs each have an entropy change, but the sum of these changes—that is, the total entropy change of the system's environment—is zero.

These results apply to the special case of the Carnot cycle, for which *all* of the processes are reversible. In this case we find that the total entropy change of the system and the environment together is zero. We will see that if the cycle includes irreversible processes (as is the case for the Otto and Diesel cycles of Section 20.3), the total entropy change of the system and the environment *cannot* be zero, but rather must be positive.

### Example 20.10 Entropy change in an irreversible process

Suppose 1.00 kg of water at 100°C is placed in thermal contact with 1.00 kg of water at 0°C. What is the total change in entropy? Assume that the specific heat of water is constant at 4190 J/kg · K over this temperature range.

#### SOLUTION

**IDENTIFY and SET UP:** This process involves irreversible heat flow because of the temperature differences. There are equal

masses of 0°C water and 100°C water, so the final temperature is the average of these two temperatures: 50°C = 323 K. Although the processes are irreversible, we can calculate the entropy changes for the (initially) hot water and the (initially) cold water by assuming that the process occurs reversibly. As in Example 20.6, we must use Eq. (20.19) to calculate  $\Delta S$  for each substance because the temperatures are not constant.

*Continued*

**EXECUTE:** The entropy changes of the hot water (subscript H) and the cold water (subscript C) are

$$\begin{aligned}\Delta S_H &= mc \int_{T_1}^{T_2} \frac{dT}{T} = (1.00 \text{ kg})(4190 \text{ J/kg} \cdot \text{K}) \int_{373 \text{ K}}^{323 \text{ K}} \frac{dT}{T} \\ &= (4190 \text{ J/K}) \left( \ln \frac{323 \text{ K}}{373 \text{ K}} \right) = -603 \text{ J/K} \\ \Delta S_C &= (4190 \text{ J/K}) \left( \ln \frac{323 \text{ K}}{273 \text{ K}} \right) = +705 \text{ J/K}\end{aligned}$$

The *total* entropy change of the system is

$$\Delta S_{\text{tot}} = \Delta S_H + \Delta S_C = (-603 \text{ J/K}) + 705 \text{ J/K} = +102 \text{ J/K}$$

**EVALUATE:** An irreversible heat flow in an isolated system is accompanied by an increase in entropy. We could reach the same

end state by mixing the hot and cold water, which is also an irreversible process; the total entropy change, which depends only on the initial and final states of the system, would again be 102 J/K.

Note that the entropy of the system increases *continuously* as the two quantities of water come to equilibrium. For example, the first 4190 J of heat transferred cools the hot water to 99°C and warms the cold water to 1°C. The net change in entropy for this step is approximately

$$\Delta S = \frac{-4190 \text{ J}}{373 \text{ K}} + \frac{4190 \text{ J}}{273 \text{ K}} = +4.1 \text{ J/K}$$

Can you show in a similar way that the net entropy change is positive for *any* one-degree temperature change leading to the equilibrium condition?

### Example 20.8 Entropy change in a free expansion

A partition divides a thermally insulated box into two compartments, each of volume  $V$  (Fig. 20.18). Initially, one compartment contains  $n$  moles of an ideal gas at temperature  $T$ , and the other compartment is evacuated. We break the partition and the gas expands, filling both compartments. What is the entropy change in this free-expansion process?

#### SOLUTION

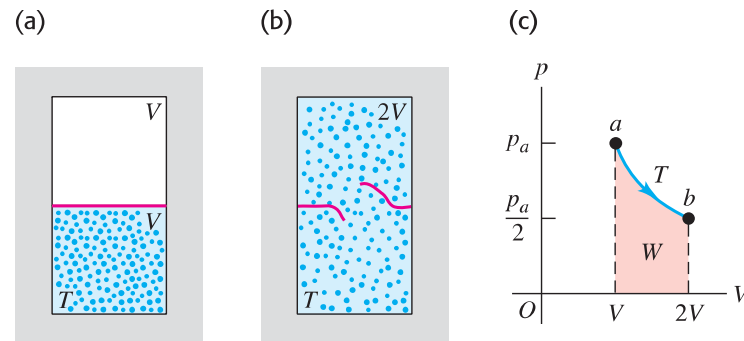
**IDENTIFY and SET UP:** For this process,  $Q = 0$ ,  $W = 0$ ,  $\Delta U = 0$ , and therefore (because the system is an ideal gas)  $\Delta T = 0$ . We might think that the entropy change is zero because there is no heat exchange. But Eq. (20.19) can be used to calculate entropy changes for *reversible* processes only; this free expansion is *not* reversible, and there *is* an entropy change. As we mentioned at the beginning of this section, entropy increases in a free expansion because the positions of the molecules are more random than before the expansion. To calculate  $\Delta S$ , we recall that the entropy change depends only on the initial and final states. We can devise a

An appropriate reversible process is an *isothermal* expansion from  $V$  to  $2V$  at temperature  $T$ , which allows us to use the simpler Eq. (20.18) to calculate  $\Delta S$ . The gas does work  $W$  during this expansion, so an equal amount of heat  $Q$  must be supplied to keep the internal energy constant.

