Chapter 18

The First and Second Laws of Thermodynamics

18.1 THE FIRST LAW OF THERMODYNAMICS

We have seen that *work* is the mechanical transfer of energy from one system to another and that *heat* is the nonmechanical transfer of energy from one system to another. The **first law of thermodynamics** is the statement of the law of conservation of energy in its most general form. It presumes, as we have already described, that every system has a definite total energy content, called the internal energy of the system U, and that U changes only as a consequence of the transfer of energy into or out of the system from the "other" systems which represent the rest of the universe. Thus, the overall energy of the universe remains the same.

Let W represent the algebraic work done *by* the system on the outside world during some process; that is, W is positive when the system does positive work and thereby loses energy, and W is negative when the system does negative work and thereby gains energy. Let Q represent the algebraic heat *entering* the system during the same process; that is, Q is positive when energy is added to the system by nonmechanical means, and Q is negative when energy leaves the system by nonmechanical means. Then, if U_i and U_f are, respectively, the initial and final total internal energy of the system at the beginning and at the end of the process, we must have

$$U_f - U_i = Q - W \tag{18.1}$$

This is the mathematical statement of the first law. It is schematically represented in Fig. 18-1. Equation (*18.1*) holds whether the process is turbulent and chaotic or gentle and quasistatic. The sign conventions for Q and W are historical, and they are standard in physics and most engineering.

> ***Note.*** Only the *difference* in internal energies of two states appears in Eq. (*18.1*). It is the difference in internal energies between states that is important, not the actual values. The actual values of the internal energy for the states of a system are obtained by arbitrarily assigning a numerical value to some chosen reference state, much as in the case of mechanical potential energy. Once such a value is assigned, the values of all the other states of the system are then fixed relative to that value.

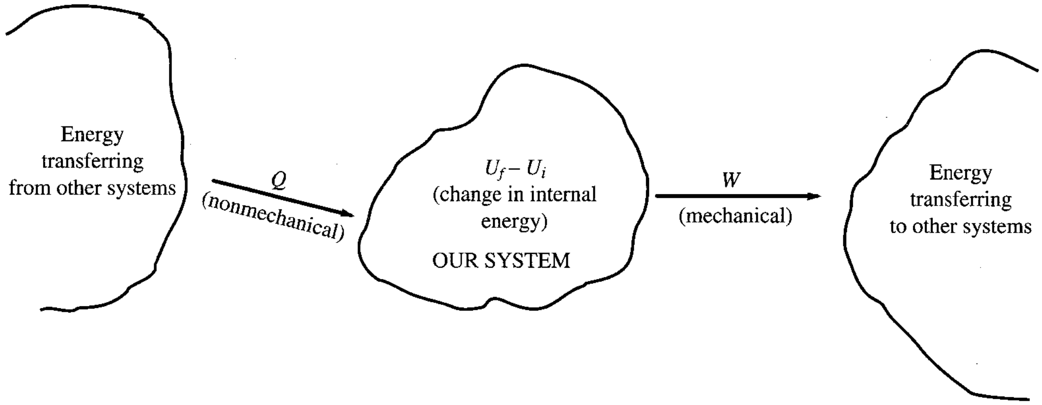


Fig. 18-1

Work and the P-V Diagram

In the case of a quasistatic process for a chemical system, the evolving states of the system can be tracked as a path on a *P-V* diagram (Fig. 18-2). In this situation, the initial and final states (points *i* and *f*, respectively) are completely defined by the thermodynamic variables, as are all the states passed through in between. Each state thus has a definite value for the internal energy. Such a track on a *P-V* diagram allows a simple calculation of the work *W* done by the system. To see this, assume that Fig. 18-2 refers to a system consisting of a gas in a cylinder with a close-fitting piston (Fig. 18-3). Suppose the piston is allowed to slowly move out under the pressure of the gas inside. If A is the area of the piston face, the force exerted by the gas (the system) on the piston (part of the environment) is $F = PA$. If the piston moves a small distance Δx, as shown, then the small amount of work done by the gas is $\Delta W = F\,\Delta x = PA\,\Delta x$. But $A\,\Delta x$ is just the change in volume of the gas: $\Delta V = A\,\Delta x$. So

$$\Delta W = P\,\Delta V \qquad (18.2)$$

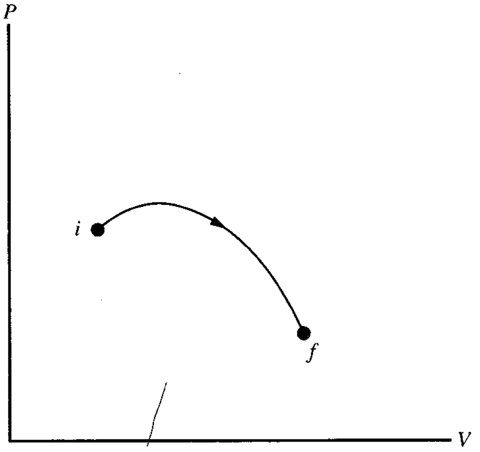


Fig. 18-2

As the gas continues to expand against the piston, the pressure of the gas will change, and the next small amount of work will be $P'\,\Delta V'$; this is followed by $P''\,\Delta V''$, and so on. The total work done will be the sum of all these increments. If Fig. 18-2 represents the change of states of the gas during the expansion, we can see what the pressure is for each volume, and the work done between points *i* and *f* is clearly the total area under the curve on the *P-V* diagram (Fig. 18-4).

It is important to realize that the way the pressure changes with volume is not predetermined by the change in volume alone, since the pressure also depends on the temperature. The temperature can be separately manipulated as the gas in the cylinder slowly expands against the piston, by slowly heating or cooling the gas at various rates during the process. Thus, there are an infinite number of paths the gas can take on a *P-V* diagram in going between the same initial and final states. Figure 18-5 shows a number of alternative paths the system can take in going between the states *i* and *f*, in addition to the original path shown in Fig. 18-2.

For each of these paths the area under the curve is different, and, therefore, so is the work done. For that reason, we say that the work done in going between two states of a system "depends on path." However, the total change in energy depends only on the final and initial states and is just $U_f - U_i$ for all possible paths. Thus, the work done depends on the path, but the total energy change stays the same! How can this happen? The answer lies in Eq. (*18.1*), which implies that the value of Q will also depend on the path in such a way that $Q - W$ always is the same for given initial and final states.

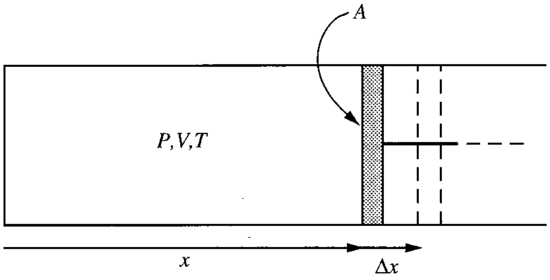


Fig. 18-3

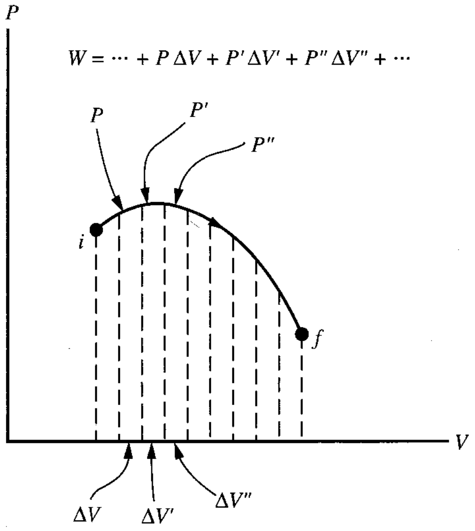


Fig. 18-4

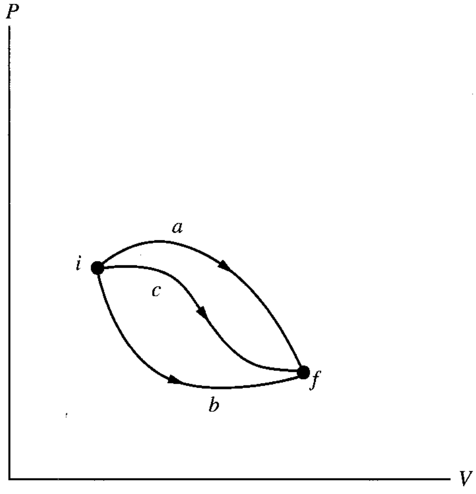


Fig. 18-5

(That Q depends on path is also implied by our description above of how to manipulate the pressure during the process by heating and/or cooling.)

What happens if one reverses the quasistatic process and returns from state f to state i? If, in Fig. 18-5, we retrace path a in the other direction, this corresponds to the piston slowly moving in, and the heat being added and subtracted in the exact reverse of the original process along path a. Clearly, from the P-V diagram (Fig. 18-4), we have

$$W_{a,fi} = -W_{a,if} \tag{18.3a}$$

where the subscripts fi and if mean, respectively, from the final to initial state and from the initial to final state. From Eq. (*18.1*) and the fact that $U_i - U_f = -(U_f - U_i)$, it follows that

$$Q_{a,fi} = -Q_{a,if} \tag{18.3b}$$

Reversing a given quasistatic path thus reverses the signs of the work done and the heat transferred.

Finally, it should be noted that while (*18.2*) was derived for the special case of a gas expanding against a piston, the result is true for any arbitrary shaped, flexible container that slowly changes shape.

Problem 18.1.

(*a*) Assuming that in Fig. 18-5 ~~the~~ work done along path a is 400 J and $U_f - U_i = -180$ J, how much heat entered or left the system during the process?

(*b*) If 60 J of heat enters the system along path b, how much work is done in that process?

Solution

(*a*) From Eq. (*18.1*) we have $-180\text{ J} = Q_{a,if} - 400\text{ J}$ or $Q_{a,if} = 220$ J

(*b*) The change in internal energy is the same, so

$$-180\text{ J} = 60\text{ J} - W_{b,if} \qquad \text{or} \qquad W_{b,if} = 240\text{ J}$$

Problem 18.2.

(*a*) If the heat entering the system along path c of Fig. 18-5 is the arithmetic mean of that entering along paths a and b (see Problem 18.1), then how much work is done in going from i to f along path c?

(*b*) How much heat leaves the system as it returns to state i by the reverse of path c?

Solution

(*a*) From Problem 18.1, the arithmetic mean is $Q_{c,if} = (220\text{ J} + 60\text{ J})/2 = 140$ J. Then, by applying (*18.1*),

$$-180\text{ J} = 140\text{ J} - W_{c,ij} \qquad \text{or} \qquad W_{c,ij} = 320\text{ J}$$

(*b*) $Q_{c,fi} = -Q_{c,if} = -140$ J; that is, 140 J of heat leaves the system.

