

3

The first law of thermodynamics

The first law of thermodynamics is essentially a ‘balance sheet of energy’. It gives the precise relationship between the familiar concept of work and the new concepts of internal energy and heat, both of which we shall be defining shortly.

It is interesting to approach the first law historically.

3.1 JOULE'S EXPERIMENTS

At the beginning of the nineteenth century, the dominant theory as to the nature of heat was that it was an indestructible substance (*caloric*) which flowed from a hot body, rich in caloric, to a cold body which had less caloric. Heat was quantified by the temperature rise it produced in a unit mass of water, taken as a standard reference substance. The experiments of Black at the end of the eighteenth century had shown that, when two bodies were put in thermal contact, the heat lost by one in this ‘method of mixtures’ was equal to the heat gained by the other. This seemed to confirm that heat was a conserved entity.

However, when Benjamin Thompson (who became Count Rumford of Bavaria and founded the Royal Institution of Great Britain) was working in the arsenal in Munich supervising the boring of cannon, he noticed that great heat was produced, as measured by the temperature rise in the cooling water. Further, when he used a blunt boring tool, he found that he could even *boil* the water, with the supply of heat being apparently inexhaustible. He concluded that heat could not be a finite substance such as caloric and that there was a direct relation between the work done and the heat produced.

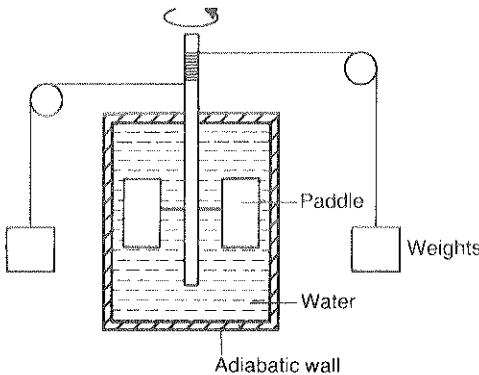


Figure 3.1 A schematic representation of Joule's apparatus.

The precise relation was established by Joule some fifty years later in a careful series of experiments between 1840 and 1849.

Joule, a Manchester brewer, constructed a tub containing a paddle wheel which could be rotated by the action of weights falling outside the tub, as in Fig. 3.1. Water inside the tub could thus be stirred (irreversibly because of turbulence), raising its temperature between two equilibrium states. The walls of the tub were insulating, so the work was performed under adiabatic conditions; we call such work *adiabatic work*. Working with extraordinary accuracy, Joule found the following.

1. That it required 4.2 kJ of work to raise the temperature of one kg of water through one degree kelvin (we have converted his British units to the modern SI units). This is known as the *mechanical equivalent of heat* J . It is interesting to note that, when Joule examined Rumford's results, he obtained a value for J that was consistent with his own.
2. That no matter how the adiabatic work was performed, it always required the *same* amount of work to take the water system between the same two equilibrium states. Joule varied his adiabatic work by changing the weights and the number of drops. He also performed the same amount of adiabatic work electrically by allowing the current produced by an electrical generator to be dissipated in a known resistance immersed in the water.

3.2 THE FIRST LAW OF THERMODYNAMICS AND THE INTERNAL ENERGY FUNCTION

We may summarize these findings in the following statement of the first law:

If a thermally isolated system is brought from one equilibrium state to another, the work necessary to achieve this change is independent of the process used.

This is saying that the adiabatic work $W_{\text{adiabatic}}$ expended in a process is path independent, depending only on the end equilibrium points; and this is true whether or not the process is reversible. So there must exist a state function whose difference between the two end points 2 and 1 is equal to the adiabatic work. We call this state function the *internal energy* U with

$$W_{\text{adiabatic}} = U_2 - U_1 \quad (3.1)$$

In mechanics, we are familiar with the idea of the work done on a system increasing the kinetic and potential energies. In our discussion we have *excluded* any change in these bulk energies: Joule's tub was neither lifted up nor was it set in motion across the floor of the laboratory. From a molecular viewpoint, however, the external work does in fact go into increasing kinetic and potential energies—those of the individual molecules which have kinetic energy because of their *random* motion and potential energy because of their mutual attraction. This viewpoint is helpful in understanding the physical meaning of internal energy.

3.3 HEAT

If the system is not thermally isolated, it is found that the work W done in taking the system between a pair of equilibrium points depends on the path. Now, for a given change, $\Delta U = U_2 - U_1$, is fixed but W is not now equal to ΔU . In other words there is a difference between the adiabatic work required to bring about a change between two equilibrium states and the non-adiabatic work required to effect the same change, with the latter having an infinite number of possible values.

We call the difference between ΔU and W the *heat*, Q . The generalization of equation (3.1) is then

$$\boxed{\Delta U = W + Q} \quad (3.2)$$

which is the mathematical statement of the first law. It tells us that the internal energy can be increased either by doing work on or by supplying heat to the system. In this form, it is true for all processes whether reversible or irreversible. Now we have seen that all forms of work are equivalent to the mechanical raising or lowering of a weight in the surroundings so we conclude that

Heat is the non-mechanical exchange of energy between the system and the surroundings because of their temperature difference.

(Here we are considering closed systems. The transfer of energy in open systems is discussed in Chapter 10.)

There has to be a sign convention for heat, just as we have one for work. We define Q as positive when it enters the system, so equation (3.2) is correct as it stands, with U increasing if we do work on the system and if we allow heat to flow in.

For an infinitesimal process, the first law takes the form

$$\bar{d}U = \bar{d}W + \bar{d}Q$$

where we write both $\bar{d}Q$ and $\bar{d}W$ with bars through them to indicate that W , and therefore Q , are in general path dependent. In the language of Appendix B, we say they are *inexact differentials*. Although in the special case of adiabatic work $\bar{d}W_{\text{adiabatic}}$ is path independent and in that sense $\bar{d}W_{\text{adiabatic}}$ is an exact differential, we shall consistently write the infinitesimal work term as $\bar{d}W$ with a bar for all cases, as W is not a state function.

If we have a compressible fluid, where $\bar{d}W = -P\bar{d}V$ for an infinitesimal reversible process, the first law becomes

$$\bar{d}U = -P\bar{d}V + \bar{d}Q$$

or

$$\boxed{\bar{d}Q = \bar{d}U + P\bar{d}V} \quad (\text{reversible}) \quad (3.3)$$

It is very important to realize that this form applies to a reversible infinitesimal process, and so we have added reversible in brackets to remind us.

Let us give an example which illustrates the difference between heat and work. In Fig. 3.2 we have a gas in a container with rigid diathermal walls. A current I flows through the heating coils of resistance R wrapped round the container. In Fig. 3.2(a) the system, denoted by the dotted line, includes the heating coils. Now we know, from our discussion at the end of section 2.9, that work is being done on the system at the rate $I^2 R$ because the current I enters the

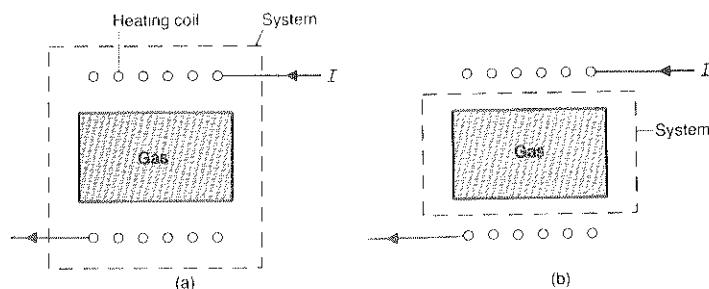


Figure 3.2 An illustration of the difference between work and heat. The input of energy into the system is in (a) as work and in (b) as heat.

system. The energy crossing the system boundary is in the form of *work*. In Fig. 3.2(b) the system is the gas and container alone, excluding the coils. Here, no work is done on the system but there is energy flow across the system boundary in the form of *heat* because the temperature of the coils is higher than that of the gas. This simple example shows that, in differentiating between heat and work, it is very important to be clear as to what constitutes the system.

It is helpful to differentiate between heat and work from a microscopic viewpoint. When we add energy to the system in the form of heat, we increase the *random* motion of the constituent molecules. However, when we increase the energy by performing work, we displace the molecules in an *ordered* way. Consideration of the stretching of a spring immediately illustrates this point. Work then results in organized motion while heat results in random motion. It is interesting to apply these ideas to a gas in a cylinder and to see how a rise in temperature can be achieved either by the addition of heat or the performance of work. If heat is added through diathermal walls, this increases the random kinetic energy of the molecules, which means a rise in temperature. Why is there a rise in temperature if work is performed on the gas which we now consider to be in a cylinder with adiabatic walls? When the piston is pushed in, the molecules striking the piston are accelerated in the direction of its travel. If these molecules strike the walls of the cylinder, they cannot lose energy to the surroundings because the walls are adiabatic. However, any organized motion initially imparted to these molecules is rapidly randomized by collisions, either with the walls or with other molecules. This increase in the random kinetic energy appears again as a temperature rise.

Finally, we should remark that the most illuminating distinction between heat and work as different ways of increasing the internal energy of a system is given by statistical mechanics. The reader is recommended to read section 2.3.2 of the companion book to this by Guenault for a complete discussion but we shall give an outline of the ideas here. Briefly, it is a result of quantum mechanics that each of the N particles in the system can exist in a series of discrete energy levels. We refer ahead to Fig. 6.5. If there is a population of n_i particles in the i th energy level ε_i , the total internal energy of the system will be $U = \sum_{i=1}^N n_i \varepsilon_i$. Now U can be increased in two ways: either the energies ε_i can be changed, with the populations remaining the same—this is work; or the populations n_i can be changed with the energies remaining the same—this is heat.

