2 THE SIGNPOST OF CHANGE

This is where we begin to define and refine corruption. So far we have seen that the immediate successors of Carnot were able to disentangle a rule about the quantity of energy from a rule about the direction of its conversion. Energy displaced heat as the eternally conserved; heat and work, hitherto regarded as equivalent, were shown to be dissymmetric. But these are bald, imprecise, and incomplete remarks: we must now sharpen them and put ourselves in a position to explore their ramifications. This we shall do in two stages. First, briefly, we shall refine the notions of heat and work, which so far we have regarded as "obvious" quantities. Then, with the precision such refinement will bring to the discussion, we shall start our main business, the refinement of the statement of the Second Law. With that refinement will come power and, as often happens, corruption too. We shall see that the domain of the Second Law is corruption and decay, and we shall see what extraordinarily wonderful things take place when quality gives way to chaos.

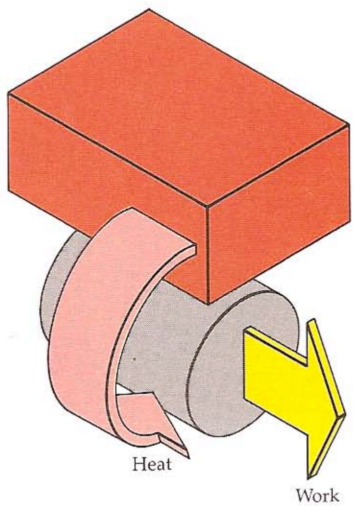
The Nature of Heat and Work

Central to our discussion so far, and for the next couple of chapters, are the concepts of *heat* and *work*. Perhaps the most important contribution of nineteenth-century thermodynamics to our comprehension of their nature has been the discovery that they are names of *methods*, not names of *things*. The early nineteenth-century view was that heat was a thing, the imponderable fluid "caloric"; but now we know that there is no such "thing" as heat. You cannot isolate heat in a bottle or pour it from one block of metal to another. The same is true of work: that too is not a thing; it can be neither stored nor poured.

Both heat and work are terms relating to the transfer of energy. *To heat* an object means to transfer energy to it in a special way (making use of a temperature difference between the hot and the heated). *To cool* an object is the negative of heating it: energy is transferred out of the object under the influence of a difference in temperature between the cold and the cooled. It is most important to realize, and to remember throughout the following pages (and maybe beyond), that *heat is not a form of energy: it is the name of a method for transferring energy.*

The same is true of work. Work is what you do when you need to change the energy of an object by a means that does not involve a temperature difference. Thus, lifting a weight from the floor and moving a truck to the top of a hill involve work. Like heat, *work is not a form of energy: it is the name of a method for transferring energy.*

All that having been established, we are going to return to informality again. In chapter 1 we said things like "heat was converted into work." If we were to speak precisely, we would have to say "energy was transferred from a source by heating and then transferred by doing work." But such precision would sink this account under a mass of verbiage; so we shall use the natural English way of talking about heat and work, and use expressions such as "heat flows into the system." But whenever we do, we shall always add in a whisper, "but we know what we really mean."



The Kelvin statement of the Second Law denies the possibility of converting a given quantity of heat completely into work without other changes occurring elsewhere.

The Seeds of Change

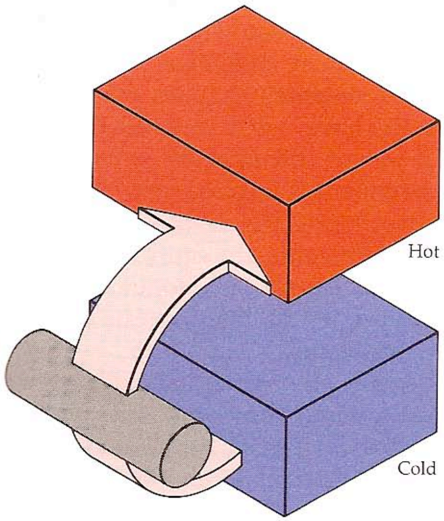
Now we refine the Second Law into a constructive tool. So far it has crept mouselike into the discussion as a not particularly impressive commentary on some not particularly interesting experience with engines. Cold sinks, we have seen, are necessary when we seek to convert heat into work. The formal restatement of this item of experience is known as the *Kelvin statement* of the Second Law:

> **Second Law:** No process is possible in which the *sole result* is the absorption of heat from a reservoir and its *complete conversion* into work.

The most important point to pick out of this statement of the Second Law is the dissymmetry of Nature that we have already mentioned. It states that *it is impossible to convert heat completely into work* (see figure on left); it says nothing about the complete conversion of work into heat. Indeed, as far as we know, there is no constraint on the latter process: work may be completely converted into heat without there being any other discernable change. For example, frictional effects may dissipate the work being done by an engine, as when a brake is applied to a wheel. *All* the energy being transferred into the outside world by the engine may be dissipated in this way. Here, then, is Nature's fundamental dissymmetry; for although work and heat are equivalent in the sense that each is a manner of transferring energy, they are *not* equivalent in the manner in which they may interchange. We shall see that the world of events is the manifestation of the dissymmetry expressed by the Second Law.

The Kelvin statement should not be construed too broadly. It denies the existence of processes in which heat is extracted from a source and converted completely into work, there being no other change in the Universe. It does not deny that heat can be completely converted into work when other changes are allowed to take place too. Thus cannons can fire cannonballs: the heat generated by the combustion of the charge is turned completely into the work of lifting the ball; however, cannons are literally one-shot processes, and the state of the system is quite different after the conversion (for instance, the volume of the gas that propelled the ball from the cannon remains large, and is not recompressed; cannons are not cycles).

One delight of thermodynamics is the way in which quite unrelated remarks turn out to be equivalent. This is the way the subject creeps over the landscape of events and digests them. Now the mouse can begin to grow and claim its own.



The Clausius statement of the Second Law denies the possibility of heat flowing spontaneously from a cold body to one that is hotter.

As an example of this process of incorporation, which allows the Second Law to spread away from the steam engine, we shall set in apparent opposition to the Kelvin statement of the Second Law the rival formulation devised by Clausius:

> **Second Law:** No process is possible in which the *sole result* is the transfer of energy from a cooler to a hotter body.