Problem 18.3. Suppose that the system described in Problems 18.1 and 18.2 goes along path a from state i to f in Fig. 18-5, and then returns to i along the reverse of path b. For such a **cyclical process**, find (*a*) the net change in internal energy; (*b*) the net amount of heat that enters or leaves the system; (*c*) the net work done.

Solution

(*a*) Since the initial and final states are the same, there is no change in internal energy: $U_i - U_i = 0$.

(*b*) From Problem 18.1, $Q_{a,if} = 220$ J and $Q_{b,fi} = -Q_{b,if} = -60$ J. The net heat in the cycle is thus $Q_{a,if} + Q_{b,fi} = 220\text{ J} - 60\text{ J} = 160$ J.

(*c*) The total, or net, work done is $W_{a,if} + W_{b,fi} = W_{a,if} - W_{b,if} = 400\text{ J} - 240\text{ J} = 160$ J. This result could also be obtained by noting that since $\Delta U = 0$, the first law gives $W = Q = 160$ J.

Problem 18.4. Show that in a cyclical process the work done is plus or minus the area enclosed by the closed cycle path on the *P*-*V* diagram.

Solution

We use Problem 18.3 as a model. The net work done in the cycle is $W_{a,if} - W_{b,if}$. In Fig. 18-5 this is just the area under path *a* minus the area under path *b*, which is the area enclosed between the two paths. This area is highlighted for more general paths *a* and *b* in Fig. 18-6. In this cycle the net work is positive because the system expanded at higher pressures (along path *a*) and contracted at lower pressures (along the reverse path *b*). If, instead, the system had expanded along path *b* and contracted along the reverse of path *a*, then the net work would have the same magnitude but a negative sign. Thus we have shown that the work in the cycle is plus or minus the area enclosed, depending on which way the cycle is traversed.

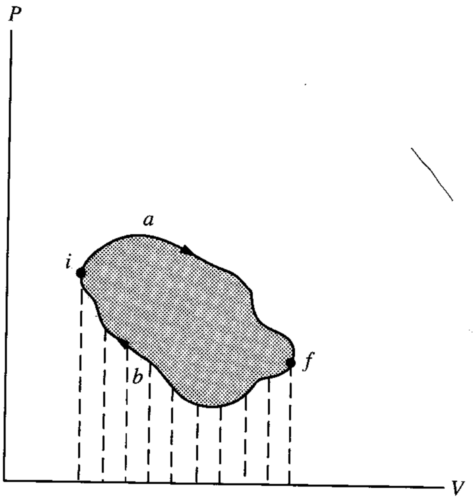


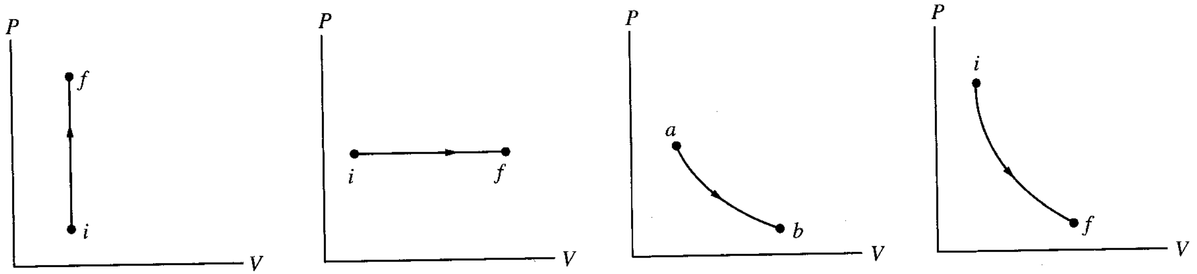
Fig. 18-6

Special Cases of Quasistatic Processes

In studying the various processes that can occur as a system evolves quasistatically, certain ones are of special interest. These (see Fig. 18-7) include a constant-volume process (isovolumic or isochoric), a constant-pressure process (isobaric), a constant-temperature process (isothermal), and a process in which no heat enters or leaves the system (adiabatic). The following problems apply the first law to these processes.

Problem 18.5.

(*a*) In an isochoric process [Fig. 18-7(*a*)], what is the work done? What is the statement of the first law for such a process?



(*a*) Isochoric (*b*) Isobaric (*c*) Isothermal (*d*) Adiabatic

Fig. 18-7

(*b*) If the system consists of n mol of a substance whose molar heat capacity at constant volume is $c_{V,\mathrm{mol}}$, find an expression for the first law that involves the temperature.

Solution

(*a*) For a chemical system the incremental work done is given by $\Delta W = P\,\Delta V$. We see that for our case of no volume change, $\Delta V = 0$, and we can have no work done ($W = 0$). From (*18.1*), the first law becomes

$$Q_{if} = U_f - U_i$$

(*b*) At constant volume we have $Q_{if} = nc_{V,\mathrm{mol}}(T_f - T_i)$, so from (*a*) we have

$$U_f - U_i = nc_{V,\mathrm{mol}}(T_f - T_i) \qquad (i)$$

Note. The direct relationship between internal energy and constant-volume heat capacities was discussed briefly in Ch. 16.

Problem 18.6. Assume that Fig. 18-7(*a*) depicts a sample of 3 mol of an ideal gas with $c_{V,\mathrm{mol}} = 2.5R$, where R is the universal gas constant. Find the change in internal energy between points i and f, given $V_i = 0.20\ \mathrm{m}^3$, $P_i = 2.0 \times 10^5$ Pa, and $P_f = 4.0 \times 10^5$ Pa.

Solution

We can use Eq. (*i*) of Problem 18.5 to obtain $U_f - U_i$. To do this we need the temperatures T_i and T_f. These can be obtained by rearranging the ideal gas law $PV = nRT$: $T_i = P_iV_i/nR$ and $T_f = P_fV_f/nR$. Since $V_f = V_i$ for a constant-volume process, the temperature interval is $T_f - T_i = V_i(P_f - P_i)/nR$. Substituting the expression into Eq. (*i*) of Problem 18.5, we get

$$U_f - U_i = nc_{V,\mathrm{mol}}\frac{V_i(P_f - P_i)}{nR} = c_{V,\mathrm{mol}}\frac{V_i(P_f - P_i)}{R} = 2.5V_i(P_f - P_i)$$

Now we can substitute in values to get

$$U_f - U_i = 2.5(0.20\ \mathrm{m}^3)\,(4.0 \times 10^5\ \mathrm{Pa} - 2.0 \times 10^5\ \mathrm{Pa}) = 1.0 \times 10^5\ \mathrm{J}$$

Problem 18.7.

(*a*) For the isobaric process of Fig. 18-7(*b*), find an expression for the first law that involves the pressure and volume.

(*b*) If the system consists of n mol of a substance with constant-pressure molar heat capacity $c_{P,\mathrm{mol}}$, find an expression for the first law that also involves the temperature.

(*c*) For the special case of an ideal gas, find an expression for the change in internal energy that depends only on the temperature change.

Solution

(*a*) Since the pressure is constant, the work done has the simple form $W_{if} = P_i(V_f - V_i)$. The first law then becomes

$$U_f - U_i = Q_{if} - P_i(V_f - V_i) \qquad (i)$$

(*b*) For a constant-pressure process we have $Q_{if} = nc_{P,\mathrm{mol}}(T_f - T_i)$. Substituting into Eq. (*i*) we have

$$U_f - U_i = nc_{P,\mathrm{mol}}(T_f - T_i) - P_i(V_f - V_i) \qquad (ii)$$

(*c*) For an ideal gas, $PV = nRT \Rightarrow P_iV_i = nRT_i$ and $P_fV_f = nRT_f$. Recalling that $P_i = P_f$, we have $P_i(V_f - V_i) = nR(T_f - T_i)$. Substituting into Eq. (*ii*) we get

$$U_f - U_i = nc_{P,\mathrm{mol}}(T_f - T_i) - nR(T_f - T_i) = n(c_{P,\mathrm{mol}} - R)(T_f - T_i) \qquad (iii)$$

Problem 18.8. Consider the isothermal process of Fig. 18-7(*c*).

(*a*) What can one say about the internal energy of the system at points *a* and *b*, if the system is an ideal gas? If the system is more general?

(*b*) Figure 18-8 shows an isotherm such as that of Fig. 18-7(*c*), with point *a* reached by an isochoric process from a point *i* and point *b* reached by an isobaric process from the same point *i*. Use the results of Problems 18.5(*b*) and 18.7(*c*) to prove that for an ideal gas $c_{P,\mathrm{mol}} = c_{V,\mathrm{mol}} + R$.

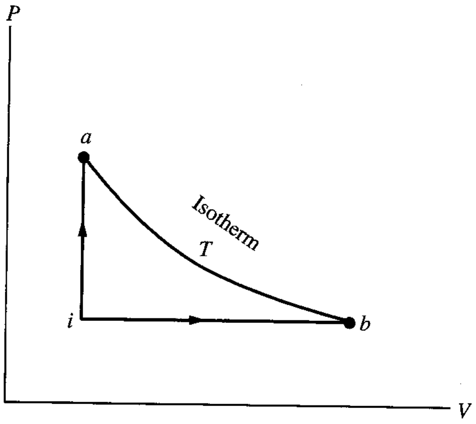


Fig. 18-8

Solution

(*a*) In Sec. 16.4 it was seen that the internal energy of a sample of ideal gas depends only on the temperature. Thus, if the temperature remains constant, so does the internal energy. It follows that, for an ideal gas, the internal energy at every point along an isotherm is the same, so $U_a = U_b$. In the case of a more general system the internal energy typically depends on pressure as well as temperature, so different points along the isotherm will have different internal energies.

(*b*) For the isochoric process, Eq. (*i*) of Problem 18.5(*b*) gives

$$U_a - U_i = nc_{V,\mathrm{mol}}(T - T_i)$$

This equation is true not only for ideal gases but for more general systems as well.

For the isobaric process, Eq. (*iii*) of Problem 18.7(*c*) gives

$$U_b - U_i = n\left[c_{P,\,\mathrm{mol}} - R\right](T - T_i)$$

for our ideal gas. But for an ideal gas, $T_b = T_a = T$ implies $U_b = U_a$. Since in our two equations the left-hand sides are the same, we can equate the right-hand sides to get the desired result. Note that this implies that c_P is greater than c_V. This makes intuitive sense, since at constant pressure positive work is done by the system as the heated ideal gas expands, giving up some of its energy to the environment. It therefore takes more heat input to get the same increase in internal energy than for a constant-volume process, where no work is done.

Problem 18.9.

(*a*) Write the special form of the first law for the case of an adiabatic process.