3.4 HEAT CAPACITY

Suppose we have a process where we allow heat Q to flow into a system, changing it from one equilibrium state to another with a temperature difference ΔT , as in Fig. 3.3. The *heat capacity* C of a system is defined as the limiting ratio of the heat introduced reversibly into the system divided by the temperature rise:

$$C = \lim_{\Delta T \rightarrow 0} (Q/\Delta T) = dQ/dT \quad (3.4)$$

The *specific heat* c is the heat capacity per unit mass:

$$c = 1/m dQ/dT \quad (3.5)$$

(We shall use lower-case symbols frequently in this book when we wish to denote specific quantities which are quantities referred to unit mass, which could be a kilogram or a mole.)

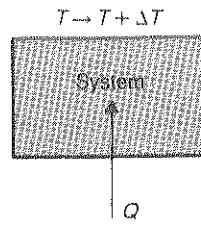


Figure 3.3 The heat capacity is $\lim_{\Delta T \rightarrow 0} Q/\Delta T$.

3.9.2 Flow through a nozzle

When a gas flowing down a pipe encounters a change in the cross-sectional area, there is a change of gas velocity. We utilize this effect frequently in engineering and in particular in a turbine where we 'throw' the gas on to the turbine blades with a high velocity. The incoming gas (steam in the case of a steam turbine) is speeded up by passing it through a nozzle, as in Fig. 3.7. No shaft work w is done, the system is assumed to be horizontal and we further assume that no heat q enters the system as the gas flow is too rapid for this to be appreciable. Equation (3.16) then becomes:

$$v_1^2 - v_2^2 = 2(h_2 - h_1) \quad (3.18)$$

which relates the velocity change to the enthalpy change.

In practice, we will be given the 'upstream' conditions P_1 , T_1 which means that we know h_1 . However, if as is usual, only the 'downstream' pressure P_2 is specified, we have insufficient information to determine h_2 . If we now assume the flow through the nozzle to be reversible as well as adiabatic and the gas is treated as ideal, then we can find the downstream temperature T_2 from the adiabatic relation

$$\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_1}{P_2}\right)^{\gamma-1}$$

This gives us sufficient information to find h_2 and therefore v_2 .

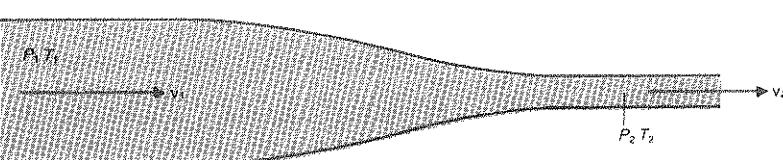


Figure 3.7 A steady flow process through a nozzle.

4

The second law of thermodynamics

The first law of thermodynamics tells us that, in any process, energy is conserved. It may be converted from one form to another but the total amount of energy is unchanged. The second law of thermodynamics imposes limits on the efficiency of processes which convert heat into work, such as steam or internal combustion engines. It will allow us to set up the thermodynamic temperature scale which is independent of the nature of the thermometric substance, and to define the concept of entropy, which we shall see is related to the microscopic disorder in the system.

Before we set up the second law we shall first discuss Carnot cycles, which are central to the discussion.

4.1 CARNOT CYCLES

At the beginning of the nineteenth century, when steam engines were in their infancy, there was enormous interest in how their efficiency could be increased. An intellectual giant in this field was a French engineer, Carnot, who published in 1824 a powerful paper on how work could be produced from sources of heat. He knew that work could be obtained from an engine if there were heat sources at different temperatures—the boiler and the surrounding air in the case of a steam engine. He also knew that it was possible for heat to flow from a hot body to a cold body with no work being performed, the flow continuing until thermal equilibrium was attained. Carnot realized then, since any return to thermal equilibrium could be used to produce work, any return to equilibrium without the production of this work must be considered a loss. So any temperature difference may be utilized in the production of work or it may be

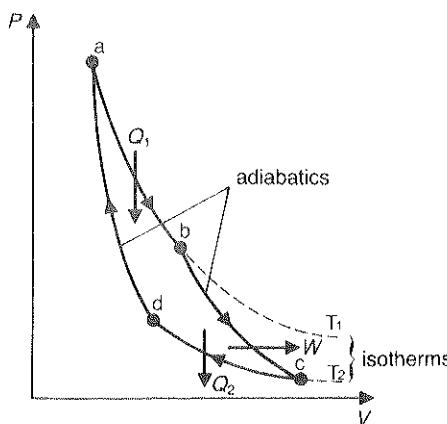


Figure 4.1 A Carnot cycle for an ideal gas.

wastefully dissipated in a spontaneous flow of heat. He concluded that, in an efficient engine, all transfers of heat should be between bodies of nearly equal temperature. With these ideas in mind, he designed an idealized engine which is of fundamental significance. The cycle for the Carnot engine is depicted in Fig. 4.1.

A working substance, which could be any substance but we have chosen it to be an ideal gas for the purpose of our discussion, is taken round the reversible cycle abcd. ab is an isotherm at the temperature T_1 and heat Q_1 enters from a heat reservoir at T_1 . cd is an isotherm at a lower temperature T_2 where heat Q_2 is rejected to another reservoir at that temperature. bc and da are adiabatics. The work W done in the cycle is the area abcd.

It is important to emphasize that a Carnot engine operates between *only two reservoirs* and that it is *reversible*. Also, if a working substance is chosen other than an ideal gas, then the shape of the Carnot cycle as depicted in Fig. 4.1 is different because the equations for the adiabatics and isotherms are no longer $PV^\gamma = \text{constant}$ and $PV = nRT$.

It is interesting to note that Carnot's ideas were conceived before the first law was formulated, using the caloric concept of heat.

4.2 EFFICIENCY OF AN ENGINE

Any general heat engine E may be represented by the schematic diagram Fig. 4.2 where the heat supplied Q_1 and the heat rejected Q_2 are not necessarily obtained from just two heat reservoirs as in

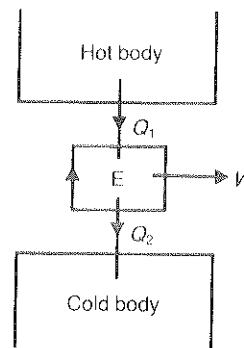


Figure 4.2 A schematic representation of an engine working in a cycle. The efficiency $\eta = W/Q_1 = 1 - Q_2/Q_1$.

the special case of the Carnot engine. W is the work done *by* the engine. The arrow around the edge of the block depicting the engine indicates that the latter works in a cycle.

As a measure of 'what we get out for what we put in', we define the efficiency η of an engine as the work performed divided by the heat put in. For the engine cycle depicted in Fig. 4.2,

$$\eta = W/Q_1$$

Applying the first law to the working substance in the engine,

$$\Delta U = Q_1 - Q_2 - W$$

In writing this, we have remembered our sign convention where the heat *into* the system and the work done *on* the system are both counted positively. As the working substance is unchanged in a cycle, $\Delta U = 0$ and our first law becomes

$$W = Q_1 - Q_2$$

so

$$\boxed{\eta = 1 - Q_2/Q_1} \quad (4.1)$$

4.3 STATEMENTS OF THE SECOND LAW OF THERMODYNAMICS

There are two statements of the second law of thermodynamics which are both based on our general experience. They were each formulated in the 1850s by Clausius and Kelvin, but the second was subsequently modified by Planck. We shall shortly show that both statements are equivalent and they are as follows, although not in the original words.

4.3.1 The Kelvin–Planck statement

It is impossible to construct a device that, operating in a cycle, will produce no effect other than the extraction of heat from a single body at a uniform temperature and the performance of an equivalent amount of work.

Schematically this statement is represented in Fig. 4.3 (a). The second law implies that some heat must also be rejected by the device to a body at a lower temperature; otherwise, as can be seen from equation (4.1), one could have an engine with 100% efficiency. Were this statement untrue, we could drive a ship across the sea just by extracting heat from the sea and converting it totally into work!

There are some key words and phrases in this statement which need further discussion.

(a) **Cycle** requires that the state of the working substance is the same at the start and end of the process, although it may change in between these end points; in other words, there is not a *net* change in the state of the working system. Many processes can be thought of which convert heat *completely* into work, but in all of them there is a *net change in the state of the working system*. For example, we could heat 1 mole of an ideal gas and allow it to expand quasistatically and isothermally (by keeping it in contact with a thermal reservoir) from a volume V_1 to $V_2 > V_1$ as in Fig. 4.4. The work done by the gas is

$$W = \int_{V_1}^{V_2} P dV = RT \int_{V_1}^{V_2} \frac{dV}{V} = RT \ln\left(\frac{V_2}{V_1}\right) > 0$$

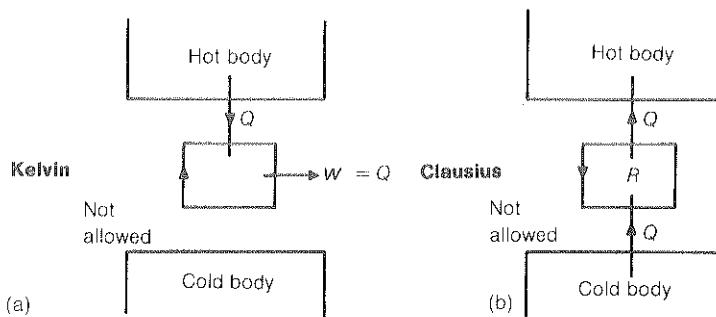


Figure 4.3 Schematic representation of the Kelvin–Planck statement.