First, note that the Clausius statement can stand on its own as a summary of experience: so far as we know, no one has ever observed energy to transfer spontaneously (that is, without external intervention) from a cool body to a hot body (see figure on left). The laws of thermodynamics ignore, of course, the sporadic reports of purported miracles, and its proven predictive power is a retrospective argument against their occurrence. The fact that we need to construct elaborate devices to bring about refrigeration and air conditioning, and must run them by using electric power, is a practical manifestation of the validity of the Clausius statement of the Second Law: for although heat will not spontaneously flow to a hotter body, we can *cause* it flow in an unnatural direction if we allow changes to take place elsewhere in the Universe. In particular, a refrigerator operates at the expense of a burning lump of coal, a stream of falling water, or an exploding nucleus elsewhere. The Second Law specifies the *unnatural*, but does not forbid us to bring about the unnatural by means of a *natural* change elsewhere.

Second, the Clausius statement, like the Kelvin statement, identifies a fundamental dissymmetry of Nature, but ostensibly a different dissymmetry. In the Kelvin statement the dissymmetry is that between work and heat; in the Clausius statement there is no overt mention of work. The Clausius statement implies a dissymmetry in the direction of natural change: energy may flow spontaneously down the slope of temperature, not up. The twin dissymmetries are the anvils on which we shall forge the description of all natural change.

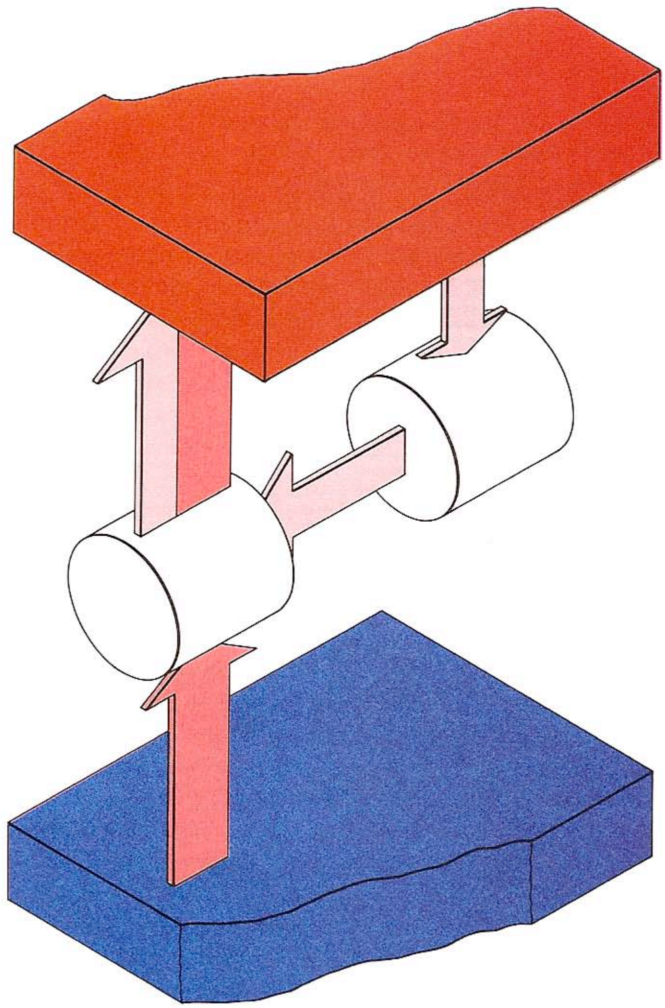
But there cannot be *two* Second Laws of thermodynamics: if the twin dissymmetries of Nature are both to survive, they must be the outcome of a *single* Second Law or at least one that should be expressed more richly than either the Kelvin or the Clausius statement alone. In fact, the two statements, although apparently different, are logically equivalent: there is indeed only one Second Law, and it may be expressed as either statement alone. The twin dissymmetries, and the anvils, are really one.

In order to show that the two statements are equivalent, we use the logical device of demonstrating that the Kelvin statement implies the Clausius statement, and that the Clausius statement implies the Kelvin. Actually, in the slippery way that logicians have, what we shall do is exactly the opposite: we shall show that if we can disprove the Kelvin statement, then the falsity of the Clausius statement is implied, and if we can disprove the Clausius, then farewell Kelvin too. If the death of either one implies the death of the other, then the statements are equivalent.

For our purposes, we bring on the family Rogue: Jack Rogue, the purveyor of anti-Kelvin devices, and Jill Rogue, whose line consists of anti-Clausius devices. First Jack will present his wares.

We take Jack's device, which he claims is an engine that contravenes Kelvin's experience, and can convert heat entirely into work and produce no change elsewhere, and we connect it between a hot source and a cold sink (see figure on facing page). We also connect it to another (conventional) engine, which will be run as a refrigerator and used to pump energy from the same cold sink to the same hot source. According to Jack, all the heat drawn from the hot source is converted into work. Suppose, then, that we run the engine long enough to remove 100 joules of energy* as heat, in which case, according to Jack, 100 joules of work are produced by his excellent machine. If that is so, then our other engine uses that 100 joules, and with it can transfer some energy from the cold sink to the hot source; the total energy it dumps as heat into that source is the sum of whatever it draws from the cold sink plus the 100 joules of energy that Jack's engine supplies. This must be so in order to accord with the First Law (which both Jack and Jill accept). These flows of energy are illustrated in the figure on the facing page. The overall effect, therefore, is to transfer

* The units for expressing quantities of energy, whether they are simply stored or are being shipped as heat or as work, are explained in Appendix 1. We shall use *joules*.