(*b*) Why is an adiabatic expansion of an ideal gas a steeper curve when plotted on a *P*-*V* diagram than that of an isotherm?

Solution

(*a*) Since there is no transfer of heat into or out of the system, we have $Q_{if} = 0$, and the first law takes the form

$$U_f - U_i = -W_{if} \qquad (i)$$

(*b*) In an adiabatic expansion, positive work is done by the system, and, as can be seen in Eq. (*i*), the internal energy drops. For an ideal gas this corresponds to a drop in temperature. All else being the same, lower temperature means lower pressure. Thus, as one plots *P* vs. *V* for an adiabatic process starting at some point on the *P*-*V* diagram, the pressure drops faster than it does along an isotherm starting at the same point (the temperature stays the same on the isotherm). Figure 18-9 shows a series of adiabatics and isotherms for an ideal gas. The lower isotherms correspond to lower temperatures.

Note. For an ideal gas undergoing an adiabatic process it can be shown, using the calculus, that *P* and *V* are related by $PV^\gamma = \text{constant}$, or

$$P_1V_1{}^\gamma = P_2V_2{}^\gamma \qquad (ii)$$

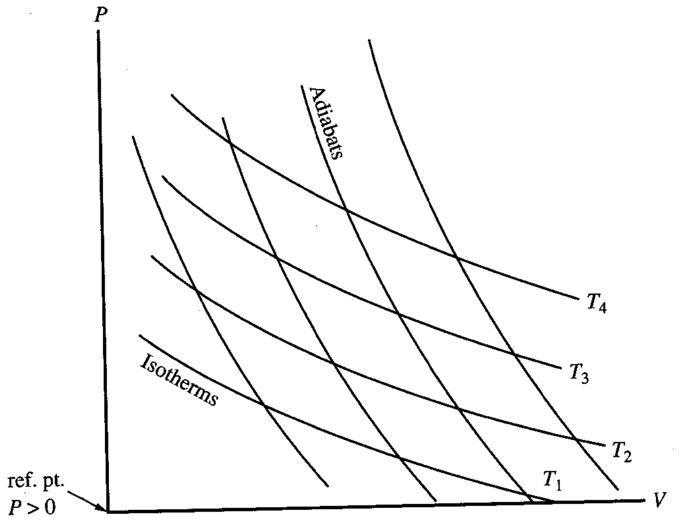


Fig. 18-9

where points 1 and 2 are anywhere along the adiabatic curve. Here $\gamma = c_{mol,P}/c_{mol,V}$, the ratio of molar heat capacities at constant pressure and constant volume. Using the ideal gas law, (*ii*) can be rewritten in terms of Kelvin temperature, as

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \qquad (iii)$$

Since from the previous problem we saw $c_{\mathrm{mol},P} > c_{\mathrm{mol},V}$, we have $\gamma > 1$. Equation (*ii*) is the adiabatic analog of Boyle's law for an isothermal process of an ideal gas: $P_1V_1 = P_2V_2$.

Problem 18.10. Consider a system that is taken along the paths shown on the *P*-*V* diagram in Fig. 18-10. Assume $U_a = 30{,}000$ J.

(*a*) Find the work done by the system in going from *a* to *b*.

(*b*) Find the work done by the system in going from *b* to *c*.

(*c*) If 20,000 J of heat enters the system along the path from *a* to *b*, what is the internal energy at point *b*?

(*d*) If the internal energy at point *c* is 95,000 J, how much heat enters or leaves the system along the path from *b* to *c*?

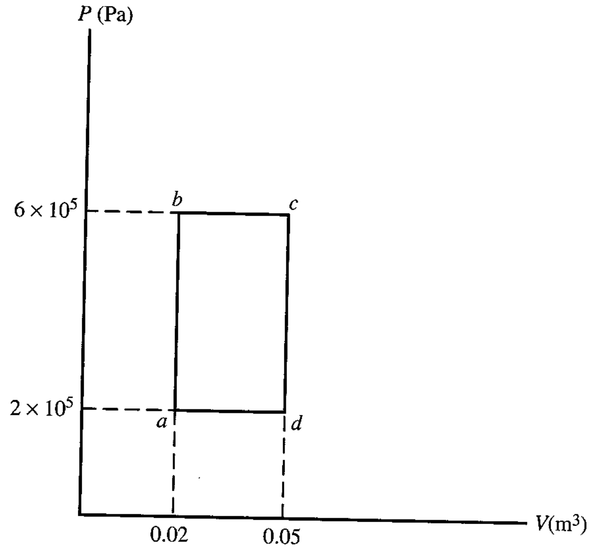


Fig. 18-10

Solution

(*a*) There is no change in volume, so $W_{ab} = 0$.

(*b*) $W_{bc} = P_b(V_c - V_b) = (6 \times 10^5\ \mathrm{Pa})(0.050\ \mathrm{m}^3 - 0.020\ \mathrm{m}^3) = 1.80 \times 10^4$ J.

(*c*) From the first law, $U_b - U_a = Q_{ab} - W_{ab} \Rightarrow U_b - 30{,}000\ \mathrm{J} = 20{,}000\ \mathrm{J} - 0\ \mathrm{J} \Rightarrow U_b =$ 50,000 J.

(*d*) Here we have $U_c - U_b = Q_{bc} - W_{bc} \Rightarrow 95{,}000\ \mathrm{J} - 50{,}000\ \mathrm{J} = Q_{bc} - 18{,}000\ \mathrm{J} \Rightarrow Q_{bc} =$ 63,000 J.

Problem 18.11. Refer to Problem 18.10 and Fig. 18-10.

(*a*) If 21,000 J of heat enters the system in going from *a* to *d*, what is the internal energy at point *d*?

(*b*) Find the heat that enters the system along the path from *d* to *c*.

(*c*) If the system is taken along the closed loop $a \to b \to c \to d \to a$, how much work is done? What is the net heat that enters the system?

Solution

(*a*) The first law gives $U_d - U_a = Q_{ad} - W_{ad}$. We first obtain the work W_{ad}. From Fig. 18-10, we have

$$W_{ad} = P_a(V_d - V_a) = (2.0 \times 10^5 \text{ Pa})\,(0.050 \text{ m}^3 - 0.020 \text{ m}^3) = 6000 \text{ J}$$

Then, using information given above and in Problem 18.10, we have

$$U_d - 30{,}000 \text{ J} = 21{,}000 \text{ J} - 6000 \text{ J} \qquad \text{or} \qquad U_d = 45{,}000 \text{ J}$$

(*b*) We now have $U_c - U_d = Q_{dc} - W_{dc}$. We see that there is no change in volume along the path from *d* to *c*, so $W_{dc} = 0$. Recalling from Problem 18.10(*d*) that $U_c = 95{,}000$ J, we get

$$95{,}000 \text{ J} - 45{,}000 \text{ J} = Q_{dc} - 0 \text{ J} \qquad \text{or} \qquad Q_{dc} = 50{,}000 \text{ J}$$

(*c*) Here, we add up the portions of the net work: $W_{\text{net}} = W_{ab} + W_{bc} + W_{cd} + W_{da}$. Recalling that $W_{ab} = 0$, $W_{bc} = 18{,}000$ J, $W_{cd} = -W_{dc} = 0$, and $W_{da} = -W_{ad} = -6000$ J, we have

$$W_{\text{net}} = 0 \text{ J} + 18{,}000 \text{ J} + 0 \text{ J} - 6000 \text{ J} = 12{,}000 \text{ J}$$

It is possible to obtain Q_{net} from the first law. Since we have returned to the starting point, the change in internal energy in the process is zero, and we must have $0 \text{ J} = Q_{\text{net}} - W_{\text{net}} \Rightarrow Q_{\text{net}} = W_{\text{net}} = 12{,}000$ J.

Problem 18.12. A system consists of a sealed steel cylinder containing a volatile gas mixture. The system is surrounded by a thermal insulating material such as asbestos so that no heat can enter or leave the system (assume radiative losses are negligible). The mixture explodes, but the cylinder stays intact, and the system is allowed to settle down.

(*a*) How has the temperature of the system changed?

(*b*) What is the change in the internal energy of the system as a consequence of the explosion?

(*c*) How would one describe the overall process on a *P-V* diagram?

Solution

(*a*) In the explosion, stored chemical potential energy has been converted into thermal energy. Unless this thermal energy leaves the system or is converted to another form of energy, there will be a rise in temperature.

(*b*) Since the sealed steel cylinder stays intact, there is essentially no change in volume and consequently no work done. Similarly, the insulation stops any transfer of heat to the outside world. From the first law, the amount of internal energy must be unchanged. Of course, the form of the internal energy has changed as described in (*a*).

(*c*) The change in the system cannot be plotted on a *P-V* diagram, because the explosion is not quasistatic. One may be tempted to say that the system is describable by a vertical line on the diagram, corresponding to a constant-volume (isovolumic) process, but that would be wrong. The process is indeed isovolumic, but there is no well-defined "systemwide" pressure at any moment of the explosion. All one can do is to represent the initial and final states by two points (one directly above the other) on a P-V diagram, since these are equilibrium states of the system.

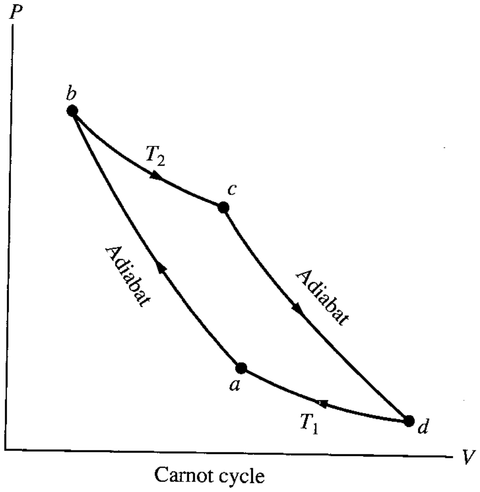
Problem 18.13. Consider a system undergoing a quasistatic cyclical process involving four legs, with two being isotherms and two being adiabats. Such a process is represented on the P-V diagram of Fig. 18-11 and is called a **Carnot cycle.**

(*a*) If the system goes along path $a \to b \to c \to d \to a$, describe qualitatively the net work done.

(*b*) Describe qualitatively the work done along each leg of the cycle.

(*c*) Describe qualitatively the heat that enters or leaves the system along each leg of the cycle, and the net heat transferred by the system over the complete cycle.

(*d*) How would the above answers change if the cycle were in the reverse direction: $a \to d \to c \to b \to a$?



Carnot cycle

Fig. 18-11

Solution

(*a*) From the discussion in the text and earlier problems, we note that the net work is the positive area enclosed by the cycle on the P-V diagram.