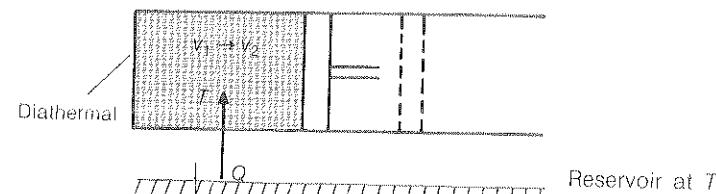


Figure 4.4 An isothermal expansion of an ideal gas. $W = Q$.

As the expansion is isothermal, $T_1 = T_2$ and so $\Delta U = 0$. The first law then shows that $Q = W > 0$ where Q is the net heat supplied, and we have a 100% conversion of heat into work. However there is no violation of the second law here as there has been a net change in the state of the ideal gas working system.

- (b) **No effect other than** tells us that, in addition to the rejection of heat to a body at a lower temperature, the only other effect on the surroundings is via the work delivered by the engine. This means that the bodies delivering and accepting heat to and from the engine must do so without delivering any work. In other words, their volumes must remain constant if only P - V work is being considered. Such a body which delivers its heat with no work is sometimes called a *source of heat*.
- (c) **Single.** Suppose that the heat $Q_1 + Q_2$ was supplied from two bodies: Q_1 from a body at T_1 and Q_2 from a body at T_2 with $T_1 > T_2$ say. The cyclical engine delivers an amount of work $W = Q_1 + Q_2$ as shown in Fig. 4.5 and we appear to have a

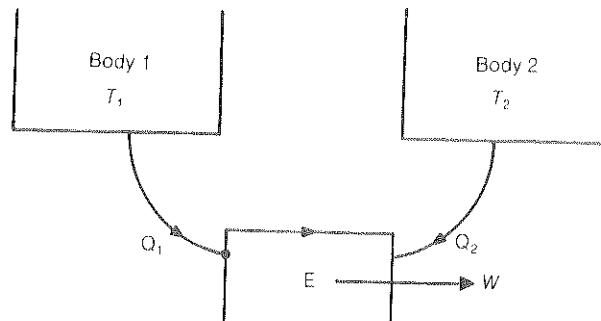


Figure 4.5 Two bodies supplying heat to an engine do not violate the Kelvin statement, as Q_2 could be negative.

complete conversion of heat into work in a cyclical process with no heat being rejected to a reservoir at a lower temperature.

However, there is no violation of the second law here because Q_2 could be negative with $W = |Q_1| - |Q_2|$. We exclude this possible type of engine from the Kelvin statement by specifying a single body.

It should be remarked here that, were we to run an engine with bodies as the sources of heat rather than reservoirs, it would eventually run down as the bodies approach each other in temperature and would not be a very useful engine; however, the second law as given above applies to both situations.

The Kelvin statement of the second law is sometimes given in the very concise form:

A process whose only effect is the complete conversion of heat into work is impossible

A few moments thought on behalf of the reader will show that the word *only* ensures that all the points we have made earlier are covered. We have preferred to give the Kelvin statement in the first more extended form, as the significance of only in the concise form is too easily overlooked.

4.3.2 The Clausius statement

It is impossible to construct a device that, operating in a cycle, produces no effect other than the transfer of heat from a colder to a hotter body.

Schematically, this statement is represented in Fig. 4.3 (b). What this form of the second law tells us is that work must be performed if heat is to be transferred from a colder to a hotter body. Were this not so, we could heat our houses just by cooling the ground at no cost with no work having to be done!

An engine which extracts heat from a cold body and delivers heat to a hot body when work is performed on the engine we recognize as a refrigerator. In our diagrams, we shall denote refrigerators by R .

There is one final point that should be discussed. The Kelvin statement of the second law refers to the impossibility of heat being extracted from a hot body and the performance of an equivalent amount of work, with there being no net change in the state of the working system. It does not forbid the opposite situation depicted

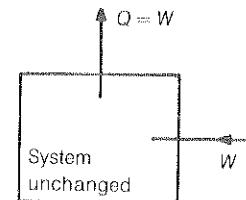


Figure 4.6 Work can be converted completely into heat, with no change in the working substance.

in Fig. 4.6 where all the work W done on an unchanged system may be converted completely into heat. Rumford's experiment with a blunt boring tool is an example of such a total conversion of work into heat. Another example would be rubbing stones together under running water.

4.4 THE EQUIVALENCE OF THE KELVIN AND CLAUSIUS STATEMENTS

The two statements of the second law of thermodynamics may be shown to be equivalent by showing that the falsity of each implies the falsity of the other.

Let us suppose first that the Kelvin statement is untrue. This means that we can have an engine E which takes Q_1 from a hot body and delivers work $W = Q_1$ in one cycle. Let this engine drive a refrigerator R as shown in Fig. 4.7(a) and let us now adjust the size of the working cycles so that W is sufficient work to drive the refrigerator round one cycle. Suppose the refrigerator extracts heat Q_2 from the cold body. Then the heat delivered by it to the hot body is $Q_2 + W$ or $Q_1 + Q_2$. We may regard the engine and the refrigerator as the composite engine enclosed by the dotted line as shown in Fig. 4.7(b). This composite engine (strictly a refrigerator) extracts Q_2 from the cold body and delivers a net amount of heat $Q_2 + Q_1 - Q_1 = Q_2$ to the hot body, but no work is done. Hence we have a violation of the Clausius statement.

Suppose now that the Clausius statement is untrue. This means that we can have a refrigerator which extracts heat Q_2 from a cold body and delivers the same heat Q_2 to a hot body in one cycle, with no work having to be done. Let us now have an engine which operates between the same two bodies and let us adjust the size of its working cycle so that, in one cycle, it extracts heat Q_1 from the hot body,

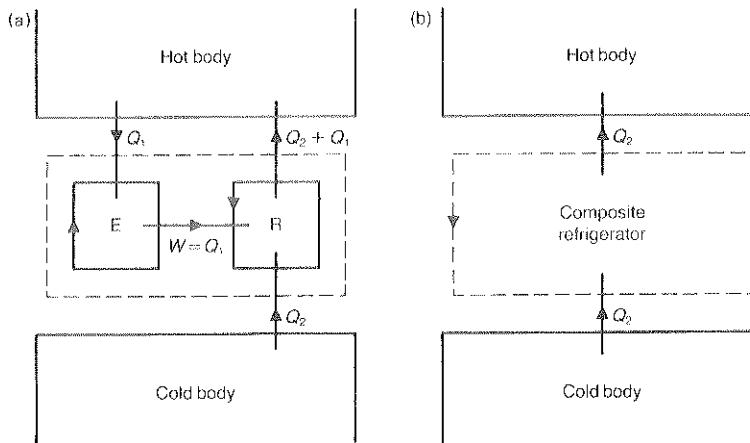


Figure 4.7 If the Kelvin statement of the second law is false, this implies that the Clausius statement is also false. We use the arrangement illustrated here to prove this.

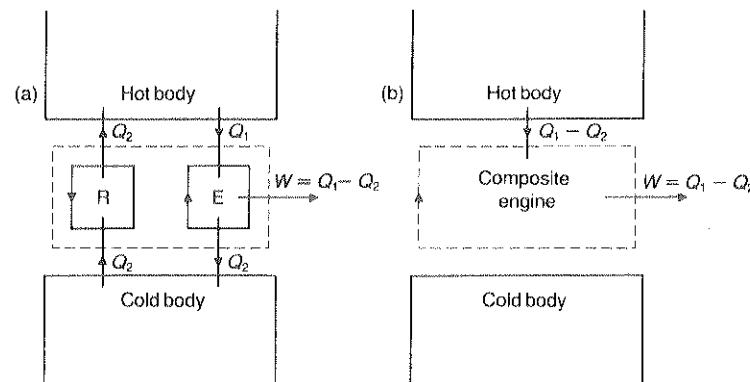


Figure 4.8 If the Clausius statement of the second law is false, this implies that the Kelvin statement is also false. We use the arrangement illustrated here to prove this.

gives up the same heat Q_2 to the cold body as was extracted by the refrigerator and so delivers the work $W = Q_1 - Q_2$. This is depicted in Fig. 4.8(a). The engine and the refrigerator may be regarded as the composite engine enclosed by the dotted line, as shown in Fig. 4.8(b), which takes in heat $(Q_1 - Q_2)$ from the hot body and delivers the

same amount of work. Hence, we have a violation of Kelvin. This proves the equivalence of the two statements.

4.5 CARNOT'S THEOREM

In the introduction to this chapter, we saw that Carnot had argued that efficient engines must be those operating as nearly as possible to a Carnot cycle. Using our Clausius statement of the second law, let us now prove Carnot's theorem which states:

No engine operating between two reservoirs can be more efficient than a Carnot engine operating between those same two reservoirs.

To prove this, let us imagine that such a hypothetical engine E' does exist with an efficiency η' . As shown in Fig. 4.9(a), this engine extracts heat Q'_1 from the hot reservoir, performs the work W' and delivers the heat $Q'_2 = (Q'_1 - W')$ to the cold reservoir.