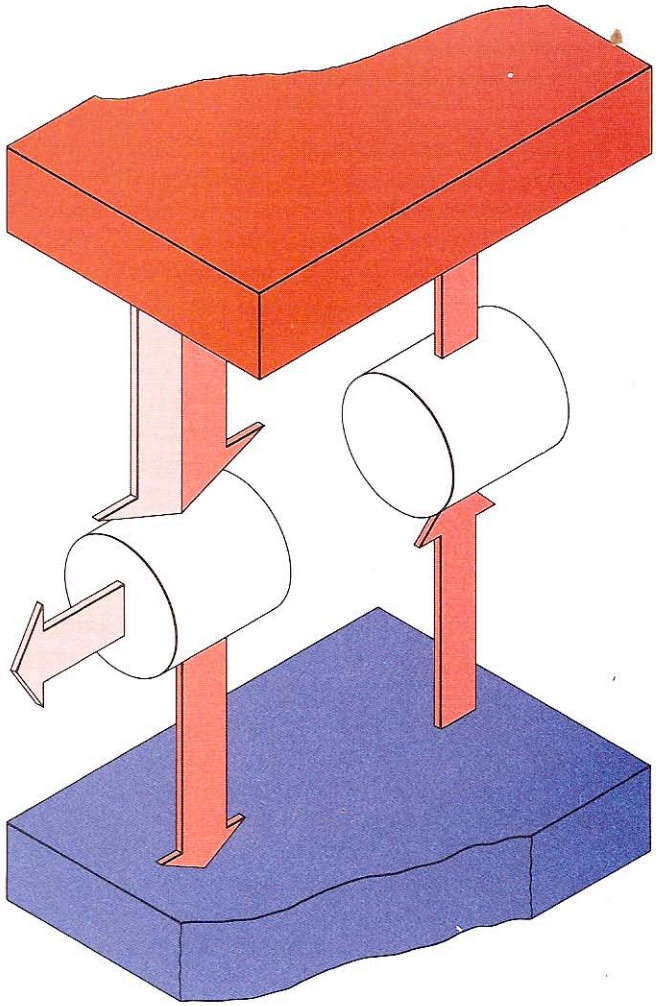


The argument to show that a failure of the Kelvin statement implies a failure of the Clausius statement involves connecting an ordinary engine between two reservoirs and driving it with an anti-Kelvin device. The net effect of the flows of energy shown here is to transport heat spontaneously from the cold to the hot reservoir, contradicting Clausius.

heat from cold to hot, there being no other change. Thus Jack's device pleases Jill.

Happy Jill now shows her device, which, she claims, spontaneously pumps heat from a cold sink to a hot source and leaves no change elsewhere. As was done with Jack's, Jill's device is connected between a hot source and a cold sink, and another engine is also connected between the two (see figure on next page). Jill runs her device, which pumps 100 joules of energy from cold to hot, and does so without any interference from outside, thus denying Clausius's experience of life. The other engine is arranged to run, and to dump 100 joules of energy into the cold sink, providing the balance of whatever it draws from the hot source as work.

In order to show that the failure of the Clausius statement implies a failure of the Kelvin statement, an ordinary engine is connected between hot and cold reservoirs which are also joined by an anti-Clausius device. The flows of energy are shown in the illustration, and the net effect is for a quantity of heat to be converted fully into work with no other change, contradicting Kelvin.



The flow of energy is shown above. Clearly, there has been no net change in the energy of the cold sink, and the overall outcome is for heat from the hot source to have been converted fully into work, with no change elsewhere, which pleases Jack.

Thus Jack and Jill are excellently matched: successful Jack, then successful Jill; successful Jill, then successful Jack. In other words, if Kelvin is false, then so is Clausius; and if Clausius is false, then so is Kelvin. Hence the Kelvin and Clausius statements are equivalent statements of experience: they are two faces of a single Second Law.

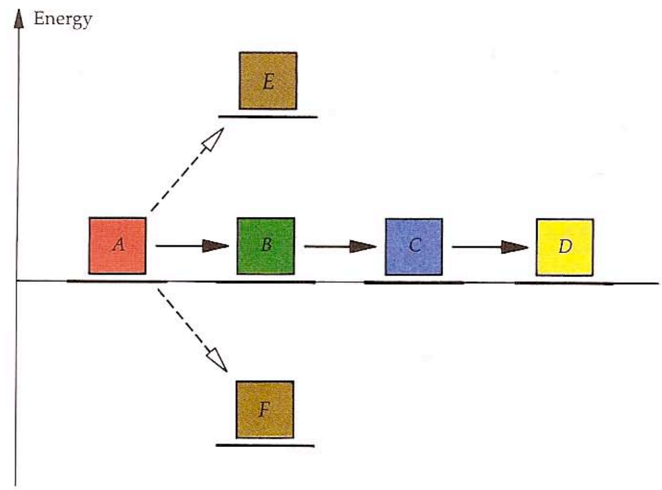
Toward Corruption

The progress of science is marked by the transformation of the qualitative into the quantitative. In this way not only do notions become turned into theories and lay themselves open to precise investigation, but the logical development of the notion becomes, in a sense, automated. Once a notion has been assembled mathematically, then its implications can be teased out in a rational, systematic way. Now, we have promised that this account of the Second Law will be nonmathematical, but that does not mean we cannot introduce a quantitative concept. Indeed, we have already met several, temperature and energy among them. Now is the time to do the same thing for spontaneity.

The idea behind the next move can be described as follows. The Zeroth Law of thermodynamics refers to the *thermal equilibrium* between objects ("objects," the things at the center of our attention, are normally referred to as *systems* in thermodynamics, and we shall use that term from now on). Thermal equilibrium exists when system *A* is put in thermal contact with system *B*, but no net flow of energy occurs. In order to express this condition, we need to introduce the idea of the *temperature* of a system, which we define as meaning that if *A* and *B* happen to have the same temperature, then we know without further ado that they are in thermal equilibrium with each other. That is, the Zeroth Law gives us a reason to introduce a "new" property of a system, so that we can easily decide whether or not that system would be in thermal equilibrium with any other system if they were in contact.

The First Law gives us a reason to carry out a similar procedure, but now one that leads to the idea of "energy." We may be interested in what states a system can reach if we heat it or do work on it. We can assess whether a particular state is accessible from the starting condition by introducing the concept of *energy*. If the new state differs in energy from the initial state by an amount that is different from the quantity of work or heating that we are doing, then we know at once, from the First Law, that that state cannot be reached: we have to do more or less work, or more or less heating, in order to bring the energy up to the appropriate value. The energy of a system is therefore a property we can use for deciding whether a particular state is accessible (see figure on next page).

This suggests that there may be a property of systems that could be introduced to accommodate what the Second Law is telling us. Such a property would tell us, essentially at a glance, not whether one state of the system is accessible from the other (that is the job of the energy acting through the First Law), but whether it is *spontaneously* accessible. That is, there ought to be a property that can act as the signpost of natural, sponta-



An isolated system may in principle change its state to any other of the same energy (the four colored boxes in the horizontal row), but the First Law forbids it to change to states of different energy (the brown-tinted boxes).