(*b*) Since the system expands along $b \to c$ and $c \to d$, the work done in each of these two paths is positive. Similarly, the system contracts along $d \to a$ and $a \to b$, and the work done is negative on each of these two legs.

(*c*) By definition, no heat enters or leaves the system along either adiabat. It is typical that heat would enter the system along path $b \to c$ because the system does positive work, and heat would have to enter the system to keep the temperature constant during the process. Likewise, along isotherm $d \to a$ heat ought to leave the system. On net, the total algebraic heat is $Q_{\text{net}} = Q_{bc} + Q_{da}$, where the first and second terms on the right are positive and negative, respectively. Furthermore, from the first law, at the end of the complete cycle the internal energy is back to its original value, so we must have $Q_{\text{net}} = W_{\text{net}}$, with both being positive quantities.

(*d*) If the cycle is reversed, each leg is reversed, and we have that the work done and heat transferred during each leg simply changes sign. Similarly, the net work and net heat in the cycle must therefore change sign. In the reversed cycle, the net work done by the system is negative and the net heat entering the system is negative.

18.2 THE SECOND LAW OF THERMODYNAMICS

As we have seen, the First Law says that energy can only shift from one system to another (by means of work and heat transfer), but the total energy of the universe stays fixed. The second law of thermodynamics addresses the separate question of the feasibility of certain types of energy transfers. The fact that energy must be conserved when there is an energy transfer from one system to another doesn't say whether the transfer will in fact take place.

As an example of feasibility, consider the conductive heat transfer of energy between two systems at different temperatures that are brought into good thermal contact. Clearly, the heat will transfer from the hotter to the cooler body. From the point of view of the first law, there is no reason why energy could not transfer from the cool body to the hot body, with the cool body getting colder as it lost thermal energy and the hot body getting even hotter as it gained thermal energy. The only constraint placed on such a process by the first law is that the amount of energy leaving the cold body precisely equal the amount of energy entering the hot body. Nonetheless, such a process does not occur naturally by direct thermal contact. To accomplish the removal of thermal energy from a cool body and its transfer to a hot body requires an intermediary system called a **refrigerator**.

Another example is the conversion of mechanical energy of a system into thermal energy of the same system, or of another system. Clearly, it is always easy to convert mechanical energy into thermal energy because of friction: a block with kinetic energy sliding on a surface slowly comes to rest because of the frictional conversion of the mechanical energy into thermal energy. But what if we wanted the reverse to occur: the thermal energy of the block and surface to somehow give itself up, to expend itself, to get the block moving again. The first law does not prohibit such a process, as long as the total energy stays the same. Nonetheless, such a conversion will not simply occur. To convert thermal energy to mechanical energy requires the services of an intermediary system, called a **heat engine**, to accomplish the goal.

The central issue here lies in the fact that thermal energy, being statistically random in nature, does not have the ability to organize itself in a way to easily convert to mechanical energy (second example), or to transfer from a less energetic environment to a more energetic environment (first example). The second law is thus deeply connected to the concept of randomness, and therefore to the subject of statistical mechanics. It is a remarkable fact that the second law was developed on an empirical basis, quite independently of any understanding of the statistical behavior of the myriad atoms and molecules making up a macroscopic system.

The Engine Statement of the Second Law

We have referred, above, to intermediary systems to effect the transfers that don't occur naturally. We have already encountered such systems in our discussion of cyclical motion on a P-V diagram. Consider the systems described by the cycles $a \rightarrow b \rightarrow c \rightarrow d \rightarrow a$ in Figs. 18-10 and 18-11. Clearly, each time either system goes through a complete cycle, net work W_{net} is done by the system. This means that mechanical energy is transferred to somewhere in the environment. In that same cycle a net amount of heat has entered the system; that is, thermal energy has been drawn from somewhere in the environment. It follows that in this cyclical process, thermal energy from somewhere has been converted to mechanical energy somewhere, since the intermediary system has returned to its original state and therefore has not changed at all. As noted, such a device is called a heat engine. Since we can repeat the cycle over and over again, we can continuously transform thermal energy to mechanical energy.

There is a catch, however. In either of the engine cycles, heat $Q_{\text{in}} > 0$ is drawn in during part of the cycle (typically at the higher temperatures), but some heat Q_{out} is exhausted to the outside during another part of the cycle (typically at the lower temperatures). (For future reference Q_{in} and Q_{out} are understood to be the magnitudes of the heats involved and are therefore always positive.) This means that the conversion of thermal energy to mechanical energy is not 100% efficient. Only part of the thermal energy Q_{in} that had been pulled in from the "hot" outside systems has been converted to mechanical energy, since some of the thermal energy Q_{out} has been dumped to "cooler" outside systems as part of the process. Indeed, from the first law

$$Q_{in} = W_{net} + Q_{out} \tag{18.4}$$

The engine, or **Kelvin-Planck**, statement of the second law is a verbal formalization of this result:

> *It is impossible for a cyclical process to have no other effect than to draw thermal energy from some system or systems, and convert it completely into mechanical energy.*

In other words, Q_{out} in Eq. (*18.4*), is always greater than zero. The engine statement of the second law is expressed schematically in Fig. 18-12(*a*).

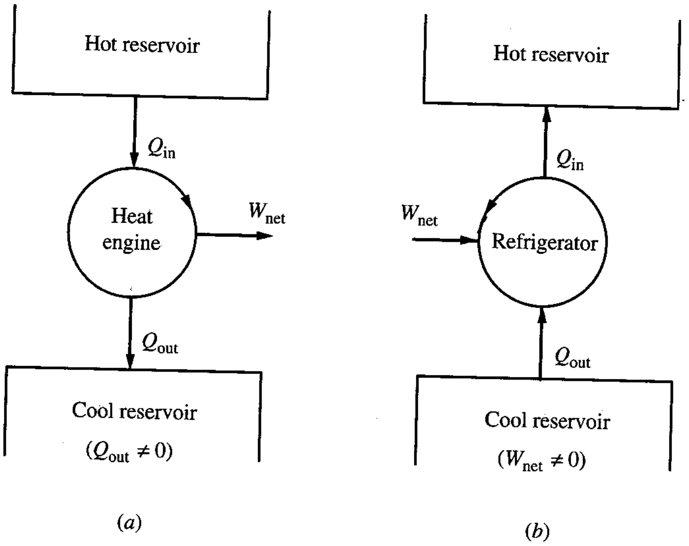


Fig. 18-12

The hotter system(s) which is the source of the thermal energy is often called the **hot reservoir(s)**, whereas the cooler system(s) to which thermal energy is exhausted is called the **cool reservoir(s)**. The efficiency e of any engine is defined as the ratio of mechanical energy obtained to the thermal energy extracted from the hot reservoir(s);

$$e = \frac{W_{net}}{Q_{in}} \tag{18.5a}$$

Using (*18.4*), this can be rewritten as

$$e = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} \tag{18.5b}$$

Problem 18.14. Referring to Problems 18.10 and 18.11, find the efficiency of the engine defined by the cycle $a \to b \to c \to d \to a$ in Fig. 18-10.

Solution

From Problems 18.11(*c*) and 18.10(*c*, *d*), we have, respectively, $W_{\text{net}} = 12{,}000$ J, $Q_{ab} = 20{,}000$ J, and $Q_{bc} = 63{,}000$ J. From Problem 18.11(*a*, *b*) we can deduce that $Q_{cd} = -50{,}000$ J and $Q_{da} = -21{,}000$ J. Then, from its definition, $Q_{\text{in}} = Q_{ab} + Q_{bc} = 83{,}000$ J. Similarly, from its definition, $Q_{\text{out}} = |Q_{cd} + Q_{da}| = 71{,}000$ J. Using (*18.5a*), we have

$$e = \frac{12{,}000\ \text{J}}{83{,}000\ \text{J}} = 0.145 = 14.5\%$$

Equivalently, we could use Eq. (*18.5b*) to get

$$e = 1 - \frac{71{,}000\ \text{J}}{83{,}000\ \text{J}} = 0.145 = 14.5\%$$

Problem 18.15. Suppose that for the Carnot cycle of Fig. 18-11 we are given $Q_{bc} = 7{,}000$ J and $Q_{da} = -4800$ J. Find (*a*) the net work done in the cycle, (*b*) the efficiency of this Carnot engine.

Solution

(*a*) Since no heat enters or leaves the system along the other two (adiabatic) legs of the cycle, $Q_{\text{net}} = Q_{bc} + Q_{da} = 2200$ J. From the first law, for the complete cycle we must have $W_{\text{net}} = Q_{\text{net}} = 2200$ J.

(*b*) The efficiency is

$$e = 1 - \frac{|Q_{\cancel{da}}|}{Q_{bc}} = 1 - \frac{4800\ \text{J}}{7000\ \text{J}} = 0.314 = 31.4\%$$

The Refrigerator Statement of the Second Law

We now examine the intermediary systems that allow us to draw thermal energy from a cool system(s) and deposit it in a hot system(s). Again we have encountered such systems in the cycles of Figs. 18-10 and 18-11. This time we consider the cycles run in reverse order: $a \to d \to c \to b \to a$. In this case Q_{out} represents the magnitude of heat that enters the cyclical system at lower temperatures, and Q_{in} represents the heat expelled from the cyclical system at higher temperatures. Thus, thermal energy Q_{out} is being extracted from a cooler reservoir(s), and thermal energy Q_{in} is being deposited in a hotter reservoir(s). This is just what we want to accomplish. Our cyclical intermediary system, which like the engine is itself unchanged over a cycle, constitutes our refrigerator.

Again, as with the engine, there is a catch. The thermal energy Q_{in} deposited in the hotter reservoir is greater than the thermal energy Q_{out} extracted from the cooler reservoir. The difference is accounted for by the work done by the system, which is now negative and equals $-W_{\text{net}}$. In other words, positive work W_{net} must be done *by outside systems* to accomplish the refrigeration process. The relation of Q_{out}, Q_{in}, and W_{net} is given by the first law, $Q_{\text{in}} = Q_{\text{out}} + W_{\text{net}}$, which is algebraically the same as (*18.4*) but now has the interpretation given above for a refrigerator: The sum of the heat drawn from the cool reservoir(s) and the work done by outside systems equals the heat entering the hot reservoir(s).

The performance of the refrigerator is thus not ideal because some outside system has to do work to accomplish the thermal energy transfer. The refrigerator, or **Clausius**, statement of the second law is a verbal statement of this result:

> *It is impossible for a cyclical process to have no other effect than to extract thermal energy from a cooler system or systems, and eject that thermal energy to a hotter system or systems.*

In other words, W_{net} is never zero. The coefficient of performance κ of a refrigerator is defined as

$$\kappa = \frac{Q_{\text{out}}}{W_{\text{net}}} \tag{18.6a}$$

Using Eq. (*18.4*) this becomes

$$\kappa = \frac{Q_{\text{out}}}{Q_{\text{in}} - Q_{\text{out}}} \tag{18.6b}$$

> ***Note.*** κ is defined so that it increases without limit as $W_{\text{net}} \to 0$ and is a measure of the amount of heat extracted from the cool reservoir per unit work done. Thus, for example, a coefficient, of performance κ of 20 means that for each joule of work done, 20 J of heat is extracted.