Let us now operate a Carnot engine, denoted by C and with efficiency η_C , between the two reservoirs extracting and delivering the heats Q_1 and Q_2 , and let us also adjust the size of the cycle to make this engine perform the same amount of work as the hypothetical engine. For this Carnot engine, $Q_2 = Q_1 - W$. As the hypothetical engine is assumed to be more efficient than the Carnot

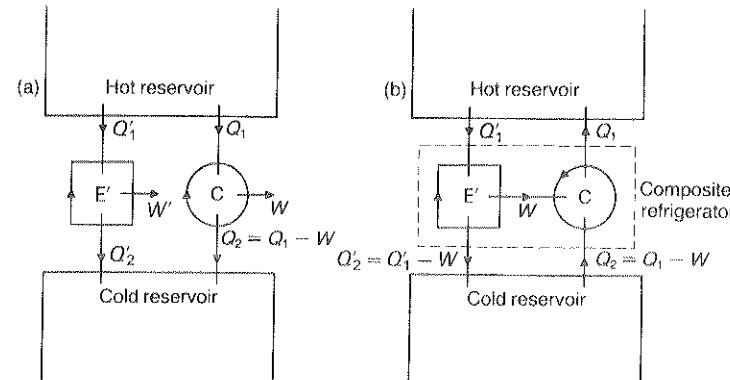


Figure 4.9 The arrangement used to prove Carnot's theorem: no engine working between two reservoirs can be more efficient than a Carnot engine working between the same two reservoirs.

engine,

$$W'/Q'_1 > W/Q_1 \quad (W' = W)$$

so

$$Q_1 > Q'_1$$

Now a Carnot engine is a reversible engine so we may drive it backwards as a refrigerator as shown in Fig. 4.9(b). The hypothetical engine and the Carnot refrigerator together act as a composite device, shown by the dotted line, which extracts *positive* heat ($Q_1 - Q'_1$) from the cold reservoir and delivers the *same* heat to the hot reservoir with no external work being required. But reservoirs are just large bodies where the temperature is unchanged upon the addition of heat. This means that we have a violation of the Clausius formulation and so the engine E' cannot exist and our original assumption that $\eta' > \eta_C$ is incorrect. Also, we could allow η' to be equal to η as then $Q'_1 = Q_1$; this means that the composite refrigerator simply transfers no net heat for no work, which is allowed.

We conclude that, for any real engine,

$$\boxed{\eta \leq \eta_C}$$

which proves the theorem.

4.6 COROLLARY TO CARNOT'S THEOREM

It follows from Carnot's theorem that:

All Carnot engines operating between the same two reservoirs have the same efficiency.

To prove this statement, let us imagine two Carnot engines C and C' operating between the same two reservoirs, and let the size of the working cycles be adjusted so that they each deliver the same amount of work.

Let C run C' backwards as in Fig. 4.10. It follows from the argument just given in the previous section that

$$\eta_C \leq \eta'_{C'}$$

If C' now runs C backwards,

$$\eta'_{C'} \leq \eta_C$$

We conclude that

$$\boxed{\eta_C = \eta'_{C'}}$$

which proves our assertion!

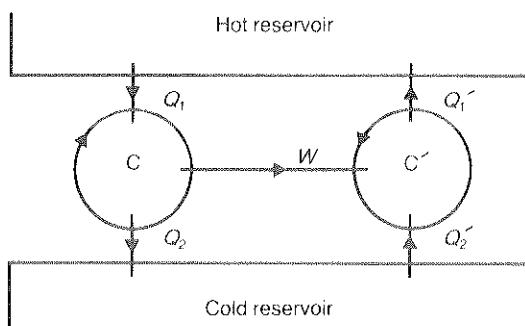


Figure 4.10 The arrangement used to prove that all Carnot engines operating between the same two reservoirs have the same efficiency.

4.7 THE THERMODYNAMIC TEMPERATURE SCALE

We have just seen that the efficiency of a Carnot engine operating between the two reservoirs is independent of the nature of the working substance and so can be dependent only on the temperatures of the reservoirs. This gives us a means of defining a temperature scale which is independent of any particular material. Let us define the thermodynamic temperature T so that T_1 and T_2 for the two reservoirs in a Carnot engine are related as

$$\eta_C = \frac{T_1 - T_2}{T_1} = 1 - T_2/T_1 \quad (4.2)$$

If we compare this with equation (4.1), we have

$$\boxed{T_1/T_2 = Q_1/Q_2} \quad (\text{Carnot}) \quad (4.3)$$

where we have written Carnot in brackets to remind us that this definition holds only for a Carnot engine. Note that here, we have defined the heat flow Q_1 in and the heat flow Q_2 out to be both positive numbers.

We can see that equation (4.3) gives a sensible definition for a scale of temperature by considering Fig. 4.11. Here, we have a Carnot engine C_{12} operating between the reservoirs at T_1 and T_2 . For this engine, equation (4.3) gives

$$T_1/T_2 = Q_1/Q_2 \quad (4.4)$$

Suppose we have a second Carnot engine C_{23} operating between the reservoir at T_2 and a third reservoir at T_3 . Let C_{23} absorb the same amount of heat Q_2 from the reservoir at T_2 as was rejected to

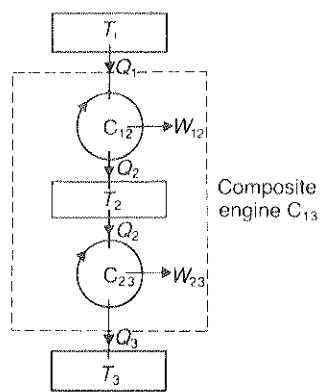


Figure 4.11 The thermodynamic temperature scale, as defined by equation (4.3), is consistent with the arrangement illustrated here.

that reservoir by C_{12} . When the two engines operate together, the reservoir at T_2 is thus unchanged. Equation (4.3) gives

$$T_2/T_3 = Q_2/Q_3 \quad (4.5)$$

Multiplying equation (4.4) by equation (4.5),

$$T_1/T_3 = Q_1/Q_3$$

which does not involve the intermediate temperature T_2 . As the reservoir at T_2 is unchanged, we may consider the two engines C_{12} and C_{23} , acting together, to be a composite Carnot engine C_{13} operating between the two reservoirs at T_1 and T_3 . This composite engine is denoted by the dotted line in Fig. 4.11. The application of equation (4.3) again shows that the previous relation is precisely the one that holds for this composite Carnot engine. It follows that, by taking a whole series of Carnot engines, any range of temperatures may be defined in a self-consistent way.

This temperature scale is **independent of the choice of working substance**, which was one of our objectives in our discussion of scales of temperature in Chapter 1. The thermodynamic scale of temperature will now be shown to be identical to the familiar ideal gas scale.

4.8 THE EQUIVALENCE OF THE THERMODYNAMIC AND THE IDEAL GAS SCALES

Until now, we have used the symbol T for absolute temperature as defined on the ideal gas scale. In this section, until we prove them to

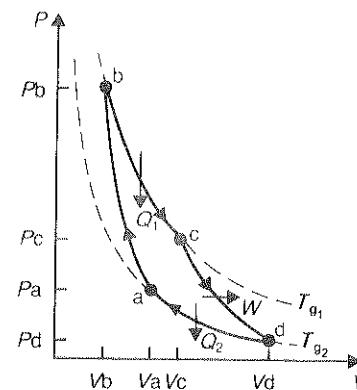


Figure 4.12 A Carnot cycle with an ideal gas as the working substance. Using this figure, we show in the text that the ideal gas scale temperature is identical to the thermodynamic temperature T .

be identical, we shall use the symbol T_g for the gas scale temperature and T for the thermodynamic temperature as just defined.

Consider a Carnot engine, with an ideal gas as the working substance, operating between the two reservoirs at the ideal gas scale temperatures T_{g_1} and T_{g_2} . Let us follow the operating cycle abcd shown in Fig. 4.11. For the isotherm bc, we have the empirical equation of state involving the gas scale temperature T_{g_1}

$$PV = nRT_{g_1} \quad (4.6)$$

The first law gives for an infinitesimal part of this reversible process

$$dQ = dU + PdV = PdV \quad (4.7)$$

as $dU = 0$ because the temperature is constant. The heat Q_1 entering the engine in this portion of the cycle is

$$\begin{aligned} Q_1 &= \int_{V_b}^{V_c} PdV = nRT_{g_1} \int_{V_b}^{V_c} dV/V \\ &= nRT_{g_1} \ln(V_c/V_b) \end{aligned} \quad (4.8)$$

This is positive if $V_c > V_b$, which is consistent with our idea that heat enters the engine in this portion of the cycle. Similarly, the heat entering the engine along the da isotherm part of the cycle is $nRT_{g_2} \ln(V_a/V_d)$. This is negative if $V_a < V_d$, which means that heat

flows out of the engine. But we have defined positive Q_2 as the heat flow out of the engine here, so

$$Q_2 = -nRT_{g_2} \ln(V_a/V_d) = nRT_{g_2} \ln(V_d/V_a) \quad (4.9)$$

Dividing equation (4.8) by equation (4.9),

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} = \frac{T_{g_1} \ln(V_c/V_b)}{T_{g_2} \ln(V_d/V_a)} \quad (4.10)$$

But ab and cd are adiabatics where $T_g V^{\gamma-1} = \text{a constant}$, holds so:

$$T_{g_1} V_c^{\gamma-1} = T_{g_2} V_d^{\gamma-1} \quad (\text{cd adiabatic}) \quad (4.11)$$

$$T_{g_1} V_b^{\gamma-1} = T_{g_2} V_a^{\gamma-1} \quad (\text{ab adiabatic}) \quad (4.12)$$

Dividing equation (4.11) by equation (4.12),

$$\frac{V_c}{V_b} = \frac{V_d}{V_a}$$

or

$$\ln \left\{ \frac{V_c}{V_b} \right\} = \left\{ \frac{V_d}{V_a} \right\}$$

Substituting this in equation (4.10),

$$\frac{T_1}{T_2} = \frac{T_{g_1}}{T_{g_2}}$$

This means that

$$T_g = \varepsilon T$$

where ε is a constant. But we know that all temperature scales agree at the fixed point of 273.16 K so ε must be unity. We conclude then that

$$T_g \equiv T \quad (4.13)$$

That is, the thermodynamic and the ideal gas scales of temperature are identical.