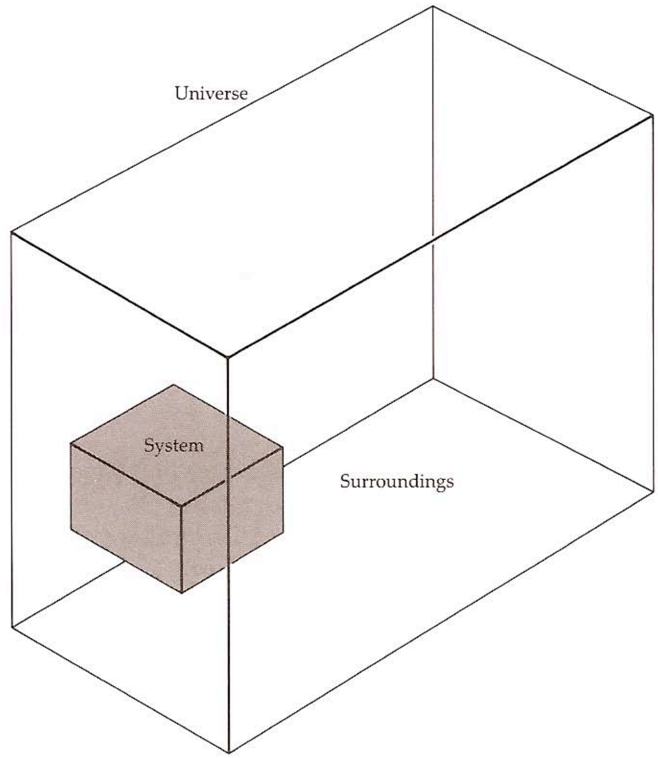
neous change, change that may occur without the need for our technology to intrude into the system in order to drive it.

There is such a property. It is the *entropy* of the system, perhaps the most famous and awe-inspiring thermodynamic property of all. Awe-inspiring it may be: but the awe should not be misplaced. The awe for entropy should be reserved for its power, not for its difficulty. The fact that in everyday discourse "entropy" is a word far less common than "energy" admittedly makes it less familiar, but that does not mean that it stands for a more difficult concept. In fact, I shall argue (and in the next chapter hope to demonstrate) that the entropy of a system is a simpler property to grasp than its energy! The exposure of the simplicity of entropy, however, has to await our encounter with atoms. Entropy is difficult only when we remain on the surface of appearances, as we do now.

Entropy

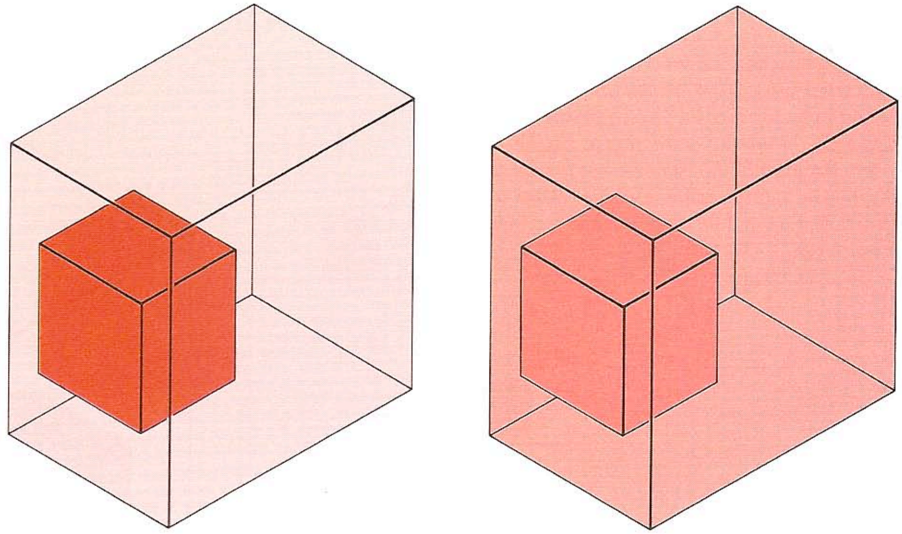
We are now going to build a working definition of entropy, using the information we already have at our disposal. The First Law instructs us to think about the energy of a system that is free from all external influences; that is, the constancy of energy refers to the energy of an *isolated system,* a system into which we cannot penetrate with heat or with work, and which for brevity we shall refer to as the *universe* (see figure on facing page). Similarly, the entropy we define will also refer to an isolated system, which we shall call the universe. Such names reflect the hubris of thermodynamics: later we shall see to what extent the "universe" is truly the Universe.

In thermodynamics we focus attention on a region called the system. *Around it are the* surroundings. *Together the two constitute the* universe. *In practice, the universe may be only a tiny fragment of the Universe itself, such as the interior of a thermally insulated, closed container, or a water bath maintained at constant temperature.*

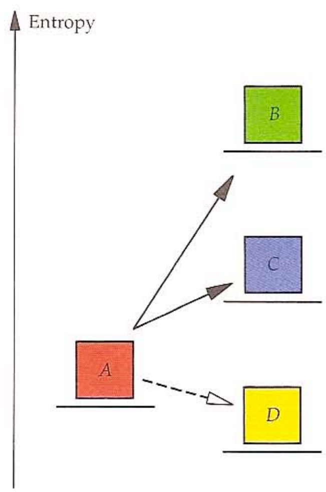


Suppose there are two states of the universe; for instance, in one a block of metal is hot, and in the other it is cold (see top figure on next page). Then the First Law tells us that the second state can be reached from the first only if the total energy of the universe is the same for each. The Second Law examines not the label specifying the energy of the universe, but another label that specifies the entropy. We shall define the entropy so that if it is *greater* in state B than in state A, then state B *may* be reached *spontaneously* from state A (see lower figure on next page). On the other hand, even though the energy of states A and B may be the same, if the entropy of state B is less than the entropy of state A, then state B cannot be reached spontaneously: in order to attain it, we would have to unzip the insulation of the universe, reach in with some technology (such as a refrigerator), and *drive* the universe from state A to state B (at the expense of a change in our larger Universe).

We have to construct a definition of entropy in such a way that in any universe entropy increases for natural changes, and decreases for changes that are unnatural and have to be contrived. Furthermore, we want to



An isolated system (a universe) containing a hot block of metal is in a different state from one containing a similar but cold block, even if the total energy is the same in each. There must be a property other than total energy that determines the direction of spontaneous change will be hot ⟶ cold *rather than the reverse.*



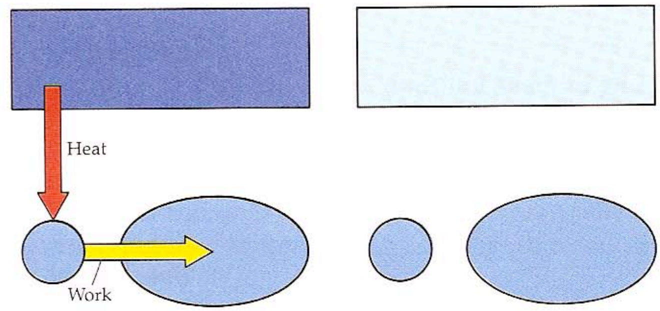
The states A, B, C, *and* D *in the illustration on page 30 have the same energy, but different* entropies. *The changes* A *to* B *and* A *to* C *may occur spontaneously, because each involves an increase of entropy; the change from* A *to* D *does not occur spontaneously, because it would require the entropy of the universe to drop. The universe always falls* upward *in entropy.*

define it so that we capture the Clausius and Kelvin statements of the Second Law, and arrive at a way of expressing them both simultaneously in the following single statement:

> **Second Law:** Natural processes are accompanied by an increase in the entropy of the universe.