The refrigerator statement of the second law is expressed schematically in Fig. 18-12(*b*).

Problem 18.16. Referring to Problems 18.10 and 18.11, find the coefficient of performance κ of the refrigerator defined by the cycle $a \to d \to c \to b \to a$ in Fig. 18-10.

Solution

This is almost identical to Problem 18.14, except that the cycle is running in reverse. Recalling that Q_{out} and Q_{in} are defined as positive quantities, from Problem 18.14, we have $Q_{\text{out}} = 71{,}000$ J, $Q_{\text{in}} = 83{,}000$ J. Similarly the positive work done by outside systems is $W_{\text{net}} = 12{,}000$ J. From Eq. (*18.6a*), we get

$$\kappa = \frac{71{,}000\ \text{J}}{12{,}000\ \text{J}} = 5.92$$

Problem 18.17. Referring to Problem 18.15, suppose the same Carnot cycle is run in reverse. Find the coefficient of performance of the Carnot refrigerator.

Solution

$Q_{\text{out}} = |Q_{da}| = 4800$ J, and $Q_{\text{in}} = Q_{bc} = 7000$ J. From Problem 18.15, $W_{\text{net}} = 2200$ J. Then, from (*18.6a*) we have

$$\kappa = \frac{4800\ \text{J}}{2200\ \text{J}} = 2.18$$

Problem 18.18. Show that the engine and refrigerator statements of the second law imply each other and therefore are equivalent statements.

Solution

Both statements come from analysis of cyclical processes, but these processes operate in opposite directions. The standard method is to show that if either of the statements were false, then the other would also have to be false. Suppose the engine statement to be true and the refrigerator statement to be false. We will show that this cannot happen. Consider the engine operating between a hot reservoir and a cool reservoir, as shown schematically in Fig. 18-13(*a*). Since the engine statement is true, we must have that Q_{out} is not zero. We next construct a refrigerator that takes Q_{out} from the same cool reservoir and expels it to the same hot reservoir as that of the engine, with no outside work necessary, as depicted in Fig. 18-13(*b*). This is possible since the refrigerator statement of the second law is presumed false. The

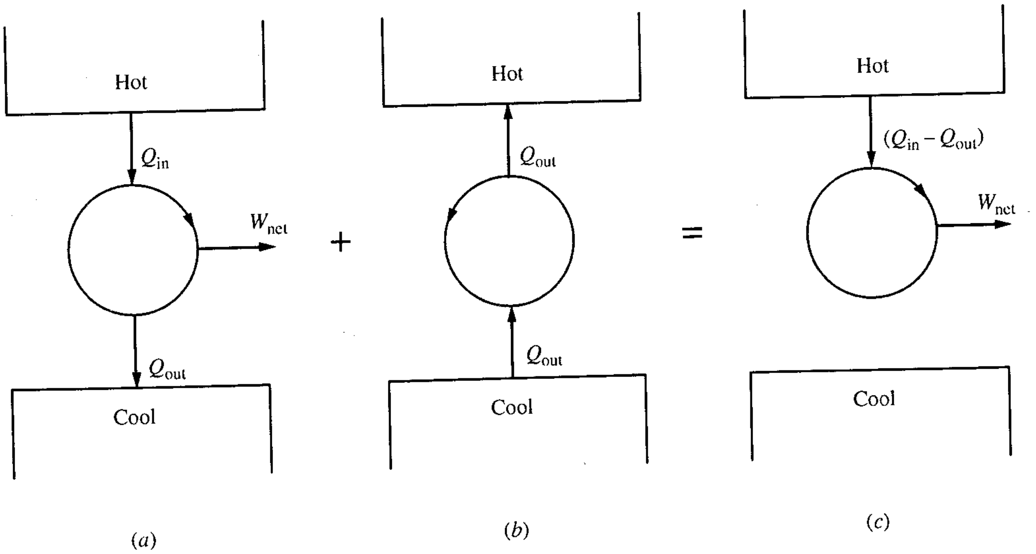


Fig. 18-13

combination of these two cycles is also a cyclical process between the same two reservoirs. The effect of the two cycles together is to take $Q_{in}' = Q_{in} - Q_{out}$ from the hot reservoir and convert it completely into work W_{net}, with no ejection of heat to any other place. This is shown in Fig. 18-13(*c*) and clearly represents an engine that violates the engine statement of the second law. Thus, if the refrigerator statement is false, so is the engine statement. The truth of the engine statement therefore implies the truth of the refrigerator statement.

A similar argument shows that if the refrigerator statement is assumed true and the engine statement false, a contradiction is again obtained.

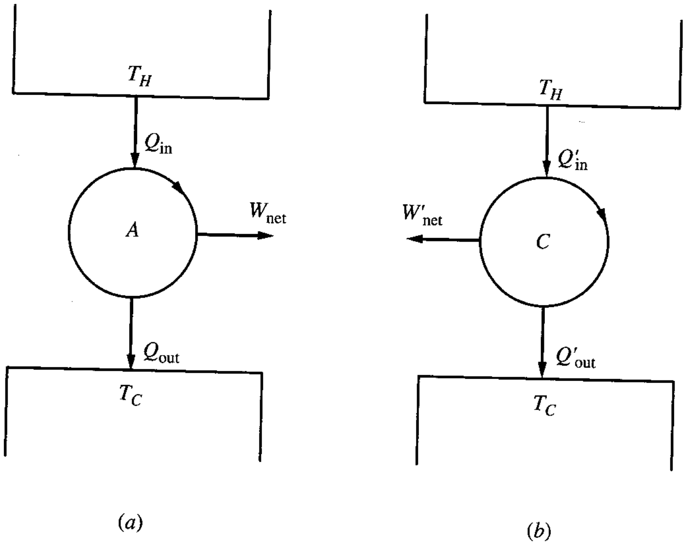
Engine Efficiency and the Carnot Cycle

In any quasistatic cyclical process such as that of Fig. 18-10, one cannot have a single hot reservoir and a single cool reservoir interacting with the engine (or refrigerator) because the cycle generally passes through a range of temperatures; if the only reservoirs in contact with the cyclical system were at two fixed temperatures, there would be a finite temperature difference between the system and the reservoirs for most of the cycle. In that case the heat-transfer rate would not be infinitesimal and there would be no single temperature for the whole system at each instant. In other words the system would not be quasistatic and could not be represented on a *P*-*V* diagram. For such a cyclical process to be quasistatic, it is necessary to have a whole series of reservoirs, at incrementally different temperatures from one another, that are successively brought into contact with the system. Each such contact is allowed to occur as the system temperature just passes the temperature of that particular reservoir, and an infinitesimal thermal energy transfer takes place between the two. Such a cycle is an "ideal" cycle for theoretical analysis or possible laboratory study but is not practical as an actual engine or refrigerator.

There is, however, one quasistatic cyclical process that can indeed operate between a single hot reservoir and a single cool reservoir, and that is the Carnot cycle. The reason is easy to understand. Since the Carnot cycle is made up of two isotherms and two adiabats, heat transfers in or out of the cyclical system only at two temperatures, and these are the temperatures of the reservoirs that serve as the source and sink of the thermal energy being transferred. During the other parts of the cycle, the adiabats, when the temperature of the system is indeed changing, and different from that of the reservoirs, the system can remain quasistatic because no heat can enter or leave the system, and the finite difference in temperature compared with outside systems does not lead to the occurrence of nonequilibrium processes.

We now show that the second law implies that the most efficient engine operating between two fixed temperature reservoirs is a Carnot engine. Consider an arbitrary engine A operating between a hot reservoir at temperature T_H and a cool reservoir at temperature T_C, as shown in Fig. 18-14(*a*). We assume the reservoirs are sufficiently large that their temperatures are not noticeably changed as a consequence of any heat transfers that take place. Assume that the efficiency e_A of this engine is greater than the efficiency e_C of a Carnot engine operating between the same two reservoirs, as shown in Fig. 18-14(*b*). Let us assume that the engines are adjusted so that $Q_{\text{out}} = Q'_{\text{out}}$. Then, from *(18.5b)*, $e_A > e_C \Rightarrow Q_{\text{in}} > Q'_{\text{in}}$, and hence $W_{\text{net}} > W'_{\text{net}}$. Now consider the combined cyclical system consisting of engine A, and the Carnot cycle operating in reverse, as a refrigerator $(-C)$, as shown in Fig. 18-15. The combined effect is the conversion of thermal energy $(Q_{\text{in}} - Q'_{\text{in}})$ into mechanical energy $(W_{\text{net}} - W'_{\text{net}})$, with no thermal energy exhausted to a cooler reservoir. This violates the second law, so our assumption $e_A > e_C$ must be false. Hence

$$e_C \geq e_A \tag{18.7}$$



(*a*) (*b*)

Fig. 18-14

where e_C is the efficiency of any Carnot engine operating between the two reservoirs at T_H and T_C and e_A is the efficiency of any other engine operating between the two same reservoirs.

Problem 18.19. Prove that all Carnot engines operating between the same two reservoirs, no matter what the operating substance making up the engine, are equally efficient.

Solution

Consider two Carnot engines A and B operating between the same two reservoirs. Since A is a Carnot engine, according to *(18.7)* we must have $e_A \geq e_B$. On the other hand, since B is also a Carnot engine we must have $e_B \geq e_A$. Therefore $e_A = e_B$.