4.9 THE EFFICIENCIES OF ENGINES AND REFRIGERATORS USING CARNOT CYCLES

In the next section we shall consider an example of a real engine, but it is instructive to consider first, because the analysis is so delightfully simple, an engine based on a Carnot cycle. This has a

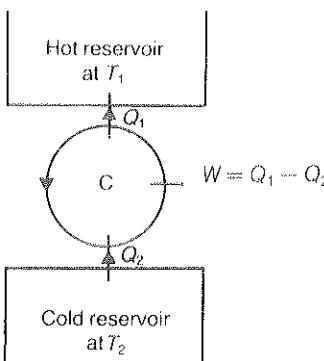


Figure 4.13 A Carnot refrigerator.

practical use in that it gives us an upper limit, by Carnot's theorem, for the efficiency of any possible engine that we might design.

A Carnot engine, such as the one depicted in Fig. 4.1, has the efficiency

$$\eta_C = 1 - Q_2/Q_1 = 1 - T_2/T_1 \quad (4.2)$$

It is then a simple matter to calculate the efficiency knowing T_1 and T_2 . It is interesting to note that the efficiency would be 100 per cent were we able to obtain a lower temperature reservoir at absolute zero; this we shall see is forbidden by the third law.

Imagine now that the Carnot engine is run backwards, as in Fig. 4.13, to act as a refrigerator. We can define the 'efficiency' η_C^R of a refrigerator as the heat extracted divided by the work expended and this is customarily known as the *coefficient of performance*. For our Carnot refrigerator,

$$\eta_C^R = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2} \quad (4.14)$$

If we take the realistic values of $T_1 = 293\text{K}$ and $T_2 = 273\text{K}$, $\eta_C^R = 13.6$. Real refrigerators have coefficients of performance of about 4 or 5.

The most interesting application of these ideas, and a first sight a rather disquieting one, is to so-called *heat pumps*. We all know that the back of a refrigerator becomes rather warm. Let us define, as a measure of how good a refrigerator is at providing heat, the 'efficiency' η^{HP} of a heat pump to be quantity Q_1/W . For a Carnot

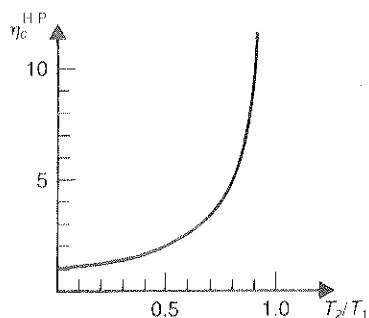


Figure 4.14 The 'efficiency' of a Carnot heat pump as a function of the ratio of the reservoir temperatures.

heat pump

$$\eta_C^{\text{HP}} = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2} = \frac{1}{1 - T_2/T_1} \quad (4.15)$$

Suppose now that $T_1 = 293\text{K}$ and $T_2 = 273\text{K}$. Then $\eta_C^{\text{HP}} = 15$, so we obtain 15 joules of heat for every joule of work we put in! Of course this is an idealized and most efficient device but real heat pumps have been produced for some forty years and, although their 'efficiencies' are not 15, they are in the region of 3 or 4, which makes them attractive propositions. Their disadvantage is their high capital cost. It is expensive to lay pipes under one's garden in order to cool this to heat one's house. The Festival Hall in London is heated by operating a heat pump between it and the Thames, and one Oxford college derived, until recently, its warmth by cooling the city sewers.

Fig. 4.14 shows the efficiency of a Carnot heat pump against (T_2/T_1) . Because the efficiency rises as the temperature difference between the reservoirs decreases, heat pumps are best used in providing background heating, with the final 'top up' being provided by a conventional source.

4.10 REAL ENGINES

The Carnot engine is an idealized engine. Real engines operate in various cycles, all different from the idealized Carnot one. At this stage we shall temporarily depart from the central thread of our

argument to discuss, for interest, the four-stroke Otto-cycle or common petrol engine.

We are all familiar with the principle of this engine.

1. Petroleum vapour and air are drawn into the cylinder on the downstroke of the piston.
2. The mixture is compressed.
3. Near top dead centre, the mixture is ignited giving rise to the power stroke.
4. The burnt mixture is expelled.

Figure 4.15(a) shows this cycle. The air standard Otto cycle is a close but simplified representation of this process which facilitates analysis; it is shown in Fig. 4.15(b). The working substance is assumed to be just air rather than air and petrol, with no chemical changes occurring in its composition. Also, instead of the heat being added internally by the burning of the fuel, heat is assumed to be added from external sources. The suction intake and the exhaust processes of the actual cycle, shown in Fig. 4.15(a), are omitted from the Otto cycle.

Let us now go round the Otto cycle.

a-b The piston rises to compress the gas reversibly and adiabatically with

$$T_a V_1^{\gamma-1} = T_b V_2^{\gamma-1} \quad (4.16)$$

b-c Heat Q_1 is added at constant volume from an external source with

$$Q_1 = C_V(T_c - T_b) \quad (4.17)$$

c-d The gas expands adiabatically and reversibly in the power stroke with

$$T_d V_1^{\gamma-1} = T_c V_2^{\gamma-1} \quad (4.18)$$

d-a At the bottom of the power stroke the gas is assumed to cool at constant volume down to the pressure P_0 by giving up heat Q_2 to external reservoirs with

$$Q_2 = C_V(T_d - T_a) \quad (4.19)$$

We may now derive an expression for the efficiency using equations (4.1), (4.17) and (4.19). For this cycle,

$$\eta = 1 - Q_2/Q_1 = 1 - \left\{ \frac{T_d - T_a}{T_c - T_b} \right\}$$

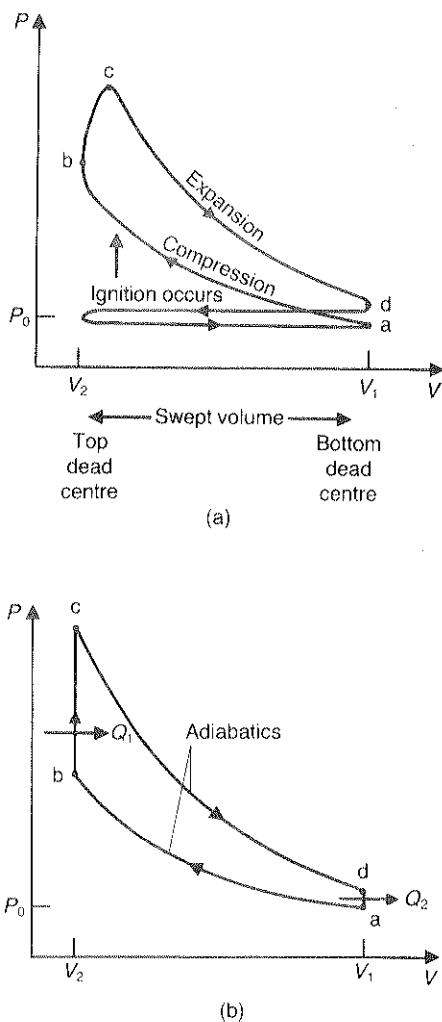


Figure 4.15 The 4-stroke internal combustion engine. (a) The actual cycle. (b) Otto cycle, which is a simplified representation of the actual cycle.

The two relations, equations (4.16) and (4.18), for the adiabatic processes, give on subtraction

$$(T_d - T_a)V_1^{\gamma-1} = (T_c - T_b)V_2^{\gamma-1}$$

$$\text{or } \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left\{ \frac{T_c - T_b}{T_d - T_a} \right\}$$

We call the ratio V_1/V_2 the compression ratio r_c , so

$$\eta = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} = 1 - \frac{1}{r_c^{\gamma-1}} \quad (4.20)$$

and it can now be seen why it is important to have as high a compression ratio as possible. Pinking or pre-ignition limits r_c to about 7 or 8 for unleaded low-octane petrol, giving a theoretical efficiency of $1 - 1/7^{0.4} = 54$ per cent. The actual efficiency of a real petrol engine is much lower than this value, being probably only about 30 per cent.

4.11 SUMMARY

This has been a very important chapter and it is useful to summarize what we have found.

1. A heat engine converts heat into work in a cyclical process in which the working substance is unchanged.
2. A Carnot engine is a reversible engine which operates between two temperatures only. In general, engines take in and reject heat at a variety of temperatures.
3. The efficiency of an engine is

$$\eta = 1 - Q_2/Q_1$$

4. The essence of the Kelvin statement of the second law is that a cyclical engine cannot convert heat from a single body at a uniform temperature completely into work. Some heat has to be rejected at a lower temperature.

The essence of the Clausius statement is that heat cannot flow from a cold body to a hot body by itself—work has to be done on a cyclical refrigerator to achieve this.

5. The most efficient engine operating between a given pair of reservoirs is a Carnot engine. All Carnot engines operating between the same reservoirs have the same efficiency, this being independent of the nature of the working substance.
6. For a Carnot engine, we can define the thermodynamic temperature as

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad \text{with} \quad \eta_C = 1 - T_2/T_1$$

The thermodynamic temperature is identical to the ideal gas temperature.

We are now in a position to meet the powerful concept of entropy.

Entropy

5.1 THE CLAUSIUS INEQUALITY

There is a very important theorem for cyclical processes which leads to the concept of entropy. This theorem is known as the Clausius inequality.

Let us consider a working substance undergoing a cycle so that, at the end of the cycle, its state is unchanged. In Fig. 5.1(a) we symbolically represent this cycle by the circle in the centre with the starting state at the temperature T_1 being represented by the point 1. We shall take the heat causing the changes as ultimately being supplied by a principal reservoir at \tilde{T} . We can take the working substance around the cycle in the following way.