**EXECUTE:** We saw in Example 19.1 that the work done by  $n$  moles of ideal gas in an isothermal expansion from  $V_1$  to  $V_2$  is  $W = nRT \ln(V_2/V_1)$ . With  $V_1 = V$  and  $V_2 = 2V$ , we have

$$Q = W = nRT \ln \frac{2V}{V} = nRT \ln 2$$

**20.18** (a, b) Free expansion of an insulated ideal gas. (c) The free-expansion process doesn't pass through equilibrium states from  $a$  to  $b$ . However, the entropy change  $S_b - S_a$  can be calculated by using the isothermal path shown or *any* reversible path from  $a$  to  $b$ .



*reversible* process having the same endpoints as this free expansion, and in general we can then use Eq. (20.19) to calculate its entropy change, which will be the same as for the free expansion.

From Eq. (20.18), the entropy change is

$$\Delta S = \frac{Q}{T} = nR \ln 2$$

**EVALUATE:** For 1 mole,  $\Delta S = (1 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(\ln 2) = 5.76 \text{ J/K}$ . The entropy change is positive, as we predicted. The factor  $(\ln 2)$  in our answer is a result of the volume having increased by a factor of 2, from  $V$  to  $2V$ . Can you show that if the volume increases in a free expansion from  $V$  to  $xV$ , where  $x$  is an arbitrary number, the entropy change is  $\Delta S = nR \ln x$ ?

### Example 20.11 A microscopic calculation of entropy change

Use Eq. (20.23) to calculate the entropy change in the free expansion of  $n$  moles of gas at temperature  $T$  described in Example 20.8 (Fig. 20.22).

#### SOLUTION

**IDENTIFY and SET UP:** We are asked to calculate the entropy change using the number of microstates in the initial and final macroscopic states (Figs. 20.22a and b). When the partition is broken, no work is done, so the velocities of the molecules are unaffected. But each molecule now has twice as much volume in which it can move and hence has twice the number of possible positions. This is all we need to calculate the entropy change using Eq. (20.23).

**EXECUTE:** Let  $w_1$  be the number of microscopic states of the system as a whole when the gas occupies volume  $V$  (Fig. 20.22a). The number of molecules is  $N = nN_A$ , and each of these  $N$  molecules has twice as many possible states after the partition is broken. Hence the number  $w_2$  of microscopic states when the gas occupies volume  $2V$  (Fig. 20.22b) is greater by a factor of  $2^N$ ; that is,  $w_2 = 2^N w_1$ . The change in entropy in this process is

$$\Delta S = k \ln \frac{w_2}{w_1} = k \ln \frac{2^N w_1}{w_1} = k \ln 2^N = Nk \ln 2$$

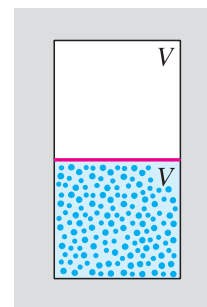
Since  $N = nN_A$  and  $k = R/N_A$ , this becomes

$$\Delta S = (nN_A)(R/N_A) \ln 2 = nR \ln 2$$

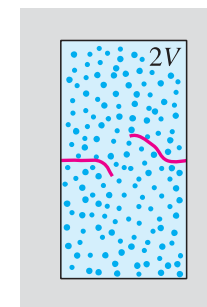
**EVALUATE:** We found the same result as in Example 20.8, but without any reference to the thermodynamic path taken.

**20.22** In a free expansion of  $N$  molecules in which the volume doubles, the number of possible microscopic states increases by  $2^N$ .

(a) Gas occupies volume  $V$ ; number of microstates =  $w_1$ .



(b) Gas occupies volume  $2V$ ; number of microstates =  $w_2 = 2^N w_1$ .