This is sometimes referred to not as the Second Law (which is properly a report on direct experience), but as the *entropy principle,* for it depends on a specification of the property "entropy," which is not a part of direct experience. (Similarly, the statement "energy is conserved" is also more correctly referred to as the *energy principle,* for the First Law itself is also a commentary on direct experience of the changes that work can bring about, whereas the more succinct statement depends on a specification of what is meant by "energy.")

The Kelvin statement is reproduced by the entropy principle if we define the entropy of a system in such a way that entropy increases when the system is heated, but remains the same when work is done. By implication, when a system is cooled its entropy decreases. Then Jack's engine is discounted by the Second Law, because heat is taken from a hot source (so that its entropy declines), and work is done on the surroundings (with the result that the entropy of the surroundings remains the same), as shown in the top figure on the facing page, and so overall the entropy of the little universe that contains his engine and its surroundings *decreases;* hence his engine is unnatural.

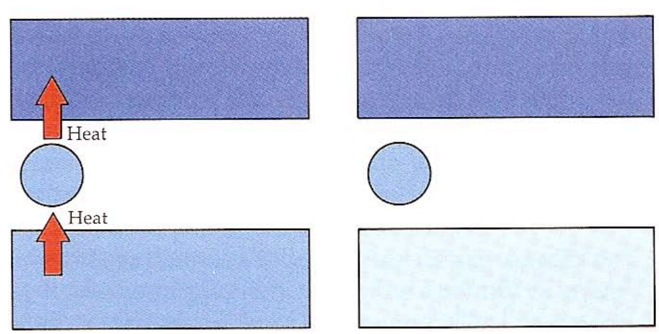


The shades of blue denote the entropies of the stored energy. When heat is withdrawn by the anti-Kelvin device, the entropy of the hot reservoir falls, but the quasistatic work does not produce entropy elsewhere. Overall, therefore, the entropy of the universe declines, which is against experience.

In order for us to discount Jill's device, the definition of entropy must depend on the temperature. We can capture her (and Clausius) if we suppose that the higher the temperature at which heat enters a system, the *smaller* the resulting change of entropy. In her anti-Clausius device, heat leaves the cold system, and the same quantity is dumped into the hot. Since the temperature of the cold reservoir is lower than that of the hot, the reduction of its entropy (see below) is greater than the increase of the entropy of the hot reservoir; so overall Jill's device reduces the entropy of the universe, and it is therefore unnatural.

Now the net is beginning to close in on natural change. We have succeeded in capturing Jack and Jill jointly on a single hook, just as we have claimed that the entropy principle captures the two statements of the Second Law. From now on we should be able to discuss *all* natural change in terms of the entropy.

Yet we are still hovering on the brink of actually defining entropy! Now is the time to take the plunge. We have seen that entropy increases when a



As in the illustration above, the shade of blue denotes the entropy. When heat is withdrawn from the cold reservoir, its entropy drops; when the same quantity of heat enters the hot reservoir, its entropy barely changes. Overall, therefore, the entropy of the universe declines, which is also against experience.

system is heated; we have seen that the increase is greater the lower the temperature. The simplest definition would therefore appear to be:

Change in entropy = (Heat supplied)/Temperature.

Happily, with care, this definition works.

First, let us make sure this definition captures what we have already done. If energy is supplied by heating a system, then *Heat supplied* is positive, and so the change of entropy is also positive (that is, the entropy increases). Conversely, if the energy leaks away as heat to the surroundings, *Heat supplied* is negative, and so the entropy decreases. If energy is supplied as work and not as heat, then *Heat supplied* is zero, and the entropy remains the same. If the heating takes place at high temperature, then *Temperature* has a large value; so for a given amount of heating, the change of entropy is small. If the heating takes place at low temperatures, then *Temperature* has a small value; so for the same amount of heating, the change of entropy is large. All this is exactly what we want.

Now for the care in the use of the definition. The temperature must be constant throughout the transfer of the energy as heat (otherwise the formula would be meaningless). Generally a system gets hotter (that is, its temperature will rise) as heating proceeds. However, if the system is extremely large (for example, if it is connected to all the rest of the actual Universe), then however much heat flows in, its temperature remains the same. Such a component of the universe is called a thermal *reservoir*. Therefore we can safely use the definition of the change of entropy *only* for a reservoir. That is the first limitation (it may seem extreme, but we shall spread the boundaries of the definition in a moment).

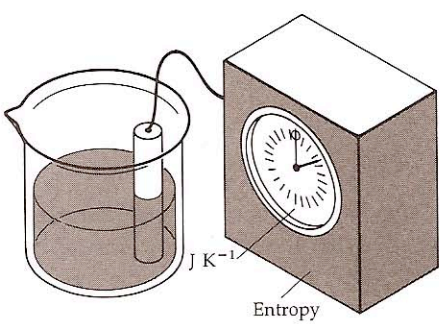
A second point concerns the manner in which energy is transferred. Suppose we allow an engine to do some work on its surroundings. Unless we are exceptionally careful, the raising of the weight, the turning of the crank, or whatever, will give rise to turbulence and vibration, which will fritter energy away by friction and in effect heat the surroundings. In that case we would expect the transfer of energy as work also to contribute to the change in entropy. In order to eliminate this from the definition (but once again only in order to clarify the definition, not to eliminate dissipative processes from the discussion), we must specify how the energy is to be transferred. The energy must be transferred without generating turbulence, vortices, and eddies. That is, it has to be done infinitely carefully: pistons must be allowed to emerge infinitely slowly, and energy must be allowed to seep down a temperature gradient infinitely slowly. Such processes are then called *quasistatic:* they are the limits of processes carried out with ever-increasing care.

Measuring the Entropy

We have a definition of entropy, but the definition does not seem to give the concept much body. Although we regard properties such as temperature and energy to be "tangible" (but we do so merely because they are familiar), the idea of entropy as (*Heat supplied*)/*Temperature* seems remote from experience. So it is, and so it will remain until the next chapter, where we shall add flesh by considering how to interpret the concept in terms of the behavior of atoms.