The state of the working substance is first changed to an infinitesimally close neighbouring state 2 at a temperature T_2 by injecting a small amount of heat δQ_1 . We do this with a Carnot engine C_1 , which operates between two auxiliary reservoirs at T_1 and \tilde{T} . The auxiliary reservoir at T_1 supplies δQ_1 to the working substance and an equal quantity of heat is supplied by C_1 to that reservoir to leave it unchanged. C_1 in its turn takes heat $\{\tilde{T}/T_1\}\delta Q_1$ from the auxiliary reservoir at \tilde{T} and performs work, δW_1 , say. If the auxiliary reservoir at \tilde{T} is to remain unchanged, heat $\{\tilde{T}/T_1\}\delta Q_1$ enters it from the principal reservoir. In this way, we can effect a change from 1 to 2 with the only other changes being the performance of the external work δW_1 and the extraction of heat $\{\tilde{T}/T_1\}\delta Q_1$ from the principal reservoir.

The process is repeated taking the working substance from 2 to 3 with the help of the Carnot engine C_2 and a new pair of auxiliary reservoirs at T_2 and \tilde{T} , and so on round the cycle.

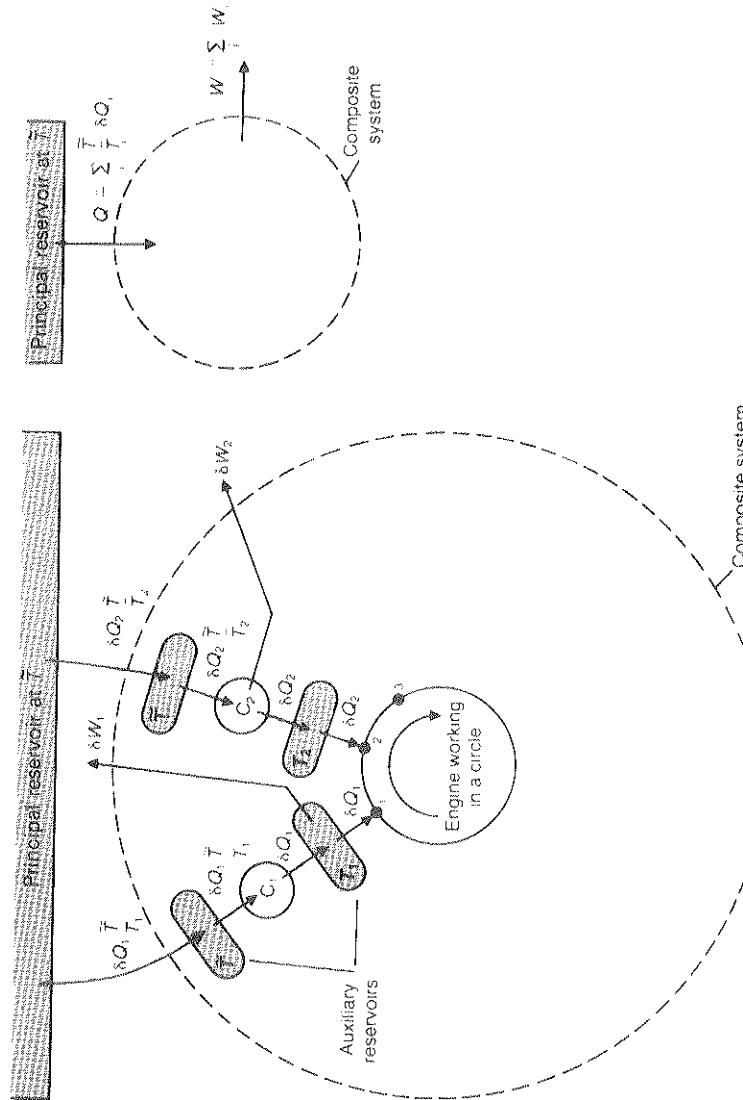


Figure 5.1 The cycle used to derive the Clausius inequality.

Consider now the composite system consisting of the working system, all the Carnot engines and all the auxiliary reservoirs. This composite system includes everything within the dashed line in Fig. 5.1(a). At the end of the cycle:

1. everything in the composite system is unchanged and so $\Delta U = 0$;
2. the heat supplied to it is

$$Q = \sum_i \delta Q_i \frac{\tilde{T}}{T_i}$$

where the summation is over the number of different Carnot engines used;

3. the external work performed is

$$\sum_i \delta W_i = W, \text{ say.}$$

Applying the first law to the composite system,

$$0 = Q - W \quad \text{or} \quad W = Q$$

This situation is represented in Fig. 5.1(b), where we can see that we have extracted heat from a *single* reservoir and have performed an equal amount of work. This is a violation of the Kelvin statement of the second law. The only way this process can occur is for both W and Q to be negative, that is, work is done *on* the system and an equal quantity of heat flows *out*. This is just the allowed situation of Fig. 4.5. Alternatively, both W and Q could be zero.

We conclude that

$$W = Q \leq 0$$

i.e.

$$\tilde{T} \sum_i \frac{\delta Q_i}{T_i} \leq 0 \quad \text{or} \quad \sum_i \frac{\delta Q_i}{T_i} \leq 0$$

In the limit,

$$\oint \frac{dQ}{T} \leq 0$$

where the circle on the integral sign indicates that the cycle is complete or closed. This is known as the *Clausius inequality* and is one of the key results in thermodynamics.

There are three important points that should be made.

1. The proof of the inequality emphasizes that the T appearing inside the integral is the temperature of the auxiliary reservoirs supplying

heat to the working substance. It is thus the *temperature of the external source of heat*. We shall always write the Clausius inequality as

$$\oint \frac{dQ}{T_0} \leq 0 \quad (\text{Clausius inequality}) \quad (5.1)$$

where we have written T_0 to remind us of this.

2. If the cycle is reversible, the cycle could be undertaken in the opposite direction and our proof would give

$$\oint \frac{dQ}{T_0} \geq 0$$

W would then be done *on* the composite system, with an equal amount of heat $\tilde{T} \sum_i \delta Q_i / T_i$ being rejected to the principal reservoir. This will not violate the Kelvin statement providing

$$W = Q = \tilde{T} \sum_i \delta Q_i / T_i \geq 0.$$

The only way for both inequalities to be satisfied is for

$$\oint_R \frac{dQ_R}{T} = 0 \quad (\text{reversible cycle only}) \quad (5.2)$$

We have added R to the bottom of the integral sign and as a subscript to dQ to remind us that this relation is valid only for a reversible process. However, we have dropped the 0 subscript on T as there is now no difference between the temperature of the external source supplying the heat and the temperature of the working substance.

3. One can never forget the sign of the inequality if one remembers that, in the proof, heat was always flowing into the engine so $T_0 > T$ and that the equality sign holds for the reversible case where $T_0 = T$. Replacing T by the large T_0 makes the inequality less than zero.

5.2 ENTROPY

This concept follows immediately from the previous section. Suppose we were to take a system along a reversible path R_1 from an initial state i to a final state f and then back again to the initial state along another reversible path R_2 , completing a reversible cycle. In Fig. 5.2 we have illustrated this for a gas system.

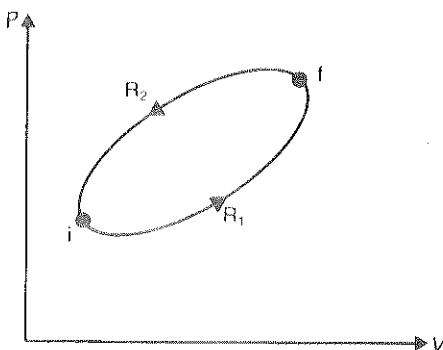


Figure 5.2 A reversible cycle. We show in the text that $\int dQ/T$ is the same for the reversible paths R_1 and R_2 connecting i and f .

As the cycle is reversible, the equality sign holds in the Clausius inequality. Remembering that the cycle is composed of the two reversible paths, R_1 and R_2 , we have

$$\oint_R \frac{dQ_R}{T} = \int_{R_1}^f \frac{dQ_R}{T} + \int_{R_2}^i \frac{dQ_R}{T} = 0$$

so

$$\int_{R_1}^f \frac{dQ_R}{T} = - \int_{R_2}^i \frac{dQ_R}{T}$$

But

$$\int_{R_2}^f \frac{dQ_R}{T} = - \int_{R_2}^i \frac{dQ_R}{T}$$

as R_2 is reversible. Thus,

$$\int_{R_1}^f \frac{dQ_R}{T} = \int_{R_2}^f \frac{dQ_R}{T}$$

which means that the integral $\int_R \frac{dQ}{T}$ is *path independent*. We conclude that there must be a state function S with

$$\Delta S = S_f - S_i = \int_{R_1}^f \frac{dQ_R}{T} \quad (5.3)$$

We call this state function the *entropy*. Notice that only entropy differences have been defined. Also, it cannot be stressed too strongly that *the defining integral for entropy differences has to be taken over a reversible path*.

For an infinitesimal reversible process,

$$dQ_R = T dS \quad (\text{reversible only}) \quad (5.4)$$

The name entropy comes from the Greek *en* meaning 'in' and *trope* meaning 'turning'. Clausius intended the word to convey the idea of heat being converted in an engine into work.

5.3 AN EXAMPLE OF A CALCULATION OF AN ENTROPY CHANGE

So that we may see how entropy changes are calculated, let us determine the entropy change of a beaker of water when it is heated at atmospheric pressure between room temperature, at 20°C , and 100°C by placing it on a reservoir at 100°C . When the water reaches 100°C , the beaker is removed from the reservoir and placed in an insulating jacket. This process is shown in Fig. 5.3. Heat passes from the reservoir into the water and it might seem that a simple application of equation (5.3) would suffice. However this equation applies to a *reversible* process, while the actual process here is *irreversible* because of the inherent finite temperature differences.