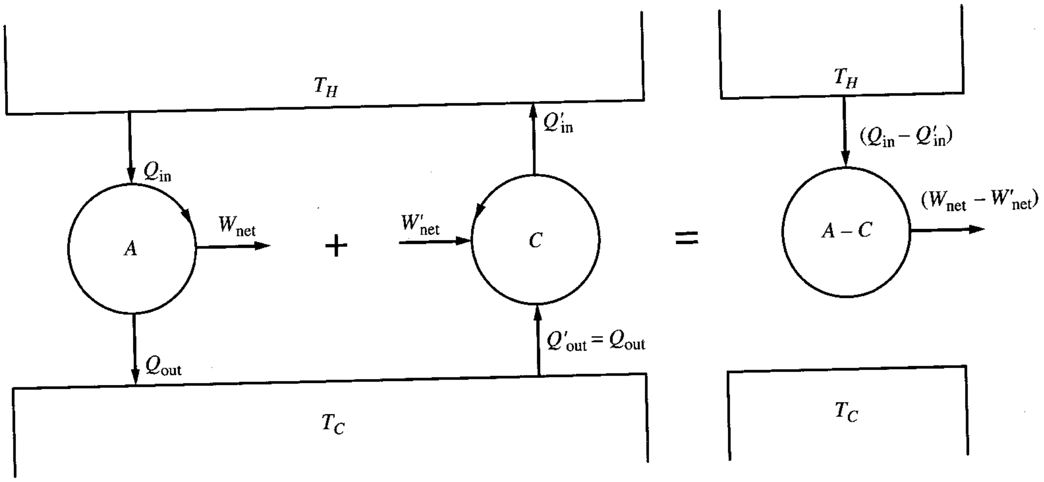


Fig. 18-15

Problem 18.20. It can be shown, using the calculus, that for a Carnot cycle in a system consisting of a confined ideal gas (e.g., in a cylinder with a close-fitting piston), there exists a simple relationship between the ratio of heats entering (or leaving) along the two isotherms and the ratio of the Kelvin temperatures of the isotherms. Using the notation of Fig. 18-11, this relationship is $Q_{bc}/Q_{ad} = T_2/T_1$. Show that this implies that the efficiency of *any* Carnot engine operating between two reservoirs at Kelvin temperatures T_H and T_C, respectively, is

$$e_C = 1 - \frac{T_H}{T_C}$$

Solution

We recall, from Fig. 18-11, that for our ideal gas Carnot engine, $Q_{in} = Q_{bc}$ and $Q_{out} = Q_{cd}$. Furthermore, we note that in the notation of the problem, $T_2 = T_H$ and $T_1 = T_C$. Then, from the information in the problem, we have

$$\frac{Q_{in}}{Q_{out}} = \frac{T_H}{T_C} \qquad (i)$$

From (*18.5b*), we have

$$e_C = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_C}{T_H} \qquad (ii)$$

While this has only been determined for the special case of an ideal gas, we recall that all Carnot engines operating between the same two temperatures have the same efficiency, so (*ii*) is true for all Carnot engines.

Problem 18.21.

(*a*) Find the efficiency of a Carnot engine that operates between two reservoirs at temperatures of 1000 K and 330 K, respectively.

(*b*) If the engine absorbs 5000 J of heat from the hot reservoir in a cycle, how much heat is ejected to the cool reservoir?

(*c*) How much work is done in the cycle?

Solution

(*a*) From (*ii*) of Problem 18.20, we have

$$e_C = 1 - \frac{T_C}{T_H} = 1 - \frac{330}{1000} = 0.670 = 67.0\%$$

(*b*) $Q_{\text{out}}/Q_{\text{in}} = T_C/T_H \Rightarrow Q_{\text{out}}/5000 \text{ J} = \frac{330}{1000} = 0.330 \Rightarrow Q_{\text{out}} = 0.330(5000 \text{ J}) = 1650 \text{ J}$.

(*c*) For the complete cycle, $W_{\text{net}} = Q_{\text{net}} = 5000 \text{ J} - 1650 \text{ J} = 3350 \text{ J}$.

Problem 18.22.

(*a*) What is the greatest efficiency we can hope for from an engine that operates between temperature reservoirs at $T_H = 900$ K and $T_C = 400$ K?

(*b*) If we know that a real engine operating between the above two temperatures has 40% of the efficiency of a Carnot engine, what is the efficiency of the real engine?

(*c*) Assuming the hot reservoir is fixed, what is an obvious way to improve the efficiency of an engine?

Solution

(*a*) The greatest efficiency is that of a Carnot engine, which is given by (*ii*) of Problem 18.20: $e_C = 1 - \frac{400}{900} = 0.556 = 55.6\%$.

(*b*) $e = (0.40)(0.556) = 0.222$.

(*c*) Again referring to (*ii*) of Problem 18.20, we see that for fixed T_H, we can increase the efficiency by decreasing T_C, the temperature of the cool reservoir (or, in other words, the temperature at which heat is exhausted). Thus, finding a cooler place to exhaust the heat improves efficiency.

Problem 18.23.

(*a*) Show how a Carnot engine can be used as a thermometer.

(*b*) We saw earlier that the Kelvin (or absolute) temperature scale was considered a "universal" scale because every constant-volume gas thermometer containing dilute gas gave rise to the same absolute scale, irrespective of the type of gas involved. Indeed the scale is defined as

$$T = (273.16 \text{ K}) \left(\frac{P}{P_{\text{tr}}}\right) \qquad (i)$$

where P_{tr} is the pressure of any dilute constant-volume gas thermometer when immersed in a bath at the triple point of water, and P is the pressure of the same thermometer at T, the temperature of interest. Of course, not every system consists of a dilute gas. Show how the Carnot cycle can make the definition of the Kelvin temperature scale truly universal.

Solution

(*a*) If we want to measure the temperature of some system X, we let that system serve as one of the two reservoirs for our Carnot "thermometer." We next choose a "reference" reservoir at the triple point of water as our other reservoir. Then we operate our Carnot engine and measure the amount of heat entering or leaving at each reservoir. From Problem 18.20 we have

$$\left|\frac{Q_X}{Q_{\text{tr}}}\right| = \frac{T_X}{T_{\text{tr}}} = \frac{T_X}{273.16 \text{ K}}$$

Since the two Q's are measured, T_X is determined.

(*b*) From part (*a*), we have

$$T_X = (273.16\ \text{K})\left|\frac{Q_X}{Q_{\text{tr}}}\right| \qquad (ii)$$

This can be used as the new definition of the Kelvin temperature, replacing (*i*) above. Now, however, not only is this true for Carnot cycles involving an ideal gas, but for Carnot cycles involving any material—gas, liquid, or solid—and both chemical and nonchemical systems, including "magnetic" systems, where the work done involves thermodynamic variables other than P and V. Thus, the Kelvin scale can be defined in a truly universal way.

Problem 18.24. One cylinder of a gasoline engine can be idealized by a quasistatic engine called the **Otto cycle**, shown in Fig. 18-16. Along path ab an ideal gas is compressed adiabatically from V_a to V_b. (In a real gasoline engine this is a rapid compression of gasoline and air, which is approximately adiabatic since there is very little time for heat to be conducted away.)

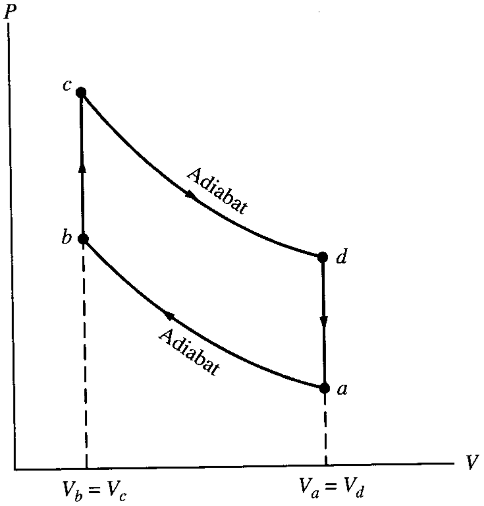


Fig. 18-16

Next, heat enters the system at constant volume along path bc, raising the temperature and pressure of the ideal gas. (In a real engine the gasoline is ignited and reacts with the oxygen in the air. The consequent explosion occurs over such a short time period that there is little expansion of the gas against the piston. The effect of the explosion is thus the isovolumic conversion of chemical potential energy to thermal energy. In the ideal engine this conversion is represented by the isovolumic absorption of heat from a series of outside reservoirs.)

Next, the heated ideal gas expands adiabatically along cd to the original volume. (This is the "power" stroke in a real engine, where the high-pressure hot gas expands rapidly against the piston, pushing it out to the end of the cylinder.)

Next, the ideal gas is allowed to cool at fixed volume along path da down to the original pressure. (In a real engine the hot exhaust gases are pushed out during another compression, and fresh gasoline and air are brought in during another expansion. This pair of steps does not involve any significant net work and accomplishes the same transfer of thermal energy out of the system as represented by the cooling of the ideal gas along da.)

(*a*) Find an expression for the efficiency e of the Otto cycle in terms of the temperatures T_a, T_b, T_c, and T_d.

(*b*) Find the efficiency of the Otto cycle in terms of the volumes V_d and V_c. [*Hint*: look at Eq. (*iii*) at the end of Problem 18.9.]

Solution

(*a*) First we note from Eq. (*18.5b*) that is suffices to determine the values of Q_{in} and Q_{out} to obtain the efficiency. In the Otto cycle, heat enters the system during the isovolumic increase in pressure along path *bc*, as is obvious from the fact that the temperature of an ideal gas at constant volume increases with pressure. The value of this can be determined from

$$Q_{bc} = nc_{\text{mol},V}(T_c - T_b) \qquad (i)$$

where n is the number of moles of gas in our system, $c_{\text{mol},V}$ is the molar heat capacity at constant volume, and T_c and T_b are the Kelvin temperatures at the respective endpoints of the path.

In similar fashion we see that heat leaves the system during the isovolumic decrease in pressure along path *da*. The algebraic heat entering along path *da* is

$$Q_{da} = nc_{\text{mol},V}(T_a - T_d) \qquad (ii)$$

where T_a and T_d are the temperatures at the two endpoints of the path. We note that, as expected, Q_{da} is negative since $T_a < T_d$. Since no heat enters the system along the two adiabats *ab* and *cd*, we can identify $Q_{\text{in}} = Q_{bc}$ and $Q_{\text{out}} = |\,Q_{da}\,|$. The efficiency is then

$$e = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{nc_{\text{mol},V}(T_d - T_a)}{nc_{\text{mol},V}(T_c - T_b)} = 1 - \frac{T_d - T_a}{T_c - T_b} \qquad (iii)$$

(*b*) Recalling (*iii*) of Problem 18.9, for our adiabats we have

$$T_c V_c^{\gamma-1} = T_d V_d^{\gamma-1} \qquad (iv)$$

$$T_b V_b^{\gamma-1} = T_a V_a^{\gamma-1} \qquad (v)$$

Noting from Fig. 18-16 that $V_a = V_d$ and $V_c = V_b$, we can subtract (*v*) from (*iv*) to get

$$(T_c - T_b)V_c^{\gamma-1} = (T_d - T_a)V_d^{\gamma-1} \qquad (vi)$$

This implies $(T_d - T_a)/(T_c - T_b) = V_c^{\gamma-1}/V_d^{\gamma-1}$, and from (*iii*) above

$$e = 1 - \left(\frac{V_c}{V_d}\right)^{\gamma-1} \qquad (vii)$$

The inverse of V_c/V_d is called the **compression ratio** and is the ratio of the largest volume to the smallest volume of the engine cylinder as the piston moves in and out. The greater the compression ratio, the more efficient the engine.