But is temperature *really* so familiar, and entropy so remote? We think of a liter of hot water and a liter of cold water as having different temperatures. *In fact*, they also have different entropies, and the "hot" water has both a higher entropy and a higher temperature than the cold water. The fact that hot water added to cold results in tepid water is a consequence of the change of entropy. Should we think then of "hotness" as denoting high temperature or as denoting high entropy? With which concept are *really* familiar?

Temperature seems familiar because we can measure it: we feel at home with pointer readings, and often mistake the reading for the concept. Take time, for instance: the pointer readings are an everyday commonplace, but the *essence* of time is much deeper. So it is with temperature; although it seems familiar, the nature of temperature is a far more subtle concept. The difficulty with accepting entropy is that we are not familiar with instruments that measure it, and consequently we are not familiar with their pointer readings. The *essence* of entropy, when we get to it, is certainly no more difficult, and may be simpler, than the essence of temperature. What we need, therefore, in order to break down the barrier between us and entropy, is an entropy meter.



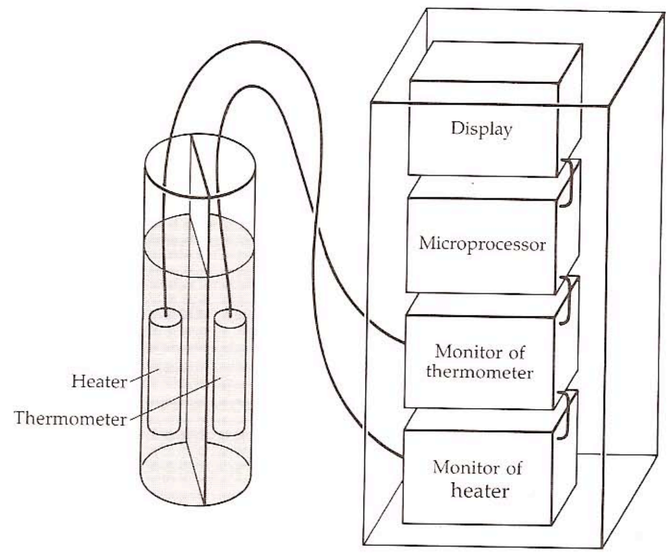
An entropy meter consists of a probe in the sample and a pointer giving a reading on a dial, exactly like a thermometer.

The figure to the left shows an entropy meter; the figure on the next page indicates the sort of mechanism that we might find inside it: it is basically a thermometer attached to a microprocessor. The readings can be taken from the digital display.

Suppose we want to measure the entropy change when a lump of iron is heated. All we need do is attach the entropy meter to the lump, and start heating: the microprocessor monitors the temperature indicated by the thermometer, and converts it directly into an entropy change. What calculations it does we shall come to in a moment. The care we have to exercise is to do the heating extremely slowly, so that we do not create hot spots and get a distorted reading: the heating must be quasistatic.

The microprocessor is programmed as follows. First, it has to work out, from the rise in temperature caused by the heating, the quantity of energy that has been transferred to the lump from the heater. That is a fairly

The interior of the entropy meter is more complicated than that of a simple mercury thermometer. The probe consists of a heater (whose output is monitored by the rest of the meter) and a thermometer (which is also monitored). The microprocessor is programmed to do a calculation based on how the temperature of the sample depends on the heat supplied by the heater. The output shown on the dial is the entropy change of the sample between the starting and finishing temperatures.



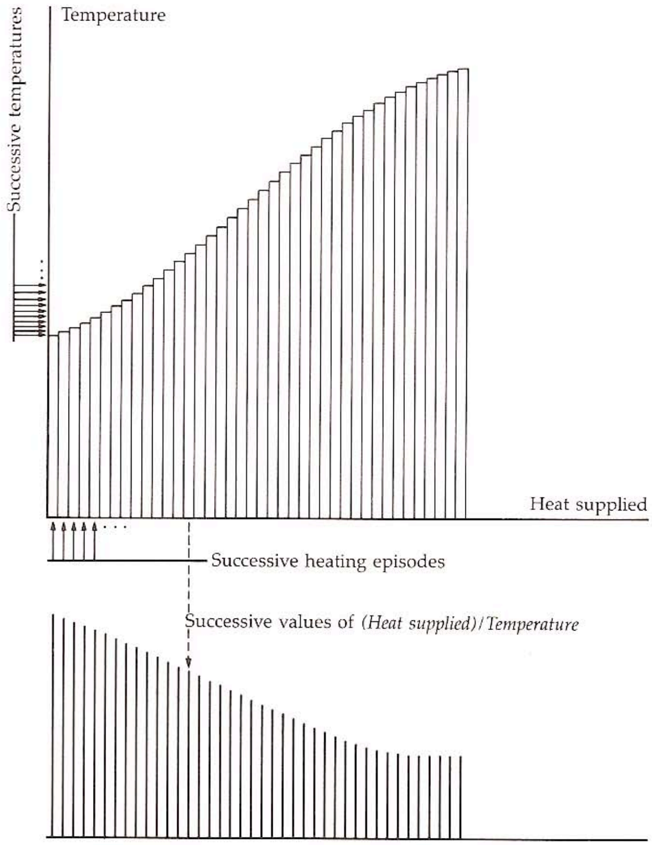
straightforward calculation once we know the *heat capacity* (the *specific heat*) of the sample, because the temperature rise is directly proportional to the heat supplied:

Temperature rise = (Proportionality coefficient) × (Heat supplied),

the coefficient being related to the heat capacity. (We could always measure the heat capacity in a separate experiment, with the same apparatus, but with a different program in the microprocessor.) The heater supplies only a trickle of energy to the sample, and the microprocessor evaluates *(Heat supplied)/Temperature,* and stores the result. If only a little heat is supplied, the temperature will hardly rise, and so the entropy formula is very accurate. However, since the sample is not an infinite reservoir, the temperature does rise a little, and the next trickle of heat takes place at a slightly higher temperature. The microprocessor therefore has to evaluate the next trickle of *(Heat supplied)/Temperature* at a marginally (in the limit, infinitesimally) higher temperature. It adds the result to the previous value (see the figure on the facing page).

The procedure continues: the thermometer records, the microprocessor goes on dividing and adding, and the heating continues until at long last (in a perfect experiment, at the other end of eternity) the temperature has risen to the final value. The microprocessor then displays the accumulated sum of all the little values of *(Heat supplied)/Temperature* as the change in entropy of the lump.