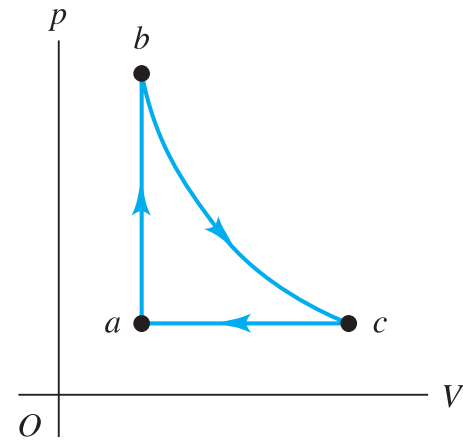
**20.3 • A Gasoline Engine.** A gasoline engine takes in  $1.61 \times 10^4$  J of heat and delivers 3700 J of work per cycle. The heat is obtained by burning gasoline with a heat of combustion of  $4.60 \times 10^4$  J/g. (a) What is the thermal efficiency? (b) How much heat is discarded in each cycle? (c) What mass of fuel is burned in each cycle? (d) If the engine goes through 60.0 cycles per second, what is its power output in kilowatts? In horsepower?

**20.11 ••** A refrigerator has a coefficient of performance of 2.25, runs on an input of 95 W of electrical power, and keeps its inside compartment at  $5^{\circ}\text{C}$ . If you put a dozen 1.0-L plastic bottles of water at  $31^{\circ}\text{C}$  into this refrigerator, how long will it take for them to be cooled down to  $5^{\circ}\text{C}$ ? (Ignore any heat that leaves the plastic.)

**20.12 ••** A freezer has a coefficient of performance of 2.40. The freezer is to convert 1.80 kg of water at  $25.0^{\circ}\text{C}$  to 1.80 kg of ice at  $-5.0^{\circ}\text{C}$  in one hour. (a) What amount of heat must be removed from the water at  $25.0^{\circ}\text{C}$  to convert it to ice at  $-5.0^{\circ}\text{C}$ ? (b) How much electrical energy is consumed by the freezer during this hour? (c) How much wasted heat is delivered to the room in which the freezer sits?

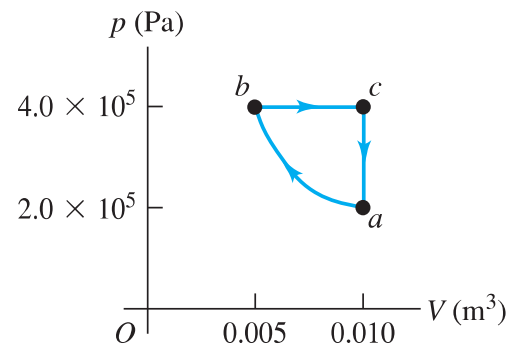
**20.43 • CALC** A heat engine operates using the cycle shown in Fig. P20.43. The working substance is 2.00 mol of helium gas, which reaches a maximum temperature of  $327^\circ\text{C}$ . Assume the helium can be treated as an ideal gas. Process  $bc$  is isothermal. The pressure in states  $a$  and  $c$  is  $1.00 \times 10^5 \text{ Pa}$ , and the pressure in state  $b$  is  $3.00 \times 10^5 \text{ Pa}$ . (a) How much heat enters the gas and how much leaves the gas each cycle? (b) How much work does the engine do each cycle, and what is its efficiency? (c) Compare this engine's efficiency with the maximum possible efficiency attainable with the hot and cold reservoirs used by this cycle.

Figure P20.43



**20.41 •• CALC** You build a heat engine that takes 1.00 mol of an ideal diatomic gas through the cycle shown in Fig. P20.41. (a) Show that segment  $ab$  is an isothermal compression. (b) During which segment(s) of the cycle is heat absorbed by the gas? During which segment(s) is heat rejected?

Figure **P20.41**



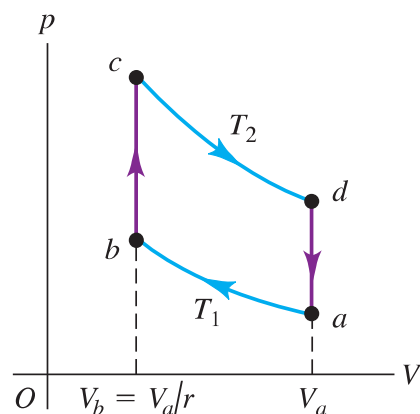
How do you know? (c) Calculate the temperature at points  $a$ ,  $b$ , and  $c$ . (d) Calculate the net heat exchanged with the surroundings and the net work done by the engine in one cycle. (e) Calculate the thermal efficiency of the engine.