Note. Problem 18.24 gives an example of a quasistatic cycle that mimics a real gasoline engine. Any real gasoline engine with the same compression ratio is much less efficient than this ideal engine because of factors such as friction, turbulent behavior, and heat-conduction losses.

Also, it can be shown that a Carnot engine operating between the highest and lowest temperatures achieved by another quasistatic engine (for example, T_c and T_a for the Otto cycle of Fig. 18-16) is always more efficient than that engine.

18.3 ENTROPY, DISORDER, AND THE SECOND LAW

The Macroscopic View

As we said at the outset, the second law is intimately related to the disordered nature of thermal energy and hence to statistical mechanics. It can be shown that for every equilibrium state of a system there is a definite quantitative measure of the disorder of the system in that state. This quantitative measure assigns a value to each equilibrium state of the system, which is called the entropy S. It follows that the entropy S, like P, V, T, and U, is a thermodynamic variable and can be expressed as a function of the other thermodynamic variables. The incremental change in entropy of a system ΔS when a small amount of heat ΔQ is slowly added can be shown to be given by

$$\Delta S = \frac{\Delta Q}{T} \tag{18.8}$$

where T is the Kelvin temperature of the system. The units of entropy are thus J/K. Equation (*18.8*) is true whether the heat is added at constant volume, at constant pressure, or in any other way. Equation (*18.8*) also implies that the entropy of a system increases with the increasing thermal energy. When heat leaves a system, ΔQ is negative, and the entropy of that system decreases. The second law of thermodynamics can be restated in terms of the overall entropy of the universe: *In any process or interaction of systems, the overall entropy change of the universe* ΔS_{univ} *obeys*

$$\Delta S_{\text{univ}} \geq 0 \tag{18.9}$$

where the equality occurs only in the case of quasistatic processes.

Problem 18.25. Use (*18.9*), the entropy statement of the second law, to derive the engine statement of the second law.

Solution

Consider the schematic diagram of an engine shown in Fig. 18-12(*a*). Suppose that at the end of a cycle, Q_{in} is pulled in from the hot reservoir and converted completely into work so that $Q_{\text{out}} = 0$. We use (*18.8*) to examine the change in entropy. Since heat leaves the hot reservoir, ΔQ for that reservoir is negative, and ΔS must be negative as well, so the entropy of the hot reservoir decreases. The entropy of the engine itself is unchanged after a cycle because the system has returned to its original state. The work W_{net} represents an increase in the *mechanical* energy of some other system, so no heat transfer is involved and according to (*18.8*) the entropy of that system is unchanged. Thus, the overall change in entropy of the universe is negative, which contradicts (*18.9*). Therefore, if (*18.9*) is to hold, there must be a nonzero Q_{out} which enters the cool reservoir and increases its entropy so that (*18.9*) for the universe can hold. The fact that Q_{out} cannot be zero is just the engine statement of the second law.

Problem 18.26. Use the law of entropy to show that the greatest possible efficiency of an engine operating between two reservoirs at temperature T_H and T_C, respectively, is that of a Carnot engine.

Solution

Consider any cyclical engine operating between two reservoirs at temperatures T_H and T_C. In a single cycle the amounts of heat Q_{in} pulled from the hot reservoir and the amount Q_{out} expelled to the cool reservoir are assumed to be sufficiently small that the temperatures of the reservoirs do not measurably change. Then, using (*18.8*), the change in entropy of the hot reservoir is $\Delta S_H = -Q_{\text{in}}/T_H$, and the change in entropy of the cool reservoir is $\Delta S_C = Q_{\text{out}}/T_C$. As discussed in Problem 18.23, there is no other change in entropy in any of the participating systems. Hence, by (*18.9*),

$$\Delta S_{\text{univ}} = \Delta S_H + \Delta S_C = \frac{Q_{\text{out}}}{T_C} - \frac{Q_{\text{in}}}{T_H} \tag{i}$$

We see that from (*18.9*) the right side of (*i*) is ≥ 0, so we have

$$\frac{Q_{\text{out}}}{T_C} \geq \frac{Q_{\text{in}}}{T_H} \tag{ii}$$

or

$$\frac{Q_{\text{out}}}{Q_{\text{in}}} \geq \frac{T_C}{T_H} \tag{iii}$$

From (*18.5b*), we have for the efficiency of the engine

$$e = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}} \tag{iv}$$

As can be seen, e is greatest when $Q_{\text{out}}/Q_{\text{in}}$ is smallest. According to (*iii*), the smallest value of $Q_{\text{out}}/Q_{\text{in}}$ is T_C/T_H, so the greatest efficiency is $e = 1 - (T_C/T_H)$, which is just the efficiency of a Carnot engine.

The Microscopic View

Considering the molecular level, the disorder of a system in equilibrium is measured by the number of different ways Γ that the molecules can arrange themselves so as to produce the value of the macroscopic variables that characterize the equilibrium state. The more such arrangements, the greater the disorder. The entropy of the system is formally defined as

$$S = k \cdot \ln \Gamma \tag{18.10}$$

where k is Boltzmann's constant and ln Γ is the natural logarithm of Γ.

To understand the concept of Γ better, consider a box filled with 100 imaginary molecules that can exist in only one of two molecular states: state a or state b. Our box of imaginary "two-state" molecules is identical to the situation of a box filled with 100 coins with the state of each coin being determined by whether it has heads or tails facing up. A state of the macroscopic system, or system state, would correspond to specifying how many molecules are in molecular state a (the rest being in state b). One such "system" state would correspond to the case of all molecules in state a. There is only one way the molecules could arrange themselves like that, so $\Gamma = 1$, and this is a highly ordered state. Another system state would be the case of 99 molecules in molecular state a and 1 in molecular state b. Clearly there are 100 different ways that this could happen, so $\Gamma = 100$, and this system state has some disorder. For the case of 50 molecules in a and 50 in b, there are more ways for this to happen than Avogadro's number! This is a highly disordered system state. This is also a much more probable system state than the previous examples given. If we were to shake up the box of coins, there would be a much greater probability of getting 50 heads and 50 tails than of getting 100 heads, or even 99 heads and one tail. The macroscopic equilibrium state of our system corresponds to the most probable system state with its specific value of Γ, and hence S.

The same reasoning can be applied to a system made up of myriad real molecules N, with many more than two possible states for each molecule. By counting how many different ways the N molecules can arrange themselves in their varying molecular states, within certain physical constraints, one can find the most probable distribution of molecules among the molecular states. This corresponds to an actual macroscopic equilibrium state of the system. The number of different ways that the molecules can arrange themselves in this most probable configuration is the value of Γ for that macroscopic state. Equation (*18.10*) can be used to determine the value of S, or the disorder, of the macroscopic state.

The quantitative relationships that allow us to determine Γ for real systems of molecules, and the proof that the entropy S defined by (*18.10*) also obeys (*18.8*) and (*18.9*) are a consequence of the laws of statistical mechanics and are beyond the scope of this book.

Problems for Review and Mind Stretching

Problem 18.27. 3.0 kg of water at 100°C and atmospheric pressure (state *a*) is converted at constant temperature and pressure to 3.0 kg of steam (state *b*). Find the change in internal energy of the system, if the volume in the vapor phase is 1670 times that in the liquid phase.

Solution

By the first law,

$$U_b - U_a = Q_{a\rightarrow b} - W_{a\rightarrow b} \tag{i}$$

Since, at atmospheric pressure and 100°C, the water is poised to undergo the phase transition to vapor, we know that the heat added is just

$$Q_{a\rightarrow b} = mL_V = (3.0\ \text{kg})\,(2256\ \text{kJ/kg}) = 6768\ \text{kJ} \tag{ii}$$

Since the process occurs at constant pressure, $W_{a\rightarrow b} = P_{\text{atm}}(V_b - V_a)$. Because the density of water is very nearly 1000 kg/m^3 over the whole range from 0°C to 100°C, the volume of 3.0 kg of liquid water is

$$V_a = \frac{3.0\ \text{kg}}{1000\ \text{kg/m}^3} = 3.0 \times 10^{-3}\ \text{m}^3$$

and the vapor volume is $V_b = (1670)V_a = 5.01\ \text{m}^3$. Then,

$$W_{a\rightarrow b} = (1.0 \times 10^5\ \text{Pa})(5.01\ \text{m}^3 - 3.0 \times 10^{-3}\ \text{m}^3) = 501\ \text{kJ} \tag{iii}$$

Substitute (*ii*) and (*iii*) in (*i*) to obtain $V_b - V_a = 6267$ kJ.

Problem 18.28. For the Otto cycle of Problem 18.24, assume that a diatomic ideal gas ($\gamma = 1.40$) is in the cylinder. Assume further that $V_c = 0.4\ V_d$.

(*a*) Find the efficiency of this Otto engine.
(*b*) Given $P_c = 20\ P_a$ find the efficiency of the Carnot cycle that operates between the highest and lowest temperatures of the Otto cycle.

Solution

(*a*) By Problem 18.24(*b*),

$$e = 1 - \left(\frac{V_c}{V_d}\right)^{\gamma - 1} = 1 - (0.4)^{0.40} = 0.307 = 30.7\%$$

(*b*) By Problem 18.21, $e_C = 1 - (T_a/T_c)$. But the ideal gas law tells us that (recalling that $V_a = V_d$)

$$\frac{P_a V_d}{T_a} = \frac{P_c V_c}{T_c} \qquad \text{or} \qquad \frac{T_a}{T_c} = \frac{P_a}{P_c}\frac{V_d}{V_c} = \left(\frac{1}{20}\right)\left(\frac{10}{4}\right) = 0.125$$

whence $e_C = 0.875 = 87.5\%$ (much superior to the Otto cycle).

Problem 18.29. A home refrigerator must remove thermal energy at the rate of 1.5 kW to keep the interior temperature at 7.0 °C. Heat is expelled to the kitchen area, which is at 30 °C.

(*a*) If the refrigerator operates in a Carnot cycle, what is its coefficient of performance κ?

(*b*) How much electrical power P is needed to run the refrigerator?

Solution

(*a*) By (*18.6*),

$$\kappa = \frac{Q_{\text{out}}}{Q_{\text{in}} - Q_{\text{out}}}$$

A Carnot refrigerator is just a Carnot engine run in reverse, so

$$\frac{Q_{\text{out}}}{Q_{\text{in}}} = \frac{T_C}{T_H} = \frac{280}{303} \quad \text{and} \quad \kappa = \frac{280/303}{1-(280/303)} = 12.2$$

(*b*) From Eq. (*18.6a*), $\kappa = Q_{\text{out}}/W_{\text{net}} \Rightarrow W_{\text{net}} = Q_{\text{out}}/\kappa$. Recalling the relationship between power and work, we have $P = (1500\ \text{J/s})/(12.2) = 123\ \text{W}$.