We resort again to the argument encountered in section 2.4. As the water is initially and finally in equilibrium states, with well-defined entropies, the entropy change for this process is also well defined. We can then *imagine any convenient reversible process* that takes the system between the same two end points and calculate, using equation (5.3), the entropy change for this imaginary process. *This entropy change is then the same as that occurring in the actual irreversible process.*

One simple reversible heating process between the end points could be affected by bringing up a whole series of reservoirs between 20°C and 100°C , keeping the pressure constant, so that the water

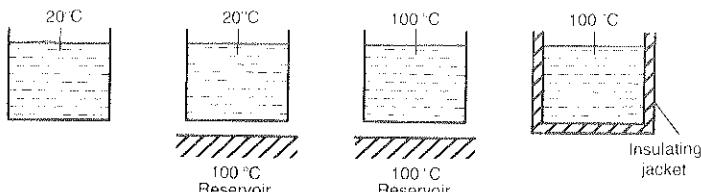


Figure 5.3 A beaker of water is heated irreversibly and isobarically between 20°C and 100°C in this process.

5.8 THE CENTRAL EQUATION OF THERMODYNAMICS

By combining the first and second laws of thermodynamics, we can obtain the most important equation in thermodynamics.

The differential form of the first law is

$$dU = dQ + dW$$

which is true for both reversible and irreversible processes. For an infinitesimal reversible process, we have

$$dW = -PdV \quad \text{and} \quad dQ_R = TdS$$

Thus

$$dU = TdS - PdV$$

or

$$TdS = dU + PdV$$

We now argue that this equation is true for all processes, whether reversible or not, and not just for reversible processes, as our argument seems to suggest. For, as all quantities in the equation are state functions whose values are fixed by the end points (P, T) and $(P + dP, T + dT)$ of the infinitesimal process, the increments dU , dS and dV are fixed and do not depend on the path joining the end points. Thus any relation between them is independent of whether or not the process is reversible.

This is a significant advance because we now have a general relation between P , V , T and S which holds for all paths between a pair of infinitesimally close equilibrium states, whether or not they are reversible. We call the relation

$$TdS = dU + PdV \quad (5.10)$$

the *central equation of thermodynamics* or, in view of what we have just said about its generality, the *thermodynamic identity*. The whole of the science of thermodynamics is consequent on this equation, just as the whole of mechanics is consequent on Newton's laws. Because it is an identity, and we do not have to enquire whether the process we are considering is reversible or irreversible, then it follows that the equations derived from it are generally true.

Two remarks should be made at this point, both of which lead to modification of equation (5.10). The first is that we have considered only PdV or volume work; if for example there were also magnetic work, this equation would have to be modified to

$$TdS = dU + PdV - B_0 dM$$

The second remark is that here we are considering only closed systems where the mass of the system is constant. If this restriction is removed, then additional terms involving the so-called *chemical potential* have to be introduced. Open systems are considered in Chapter 10.

5.9 THE ENTROPY OF AN IDEAL GAS

Although the demonstration of the power of equation (5.10) has to wait until the next chapter, we can give an example here of its use to determine an expression for the entropy of an ideal gas in terms of the volume and temperature.

For an ideal gas, where $U = U(T)$,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{dU}{dT}$$

and so equation (5.10) becomes

$$TdS = C_V dT + PdV$$

Let us consider one mole and use lower-case letters to refer to molar quantities. Using $Pv = RT$, this last equation becomes

$$Tds = c_v dT + \frac{RT}{v} dv$$

or

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}$$

Integrating, we have for the entropy per mole

$$s = c_v \ln T + R \ln v + s_0 \quad (5.11)$$

where s_0 is the integration constant which disappears when entropy differences are taken.

5.10 ENTROPY, PROBABILITY AND DISORDER

In our discussion so far, entropy has appeared as a rather mysterious quantity related to the heat flow in reversible processes. Although we have learnt how to use it, we have not really given entropy a physical interpretation. To do this, we have to resort to the microscopic picture, just as we did in Chapter 3 when we interpreted internal

energy as the random kinetic and potential energies of the constituent molecules.

How can we describe a system microscopically? We could do so exactly by specifying the position coordinates x , y and z and the momentum components p_x , p_y and p_z for each of the N constituent particles in the system. A given set of these quantities for a particle is represented as a point in the six-dimensional space spanned by x , y , z , p_x , p_y and p_z ; this space is called *phase space*. However, we cannot measure x with absolute accuracy but only to within a range Δx ; similarly we can measure p_x only to within a range Δp . So we have to be satisfied with less than an exact description by dividing the phase space up into cells of volume $(\Delta x)^3(\Delta p)^3$ and knowing how many particles are in each cell. We have assumed here that the uncertainty in y and z is also of the order of Δx and that the uncertainty in each of the momentum components is Δp . One such arrangement could be as in Fig. 5.12, where each dot represents a particle having momentum and position within the ranges appropriate to the cell. As it is impossible to draw a six dimensional phase space, we have split this up into the separate pictures: real space is shown on the left consisting of *space cells* and momentum space, consisting of *momentum cells*, is shown on the right. For simplicity, the third coordinates z and p_z have been omitted. Now, although each different arrangement of the particles amongst the cells gives rise to a definite

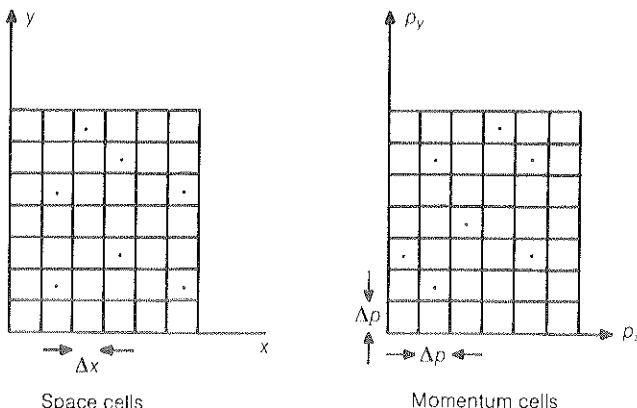


Figure 5.12 A schematic representation of phase space. A distribution of all the particles over the cells gives rise to a definite bulk state. The space cells are of volume Δx^3 and the momentum cells of volume Δp^3 .

bulk state, in general there will be many different arrangements that give rise to the same bulk state. We call the number of arrangements that give rise to a state the *thermodynamic probability*, Ω , of that state. The states with the largest Ω s will be the ones most likely to occur.

This is analogous to the game of craps where two dice are thrown. The most likely score of 7 can be realized in six ways while the least likely scores of 2 or 12 can be realized in only one way (you should work this out).

For our microscopic system, where the number of particles is huge, being of the order of 10^{23} , the thermodynamic probability becomes overwhelmingly large for a particular state, and this will be the observed equilibrium state. An isolated system will move from a state of low thermodynamic probability to the final equilibrium state of maximum thermodynamic probability, consistent with the internal energy U remaining constant. We conclude that

$$\Omega \rightarrow \text{a maximum}$$

This is our clue as to the meaning of entropy. We remember that, for an isolated system,

$$S \rightarrow \text{a maximum}$$

while U remains constant. Additionally S is an extensive quantity, so that the entropy of two separate systems is $S_1 + S_2$. If the number of ways of realizing the first system is Ω_1 and this is Ω_2 for the second, then the number of ways of realizing both systems together is

$$\Omega = \Omega_1 \Omega_2$$

We see that

$$S = k_B \ln \Omega \quad (5.12)$$

satisfies these properties. This famous equation is known as the Boltzmann relation and is carved on Boltzmann's tombstone in Vienna. k_B is the so-called Boltzmann constant.

The microscopic viewpoint thus interprets the increase of entropy for an isolated systems as a consequence of the natural tendency of the system to move from a less probable to a more probable state.

It is usual to identify Ω as a measure of 'disorder' in the system. This implies that we expect the disorder of an isolated system to increase.

To see what this means, let us consider all the particles being in one cell in phase space. This is a highly ordered arrangement in phase space which can be achieved in only one way with $\Omega = 1$ and $S = 0$. It is a highly ordered arrangement in real space, too, with all the particles being in the same place and moving with identical velocities. The particles will spread out from this highly ordered state, occupying more cells in phase space and lessening the order or increasing the disorder in that space. The thermodynamic probability will increase from 1 to a large value, with the entropy increasing accordingly. It is in this sense that Ω is a measure of disorder.

Let us now be a little more definite and see how there is complete agreement between the macroscopic and microscopic viewpoints in two specific examples.

5.10.1 The entropy change in a free expansion—microscopic approach

We know that there is no temperature change in a free expansion of an ideal gas and so the mean kinetic energy and root mean square momentum \tilde{p} of the molecules remains unchanged. Let us consider such an expansion in which the volume is doubled.

Now the momentum space is a box of volume $\sim \tilde{p}^3$ and so the number of momentum cells that can be occupied is $\sim \tilde{p}^3/\Delta p$ and this number does not change upon expansion as \tilde{p} is unchanged. However, the number of space cells doubles from $V/\Delta x^3$ to $2V/\Delta x^3$. This means that, if the number of possible arrangements for fitting the molecules in the cells before the expansion is Ω , after expansion it is now $2^N\Omega$ because each of the N molecules now has a choice of twice as many cells in phase space. Thus

$$\Delta S = k_B \ln (2^N\Omega) - k_B \ln \Omega = k_B \ln 2^N$$

or

$$\Delta S = Nk_B \ln 2 = nR \ln 2$$

for n moles as $N = nN_A$ and $N_A k_B = R$ where N_A is the Avogadro number.

This is exactly the result we obtained earlier as equation (5.6).

5.10.2 The entropy of an ideal gas—microscopic approach

We have previously derived an expression (equation (5.11)) for the entropy of an ideal gas using the central equation of thermodynamics.