**20.45** ••• An experimental power plant at the Natural Energy Laboratory of Hawaii generates electricity from the temperature gradient of the ocean. The surface and deep-water temperatures are  $27^{\circ}\text{C}$  and  $6^{\circ}\text{C}$ , respectively. (a) What is the maximum theoretical efficiency of this power plant? (b) If the power plant is to produce 210 kW of power, at what rate must heat be extracted from the warm water? At what rate must heat be absorbed by the cold water? Assume the maximum theoretical efficiency. (c) The cold water that enters the plant leaves it at a temperature of  $10^{\circ}\text{C}$ . What must be the flow rate of cold water through the system? Give your answer in kg/h and in L/h.

**20.50 •• CP Entropy Change Due to the Sun.** Our sun radiates from a surface at 5800 K (with an emissivity of 1.0) into the near-vacuum of space, which is at a temperature of 3 K. (a) By how much does our sun change the entropy of the universe every second? (Consult Appendix F.) (b) Is the process reversible or irreversible? Is your answer to part (a) consistent with this conclusion? Explain.

**20.52 •• CALC A Stirling-Cycle Engine.** The *Stirling cycle* is similar to the Otto cycle, except that the compression and expansion of the gas are done at constant temperature, not adiabatically as in the Otto cycle. The Stirling cycle is used in *external* combustion engines (in fact, burning fuel is not necessary; *any* way of producing a temperature difference will do—solar, geothermal, ocean temperature gradient, etc.), which means that the gas inside the cylinder is not used in the combustion process. Heat is supplied by burning fuel steadily outside the cylinder, instead of explosively inside the cylinder as in the Otto cycle. For this reason Stirling-cycle engines are quieter than Otto-cycle engines, since there are no intake and exhaust valves (a major source of engine noise). While small Stirling engines are used for a variety of purposes, Stirling engines for automobiles have not been successful because they are larger, heavier, and more expensive than conventional automobile engines. In the cycle, the working fluid goes through the following sequence of steps (Fig. P20.52):

Figure P20.52



- (i) Compressed isothermally at temperature  $T_1$  from the initial state  $a$  to state  $b$ , with a compression ratio  $r$ .
- (ii) Heated at constant volume to state  $c$  at temperature  $T_2$ .
- (iii) Expanded isothermally at  $T_2$  to state  $d$ .
- (iv) Cooled at constant volume back to the initial state  $a$ .

Assume that the working fluid is  $n$  moles of an ideal gas (for which  $C_V$  is independent of temperature). (a) Calculate  $Q$ ,  $W$ , and  $\Delta U$  for each of the processes  $a \rightarrow b$ ,  $b \rightarrow c$ ,  $c \rightarrow d$ , and  $d \rightarrow a$ . (b) In the Stirling cycle, the heat transfers in the processes  $b \rightarrow c$  and  $d \rightarrow a$  do not involve external heat sources but rather use *regeneration*: The same substance that transfers heat to the gas inside the cylinder in the process  $b \rightarrow c$  also absorbs heat back from the gas in the process  $d \rightarrow a$ . Hence the heat transfers  $Q_{b \rightarrow c}$  and  $Q_{d \rightarrow a}$  do not play a role in determining the efficiency of the engine. Explain this last statement by comparing the expressions for  $Q_{b \rightarrow c}$  and  $Q_{d \rightarrow a}$  calculated in part (a). (c) Calculate the efficiency of a Stirling-cycle engine in terms of the temperatures  $T_1$  and  $T_2$ . How does this compare to the efficiency of a Carnot-cycle engine operating between these same two temperatures? (Historically, the Stirling cycle was devised before the Carnot cycle.) Does this result violate the second law of thermodynamics? Explain. Unfortunately, actual Stirling-cycle engines cannot achieve this efficiency due to problems with the heat-transfer processes and pressure losses in the engine.

**20.63 •• CALC** An object of mass  $m_1$ , specific heat  $c_1$ , and temperature  $T_1$  is placed in contact with a second object of mass  $m_2$ , specific heat  $c_2$ , and temperature  $T_2 > T_1$ . As a result, the temperature of the first object increases to  $T$  and the temperature of the second object decreases to  $T'$ . (a) Show that the entropy increase of the system is

$$\Delta S = m_1 c_1 \ln \frac{T}{T_1} + m_2 c_2 \ln \frac{T'}{T_2}$$

and show that energy conservation requires that

$$m_1 c_1 (T - T_1) = m_2 c_2 (T_2 - T')$$

(b) Show that the entropy change  $\Delta S$ , considered as a function of  $T$ , is a *maximum* if  $T = T'$ , which is just the condition of thermodynamic equilibrium. (c) Discuss the result of part (b) in terms of the idea of entropy as a measure of disorder.