Problem 18.30.

(*a*) How is a quasistatic constant-entropy process represented on a *P*-*V* diagram?

(*b*) If an ideal gas undergoes an isothermal compression, does the entropy of the gas increase or decrease?

(*c*) Does the answer to (*b*) violate Eq. (*18.9*), the entropy statement of the second law?

Solution

(*a*) If the entropy of the system stays the same, then (*18.8*) implies $\Delta Q = 0$. Thus, the process is represented by an adiabat.

(*b*) In an isothermal compression, the work W done *by* the gas is negative. Since the internal energy of an ideal gas is constant during an isothermal process, the first law implies that the heat Q entering the system must equal the work done by the system: $Q = W$. Thus $Q = \Delta Q$ is also negative, and it follows from (*18.8*) that the entropy of the gas decreases.

(*c*) No: (*18.9*) refers to the entropy *of the universe.* Since Q for the gas is negative, heat must be leaving it to enter some other system. The entropy of the other system will thus be increasing; overall, (*18.9*) will hold.

Problem 18.31. An ideal gas is confined to one-half a rectangular container by a thin membrane, the other half of the container being completely empty. The container is well insulated so that no heat can enter or leave the system. When the membrane is broken, the gas rushes to occupy the whole container in a process called **free expansion** and then settles down to equilibrium in the new volume. Between the initial and final equilibrium, (*a*) what is the change in internal energy of the gas? (*b*) what is the change in temperature of the gas?

Solution

(*a*) No change. No heat enters or leaves the container, and no work is done on or by the outside world, since the volume of the container is unchanged.

(*b*) No change. For an ideal gas fixed internal energy means fixed temperature.

Problem 18.32. In the free expansion of Problem 18.31 the entropy of the gas actually increases. How can this be, in view of (*18.8*) and the fact that no heat enters or leaves?

Solution

Equation (*18.8*) does not apply here, because the free expansion is turbulent and cannot be described by means of a quasistatic path. That the entropy *does* increase can be understood intuitively—the explosive expansion can only increase molecular disorder. To prove that the entropy has increased, we mark the initial and final equilibrium states on a *P*-*V* diagram. Since the two states have the same temperature, they can be connected by an isothermal quasistatic path. We then replace the real process with an expansion along the isotherm. As we expand along any ideal-gas isotherm, heat must enter the system, so $\Delta S = \Delta Q/T > 0$. Thus our final state has higher entropy than the initial state. Since the process occurs in an isolated system (our confined gas), the entropy change of the universe is the entropy change of the gas. Thus, in this real process the entropy of the universe increases.

Supplementary Problems

Problem 18.33. In Fig. 18-5, assume the system absorbs 80 J of heat in going from $i \rightarrow f$ along path a and 50 J of heat in going from $i \rightarrow f$ along path b.

(*a*) What is the net work done in going around the complete cycle: $i \rightarrow f$ along a and $f \rightarrow i$ along b?

(*b*) If the work done by the system in going from $i \rightarrow f$ along path b is 170 J, what is the work done in going from $i \rightarrow f$ along path a?

Ans. (*a*) 30 J; (*b*) 200 J

Problem 18.34. Referring to Problem 18.33, assume the internal energy at point i is 800 J and the work done in going from $i \rightarrow f$ along path c is 180 J.

(*a*) What is the internal energy of point f?

(*b*) How much heat enters or leaves the system as the system goes from point $f \rightarrow i$ along path c?

Ans. (*a*) 680 J; (*b*) 60 J leaves.

Problem 18.35.

(*a*) Find the change in internal energy of 0.60 mol of oxygen as it is heated from $t = -50\,^\circ\mathrm{C}$ to $t = 80\,^\circ\mathrm{C}$ at constant volume. Assume the oxygen is an ideal gas. [*Hint*: See Problem 18.5.]

(*b*) Repeat (*a*) if the oxygen undergoes the same change in temperature at constant pressure.

(*c*) Find the work done by the oxygen in (*b*). [*Hint*: See Problem 18.7.]

Ans. (*a*) Increases 1650 J; (*b*) The same as part (*a*) (since U depends only on T); (*c*) 648 J

Problem 18.36. When n mol of ideal gas undergoes an isothermal expansion, depicted in Fig. 18-7(*c*), the work done is given by $W_{a\rightarrow b} = nRT\ln(V_b/V_a)$, where T is the temperature of the isotherm. If 2.0 mol of an ideal gas expands along a 300-K isotherm until the volume doubles, find (*a*) the work done; (*b*) the heat entering the gas.

Ans. (*a*) 3.46 kJ; (*b*) 3.46 kJ

Problem 18.37. Assume that 3.0 mol of a monatomic ideal gas undergoes an adiabatic expansion such as shown in Fig. 18-7(*d*). The temperature drops from $T_i = 400$ K to $T_f = 180$ K during the expansion.

(*a*) Find the work done by the gas. [*Hint*: See Problem 18.8(*b*).]

(*b*) Given $U_i = 12$ kJ, find U_f.

Ans. (*a*) 8.23 kJ; (*b*) 3.77 kJ.

Problem 18.38. Refer to Problem 18.37.

(*a*) Evaluate γ for the gas. [*Hint*: Review Chap. 16 and see note at end of Problem 18.9.]

(*b*) Given $V_i = 5.0$ L, determine V_f.

Ans. (*a*) $\frac{5}{3}$; (*b*) 16.6 L

Problem 18.39. Suppose the adiabatic process described in Problems 18.37 and 18.38 is made part of a cycle with the other two paths being a constant-pressure and a constant-volume process, as shown in Fig. 18-17, with the three paths labeled *a*, *b*, and *c*.

(*a*) Use the ideal gas law to find the pressure at points *i* and *f*, and the temperature at point *k*.

(*b*) Find the work W_{fk} done by the system along path *b* from $f \rightarrow k$.

(*c*) Find the heat Q_{fk} entering the system along path *b* from $f \rightarrow k$.

Ans. (*a*) $P_i = 1.99 \times 10^6$ Pa, $P_f = 2.70 \times 10^5$ Pa, $T_k = 54.2$ K; (*b*) $W_{fk} = -3130$ J; (*c*) -7840 J.

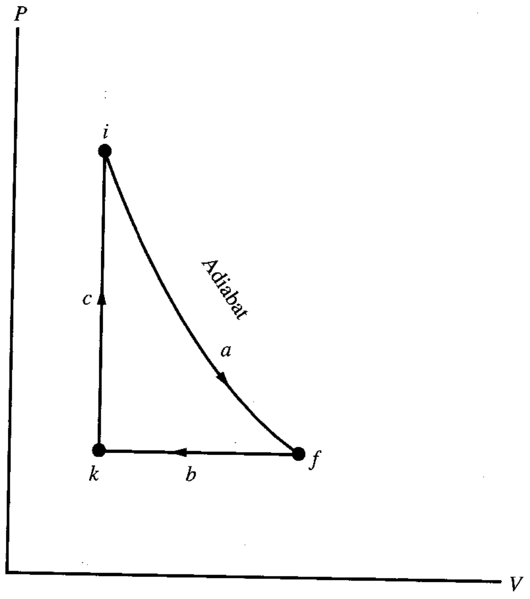


Fig. 18-17

Problem 18.40. Refer to Problem 18.39 and Fig. 18-17.

(*a*) Find the heat Q_{ki} entering the system along path *c* from $k \rightarrow i$ and the work done W_{ki} along the same path.

(*b*) Using the results of (*a*) and Problem 18.39(*c*), find the net heat entering the system in the cycle.

(*c*) Using the results of (*a*), Problem 18.39(*b*), and Problem 18.37(*a*), find the net work done in the cycle. Is this consistent with the answer to part (*b*)?

Ans. (*a*) 12,930 J, 0 J; (*b*) 5090 J; (*c*) 5100 J; in a complete cycle $W_{\text{net}} = Q_{\text{net}}$, which is our result to within rounding errors

Problem 18.41. A quasistatic engine cycle is represented on a *P*-*V* diagram by the triangle shown in Fig. 18-18. Assume that 500 J of heat enters the system along path *a* and that 300 J enters along path *b*.

(*a*) How much work is done in the cycle?

(*b*) How much heat must leave the system along path *c*?

(*c*) What is the efficiency of the engine?

Ans. (*a*) 450 J; (*b*) 350 J leaves; (*c*) 56.2%

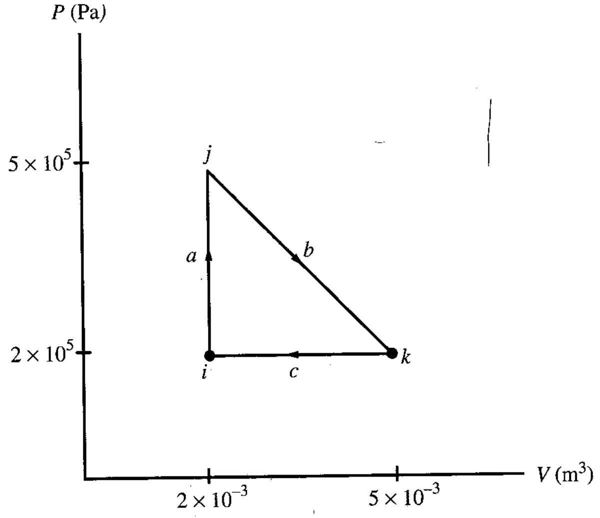


Fig. 18-18

Problem 18.42. Find the efficiency of the engines represented by the cycles of (*a*) Problem 18.33(*a*); (*b*) Problem 18.40. (Use the information given, and answers already obtained, in those problems.)

Ans. (*a*) 37.5%; (*b*) 39.4%

Problem 18.43. Find the coefficients of performance of the backward-run engines of Problem 18.42.

Ans. (*a*) 1.67; (*b*) 1.54

Problem 18.44. The efficiency of a Carnot engine is 85% and the hot reservoir is at 800 K.

(*a*) What is the temperature of the cool reservoir?

(*b*) If the engine performs 3 kJ of work per cycle, how much heat enters the system per cycle from the hot reservoir?

(*c*) How much heat is exhausted per cycle to the cool reservoir?

Ans. (*a*) 120 K; (*b*) 3.53 kJ; (*c*) 530 J

Problem 18.45. For the quasistatic process of Problem 18.36, calculate (*a*) the change in the entropy of the gas; (*b*) the change in the entropy of the rest of the universe.

Ans. (*a*) 11.5 J/K; (*b*) -11.5 J/K (since $\Delta S_{\text{unv}} = 0$)