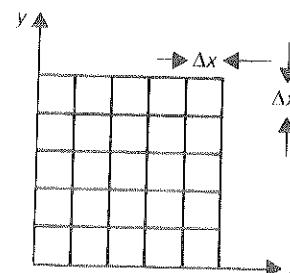


Figure 5.13 Space cells of volume Δx^3 .

Let us see if we can derive the same result from microscopic considerations using a simplified argument. We shall consider a monatomic gas where the atoms have translational degrees of freedom only.

The atoms of the gas have to be fitted into the cells of phase space subject to the following two restrictions.

1. All the atoms have to be contained in a box of volume V .
2. The total energy of the atoms of mass m is fixed at U and is all kinetic, with

$$U = \sum_i \frac{p_i^2}{2m}$$

where the summation is over the N atoms.

The total number of ways Ω of filling up the cells in phase space is the product of the number of ways Ω_{space} the space cells* of volume Δx^3 can be filled times the number of ways Ω_{momentum} the different momenta cells of volume Δp^3 can be filled. Thus

$$\Omega = \Omega_{\text{space}} \Omega_{\text{momentum}}$$

Let us calculate Ω_{space} .

In Fig. 5.13 we have drawn the box showing just two dimensions and the space cells. Each atom has $V/\Delta x^3$ distinct locations in the box. Thus

$$\Omega_{\text{space}} = \left[\frac{V}{\Delta x^3} \right]^N$$

*Strictly the use of the word cell in statistical mechanics should be confined to an elementary volume $\Delta x^3 \Delta p^3$ of phase space.

Let us now calculate Ω_{momentum} . Although each atom is not confined to a finite 'momentum box', they have a root mean square momentum \tilde{p} , given by

$$\frac{\tilde{p}^2}{2m} = \frac{U}{N}$$

and, for the purpose of this calculation, we may take them as being confined within a momentum box of side \tilde{p} as shown in Fig. 5.14. The number of cells in the momentum box is $(\tilde{p}/\Delta p)^3$ for each atom. Thus

$$\Omega_{\text{momentum}} \approx \left(\frac{\tilde{p}}{\Delta p} \right)^{3N}$$

Multiplying these two results,

$$\Omega = \Omega_{\text{space}} \cdot \Omega_{\text{momentum}} \approx \left[\frac{\tilde{p}^3 V}{\Delta x^3 \Delta p^3} \right]^N$$

However, we have over-counted our ways of filling up the cells because we have assumed that the atoms are *distinguishable*, just as if they are labelled with a number. The two situations depicted in Fig. 5.14 are clearly physically the same.

There are $N!$ ways of arranging the N identical atoms in a given set of boxes. Thus

$$\Omega_{\text{indistinguishable}} \approx \frac{1}{N!} \left[\frac{\tilde{p}^3 V}{\Delta x^3 \Delta p^3} \right]^N$$

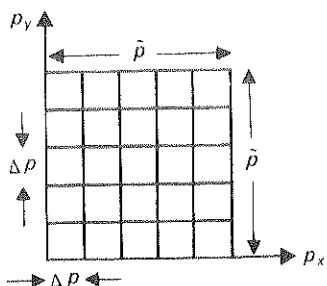


Figure 5.14 Momentum cells of volume Δp^3 .

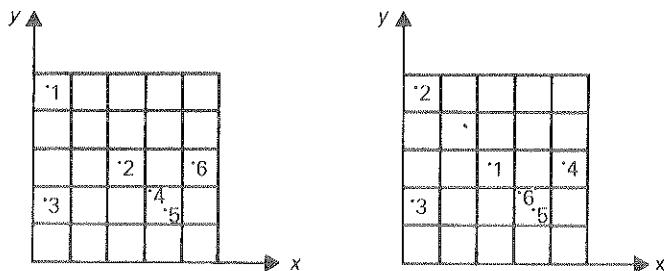


Figure 5.15 An illustration of two equivalent arrangements in phase space

If N is large, we may use Stirling's approximation for factorials:

$$N! \approx \left(\frac{N}{e} \right)^N$$

So

$$\begin{aligned} \Omega_{\text{indistinguishable}} &\approx \left[\frac{eV\tilde{p}^3}{N(\Delta x \Delta p)^3} \right]^N \\ &\approx \left[\frac{eV(2mU)^{3/2}}{N^{5/2}(\Delta x \Delta p)^3} \right]^N \quad \text{using } \tilde{p} = \left(\frac{2mU}{N} \right)^{1/2} \end{aligned}$$

If we replace the product $\Delta x \Delta p$ with \hbar , this becomes

$$\begin{aligned} \Omega_{\text{indistinguishable}} &\approx \left[\frac{eV(2mU)^{3/2}}{N^{5/2} \hbar^3} \right]^N \\ &\approx \left[\frac{eV(2mU)^{3/2}}{(nN_A)^{5/2} \hbar^3} \right]^{nN_A} \end{aligned}$$

if we have n moles with $N = nN_A$.

This result is very close to the famous result derived by Sackur and Tetrode using somewhat more rigorous and complicated arguments than the simple ones that we have employed, namely

$$\Omega_{\text{indistinguishable}} = \left[\frac{e^{5/2} V (3\pi m U)^{3/2}}{N^{5/2} \hbar^3} \right]^N$$

It is now a simple matter to obtain the entropy:

$$S = k_B \ln \Omega$$

$$= nk_B N_A \left[\ln \frac{V}{n} + \frac{3}{2} \ln \frac{U}{n} + \text{other constant terms} \right]$$

So for one mole,

$$s = R \left(\ln v + \frac{3}{2} \ln u + \text{constant terms} \right)$$

But we know from kinetic theory that

$$u = \frac{3}{2} N_A k_B T$$

for a monatomic gas, so

$$s = R \ln v + \frac{3}{2} R \ln T + s_0$$

where s_0 is a constant. As $c_v = 3/2 R$ for a monatomic gas, this is the identical result to equation (5.11) which was obtained using macroscopic ideas.

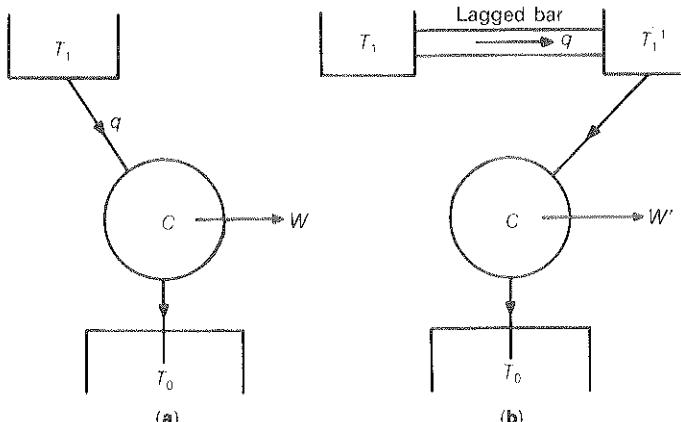
These two results are a confirmation that entropy is indeed given by

$$S = k_B \ln \Omega \quad (5.12)$$

5.11 THE DEGRADATION OF ENERGY AND THE HEAT DEATH

We conclude this important chapter on entropy by discussing the simple connection between the increase in entropy of the universe associated with an irreversible process and the decrease in the energy that is available for performing work. This can best be seen by considering an example.

In Fig. 5.16(a), a Carnot engine operates between two reservoirs



at T_1 and T_0 where the temperature T_0 of the second reservoir is the lowest temperature available. The efficiency of this engine is $\eta = 1 - (T_0/T_1)$ and so, if heat q is extracted from the hotter reservoir at T_1 , the work delivered is $w = q(1 - T_0/T_1)$. As we are considering a Carnot engine, the process is reversible and $\Delta S^{\text{universe}} = 0$. Now let us put in the *same* amount of heat q into the engine from a second reservoir at a temperature $T'_1 < T_1$. We do this, as shown in Fig. 5.16(b), by allowing the heat q first to be conducted along a lagged metal bar from the reservoir at T_1 to the reservoir at T'_1 and then being delivered to the engine. The work given out by this combined device is now $w' = q(1 - T_0/T'_1)$; this is *less* than w by an amount

$$\Delta w = w - w' = q T_0 \left\{ \frac{1}{T'_1} - \frac{1}{T_1} \right\} \quad (5.13)$$

Now this second process is irreversible because the conduction of heat along the bar is irreversible. The entropy change of the universe is

$$\Delta S^{\text{universe}} = q \left\{ \frac{1}{T'_1} - \frac{1}{T_1} \right\} \quad (5.14)$$

because of the entropy changes $-q/T_1$ and $+q/T'_1$ at the two reservoirs. We see immediately from equation 5.13 and 5.14 that the amount of work we have lost from q by using our second irreversible device is simply

$$\Delta w = T_0 \Delta S^{\text{universe}} \quad (5.15)$$

Although we have chosen to illustrate this point using this simple example, it can be shown that it is *generally* true that, in any irreversible process, the energy that becomes unavailable for work is always $T_0 \Delta S^{\text{universe}}$. This result is called the *degradation of energy*. It means simply that the quality, or potential for work, of the energy in the universe decreases by $T_0 \Delta S^{\text{universe}}$ in every irreversible process.

It is often said that the world is suffering from an *energy crisis*. We know from the first law that energy is always conserved—we can never destroy energy. What we are really suffering from is an *entropy crisis*. Every irreversible process increases the entropy of the universe and this means, as we have just discovered, a loss of capacity of energy for work. The universe is gradually running out of low entropy or order. When all the order has been destroyed, the universe will suffer a *heat death*!

Figure 5.16 An example illustrating the degradation of energy.