The entropy meter works by squirting tiny quantities of heat into the sample, and monitoring the temperature. It then evaluates (Heat supplied)/Temperature, *and stores the result. Next it monitors the new temperature, and squirts in some more heat, and repeats the calculation. This is repeated until the final temperature has been reached. In a real-life measurement, the* heat capacity *of the sample is measured over the temperature range, and the entropy change is calculated from that (see Appendix 2).*

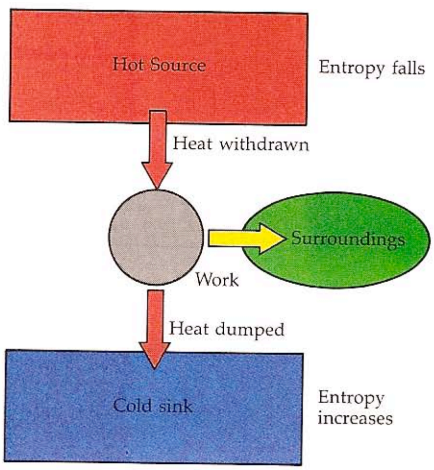


That is as far as we need go for now. What I want to establish here is not so much the details of how the entropy change is measured in any particular process, but the fact that it is a measurable quantity, exactly like the temperature, and, indeed, that it can be measured with a thermometer too!

The Dissipation of Quality

We can edge closer to complete understanding by reflecting on the implications of what this external view of entropy already reveals about the nature of the world. As a first step, we shall see how the introduction of entropy leads to a particularly important interpretation of the role of energy in events.

Suppose we have a certain amount of energy that we can draw from a hot source, and an engine to convert it into work. We know that the Second Law demands that we have a cold sink too; so we arrange for the engine to operate in the usual way. We can extract the appropriate quantity of work, and pay our tax to Nature by dumping a contribution of energy as heat into the cold sink. The energy we have dumped into the cold sink is then no longer available for doing work (unless we happen to have an even colder reservoir available). Therefore, in some sense, energy stored at a high temperature has a better "quality": high-quality energy is available for doing work; low-quality energy, corrupted energy, is less available for doing work.



Some heat must be discarded into a cold sink in order for us to generate enough entropy to overcome the decline taking place in the hot reservoir.

A slightly different way of looking at the quality of energy is to think in terms of entropy. Suppose we withdraw a quantity of energy as heat from the hot source, and allow it to go directly to the cold sink (see the figure to the left). The entropy of the universe decreases by an amount *(Heat withdrawn)/Temperature*$_{\text{HOT SOURCE}}$, but also increases by an amount *(Heat dumped)/Temperature*$_{\text{COLD SINK}}$. The sum of the two contributions to the overall change in entropy is therefore positive (because the temperature of the hot source is higher than that of the cold sink). The energy of the universe is then less available for doing work (because when energy is stored at lower temperatures, still colder sinks are needed if it is to be converted into work). It is then, in our sense, lower in quality, and the entropy associated with the energy has increased. The *entropy*, therefore, *labels the manner in which the energy is stored*: if it is stored at a high temperature, then its entropy is relatively low, and its quality is high. On the other hand, if the same amount of energy is stored at a low temperature, then the entropy of that energy is high, and its quality is low.

Just as the increasing entropy of the universe is the signpost of natural change and corresponds to energy being stored at ever-lower temperatures, so we can say that *the natural direction of change is the one that causes the quality of energy to decline:* the natural processes of the world are manifestations of this corruption of quality.

This attitude toward energy and entropy, that entropy represents the manner in which energy is stored, is of great practical significance. The First Law establishes that the energy of a universe (and maybe of the Universe itself) is constant (perhaps constant at zero). Therefore, when we burn fossil fuels, such as coal, oil, and nuclei, we are not diminishing the supply of energy. In that sense, there can never be an energy crisis, for the energy of the world is forever the same. However, every time we burn a lump of coal or a drop of oil, and whenever a nucleus falls apart, we are increasing the entropy of the world (for all these are spontaneous processes). Put another way, every action diminishes the quality of the energy of the universe.

As technological society ever more vigorously burns its resources, so the entropy of the universe inexorably increases, and the quality of the energy it stores concomitantly declines. We are not in the midst of an energy crisis: we are on the threshold of an entropy crisis. Modern civilization is living off the corruption of the stores of energy in the Universe. What we need to do is not to conserve energy, for Nature does that automatically, but to husband its quality. In other words, we have to find ways of furthering and maintaining our civilization with a lower production of entropy: the conservation of quality is the essence of the problem and our duty toward the future.

Thermodynamics, particularly the Second Law (we shall see the less than benign role of the Third in a moment), indicates the problems in this program of conservation, and also points to solutions. In order to see how this is so, we shall go back to the Carnot cycle, and apply what we have developed here to its operation.

Ceilings to Efficiency

In the first place, if the Carnot engine goes through its cycle, then the entropy change of its little world cannot be negative, for that would signify a nonspontaneous process, and useful engines do not have to be driven. Now, however, we are equipped to calculate the change in entropy, using the formula *Heat/Temperature.* In order to calculate however, we must assume that the engine is working perfectly, and that there are no losses of any kind: the cycle must be gone round quasistatically.

The engine itself returns to its initial condition (it is cyclic); so at the end of a cycle it has the same entropy as it had at the beginning. The work it does in the surroundings does not increase their entropy, because everything happens so carefully and slowly in the quasistatic operating regime. The only changes of entropy are in the hot source, the entropy of which *decreases* by an amount of magnitude

$$\textit{(Heat supplied from hot source)}/T_{\text{HOT SOURCE}},$$

and in the cold sink, the entropy of which *increases* by an amount of magnitude

$$\textit{(Heat supplied to cold sink)}/T_{\text{COLD SINK}}.$$

And, under quasistatic conditions, that is all. However, overall the change of entropy must not be negative. Therefore *the smallest value of the heat discarded into the cold sink must be large enough to increase the entropy there just enough to overcome the decrease in entropy in the hot source.* It is straightforward algebra to show that this minimum discarded energy is

Minimum heat discarded into the cold sink

$$= (\textit{Heat supplied by hot source}) \times (T_{\text{COLD SINK}}/T_{\text{HOT SOURCE}}).$$

Here is our first major result of thermodynamics: we now know how to minimize the heat we throw away: we keep the cold sink as cold as possible, and the hot source as hot as possible. That is why modern power stations use superheated steam: cold sinks are hard to come by; so the most economical procedure is to use as hot a source as possible. That is, the designer aims to use the highest-quality energy.

But we can go on, and summon up our second major result. The work generated by the Carnot engine as it goes through its cycle must be equal to the difference between the heats supplied and discarded (this is a consequence of the First Law). The work is therefore equal to *Heat supplied minus Heat discarded* (see the preceding figure). We are now, however, in a position to express this difference in terms of the *Heat supplied* multiplied by a factor involving the two temperatures. The *efficiency* of the engine is the ratio of the work it generates to the heat it absorbs. It is now very simple to arrive at the result that the efficiency of a Carnot engine, working perfectly between a hot source and a cold sink, is

$$\textit{Efficiency} = 1 - (T_{\text{COLD SINK}}/T_{\text{HOT SOURCE}}).$$

That is, the efficiency depends only on the temperatures and is independent of the working material in the engine, which could be air, mercury, steam, or whatever. Most modern power plants for electricity generation use steam at around 1,000 °F (800 K) and cold sinks at around 212 °F (373 K).* Their efficiency ceiling is therefore around 54 percent (but other losses reduce this efficiency to around 40 percent). Higher source temperatures could improve efficiencies, but bring other problems, because then materials begin to fail. For safety reasons, nuclear reactors operate at lower source temperatures (of about 600 °F, 620 K), which limits their theoretical efficiency to around 40 percent. Losses then reduce this figure to about 32 percent. Closer to home, an automobile engine operates with a briefly maintained input temperature of over 5,400 °F (around 3,300 K) and exhausts at around 2,100 °F (1,400 K), giving a theoretical ceiling of around 56 percent. However, actual automobile engines are designed to be light enough to be responsive and mobile, and therefore attain only about 25 percent efficiency.

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* Scales of temperature are described in Appendix 1. K denotes *kelvin*, the graduation of the Kelvin scale of temperature (the one of fundamental significance, in contrast to the contrived scales of Celsius and Fahrenheit). In brief, a temperature in kelvins is obtained by adding 273 to the temperature in degrees Celsius.

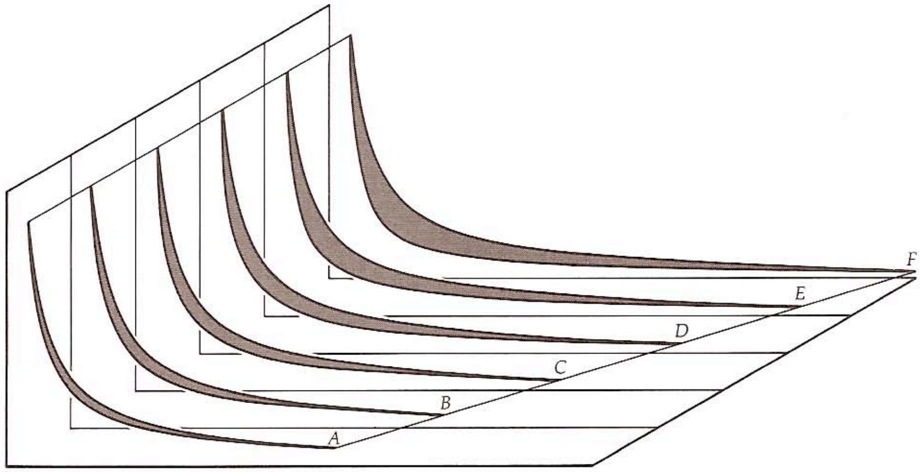
The profound importance of the preceding result is that is puts an upper limit on the efficiency of engines: whatever clever mechanism is contrived, so long as the engineer is stuck with fixed temperatures for the source and the sink, the efficiency of the engine cannot exceed the Carnot value. The reason why should by now be clear (to the external observer). In order for heat to be converted to work spontaneously, there must be an overall increase in the entropy of the universe. When energy is withdrawn as heat from the hot source, there is a reduction in its entropy. Therefore, since the perfectly operating engine does not itself generate entropy, there must be entropy generated elsewhere. Hence, in order for the engine to operate, there must be a dump for at least a little heat: there must be a sink. Moreover, that sink must be a cold one, so that even a small quantity of heat supplied to it results in a large increase in entropy.

The temperature of the cold sink amplifies the effect of dumping the heat: the lower the temperature, the higher the magnification of the entropy. Consequently, the lower the temperature, the less heat we need to discard into it in order to achieve an overall positive entropy change in the universe during the cycle. Hence the efficiency of the conversion increases as the temperature of the cold source is lowered.

There appears to be a limit to the lowness of temperature. The conversion efficiency of heat to work cannot exceed unity, for otherwise the First Law would be contravened. Therefore the value of $Temperature_{\text{COLD SINK}}$ cannot be negative. Hence there appears to be a *natural limit to the lowness of temperature,* corresponding to $Temperature_{\text{COLD SINK}} = 0$. This is the *absolute zero of temperature,* the end of getting cold. At this infinite arctic, the conversion efficiency would be unity, for even the merest wisp of heat transferred to the sink would give an enormous positive entropy (because the temperature is in the denominator, so that $1/Temperature$ becomes infinitely large and magnifies everything infinitely). But can we attain that Nirvana?

A clue to the attainability of absolute zero can be obtained by considering the Carnot cycle with an ever-decreasing temperature of its cold sink. For a given quantity of heat to be absorbed from the hot source, the piston needs to travel out a definite distance from *A* to *B* in the figure on page 18, no matter what becomes of the energy later. The cooling step, the adiabatic expansion from *C* to *D,* then involves a greater expansion the lower the temperature we are aiming to reach. Some of the expansions are illustrated in the figure on the next page: we can see that the lower the temperature aimed at, the greater the size of the stroke. In order to approach very low temperatures, we need extremely large engines. In order to reduce the temperature to zero, we would need an infinitely large engine. Absolute zero appears to be unattainable.

Carnot indicator diagrams for cycles with decreasing cold-sink temperatures (F is coldest) but constant heat input. The work output (shaded area) increases, and therefore so does the efficiency, but the stroke required becomes large.



The *Third Law* of thermodynamics generalizes this result. In a dejected kind of way it summarizes experience by the following remark:

Third Law: Absolute zero is unattainable in a finite number of steps.

This gives rise to the following sardonic summary of thermodynamics:

First Law: Heat can be converted into work.
Second Law: But completely only at absolute zero.
Third Law: And absolute zero is unattainable!

The End of the External

We have traveled a long way in this chapter. First, we drew together the skeins of experience summarized by the Kelvin and the Clausius statements of the Second Law, saw that they were equivalent, and exposed two faces of Nature's dissymmetry. We also saw that we could draw the two statements together by introducing a property of the system not readily discernable to the untutored eye, the entropy. We have seen that the entropy may be measured, and that it may be deployed to draw far-reaching conclusions about the nature of change. We have seen that the Universe is rolling uphill in entropy, and that it is thriving off the corruption of the quality of its energy.

Yet all this is superficial. We have been standing outside the world of events, but we have not yet discerned the deeper nature of change. Now is the time to descend into matter.