

The Laws of Thermodynamics

44-1 Heat engines; the first law

So far we have been discussing the properties of matter from the atomic point of view, trying to understand roughly what will happen if we suppose that things are made of atoms obeying certain laws. However, there are a number of relationships among the properties of substances which can be worked out without consideration of the detailed structure of the materials. The determination of the relationships among the various properties of materials, without knowing their internal structure, is the subject of *thermodynamics*. Historically, thermodynamics was developed before an understanding of the internal structure of matter was achieved.

To give an example: we know from the kinetic theory that the pressure of a gas is caused by molecular bombardment, and we know that if we heat a gas, so that the bombardment increases, the pressure must increase. Conversely, if the piston in a container of the gas is moved inward against the force of bombardment, the energy of the molecules bombarding the piston will increase, and consequently the temperature will increase. So, on the one hand, if we increase the temperature at a given volume, we increase the pressure. On the other hand, if we compress the gas, we will find that the temperature will rise. From the kinetic theory, one can derive a quantitative relationship between these two effects, but instinctively one might guess that they are related in some necessary fashion which is independent of the details of the collisions.

Let us consider another example. Many people are familiar with this interesting property of rubber: If we take a rubber band and pull it, it gets warm. If one puts it between his lips, for example, and pulls it out, he can feel a distinct warming, and this warming is reversible in the sense that if he relaxes the rubber band quickly while it is between his lips, it is distinctly cooled. That means that when we stretch a rubber band it heats, and when we release the tension of the band it cools. Now our instincts might suggest that if we heated a band, it might pull: that the fact that pulling a band heats it might imply that heating a band should cause it to contract. And, in fact, if we apply a gas flame to a rubber band holding a weight, we will see that the band contracts abruptly (Fig. 44-1). So it is true that when we heat a rubber band it pulls, and this fact is definitely related to the fact that when we release the tension of it, it cools.

The internal machinery of rubber that causes these effects is quite complicated. We will describe it from a molecular point of view to some extent, although our main purpose in this chapter is to understand the relationship of these effects independently of the molecular model. Nevertheless, we can show from the molecular model that the effects are closely related. One way to understand the behavior of rubber is to recognize that this substance consists of an enormous tangle of long chains of molecules, a kind of "molecular spaghetti," with one extra complication: between the chains there are cross-links—like spaghetti that is sometimes welded together where it crosses another piece of spaghetti—a grand tangle. When we pull out such a tangle, some of the chains tend to line up along the direction of the pull. At the same time, the chains are in thermal motion, so they hit each other continually. It follows that such a chain, if stretched, would not by itself remain stretched, because it would be hit from the sides by the other chains and other molecules, and would tend to kink up again. So the real reason why a rubber band tends to contract is this: when one pulls it out, the chains are lengthwise, and the thermal agitations of the molecules on the sides of the chains tend

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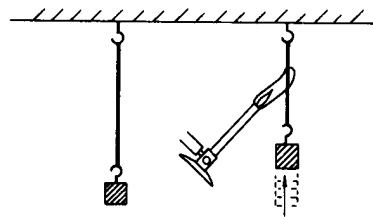


Fig. 44-1. The heated rubber band.

to kink the chains up, and make them shorten. One can then appreciate that if the chains are held stretched and the temperature is increased, so that the vigor of the bombardment on the sides of the chains is also increased, the chains tend to pull in, and they are able to pull a stronger weight when heated. If, after being stretched for a time, a rubber band is allowed to relax, each chain becomes soft, and the molecules striking it lose energy as they pound into the relaxing chain. So the temperature falls.

We have seen how these two processes, contraction when heated and cooling during relaxation, can be related by the kinetic theory, but it would be a tremendous challenge to determine from the theory the precise relationship between the two. We would have to know how many collisions there were each second and what the chains look like, and we would have to take account of all kinds of other complications. The detailed mechanism is so complex that we cannot, by kinetic theory, really determine exactly what happens; still, a definite relation between the two effects we observe can be worked out without knowing anything about the internal machinery!

The whole subject of thermodynamics depends essentially upon the following kind of consideration: because a rubber band is "stronger" at higher temperatures than it is at lower temperatures, it ought to be possible to lift weights, and to move them around, and thus to do work with heat. In fact, we have already seen experimentally that a heated rubber band can lift a weight. The study of the way that one does work with heat is the beginning of the science of thermodynamics. Can we make an engine which uses the heating effect on a rubber band to do work? One can make a silly looking engine that does just this. It consists of a bicycle wheel in which all the spokes are rubber bands (Fig. 44-2). If one heats the rubber bands on one side of the wheel with a pair of heat lamps, they become "stronger" than the rubber bands on the other side. The center of gravity of the wheel will be pulled to one side, away from the bearing, so that the wheel turns. As it turns, cool rubber bands move toward the heat, and the heated bands move away from the heat and cool, so that the wheel turns slowly so long as the heat is applied. The efficiency of this engine is extremely low. Four hundred watts of power pour into the two lamps, but it is just possible to lift a fly with such an engine! An interesting question, however, is whether we can get heat to do the work in more efficient ways.

In fact, the science of thermodynamics began with an analysis, by the great engineer Sadi Carnot, of the problem of how to build the best and most efficient engine, and this constitutes one of the few famous cases in which engineering has contributed fundamentally to physical theory. Another example that comes to mind is the more recent analysis of information theory by Claude Shannon. These two analyses, incidentally, turn out to be closely related.

Now the way a steam engine ordinarily operates is that heat from a fire boils some water, and the steam so formed expands and pushes on a piston which makes a wheel go around. So the steam pushes the piston—what then? One has to finish the job: a stupid way to complete the cycle would be to let the steam escape into the air, for then one has to keep supplying water. It is cheaper—more efficient—to let the steam go into another box, where it is condensed by cool water, and then pump the water back into the boiler, so that it circulates continuously. Heat is thus supplied to the engine and converted into work. Now would it be better to use alcohol? What property should a substance have so that it makes the best possible engine? That was the question to which Carnot addressed himself, and one of the by-products was the discovery of the type of relationship that we have just explained above.

The results of thermodynamics are all contained implicitly in certain apparently simple statements called the *laws of thermodynamics*. At the time when Carnot lived, the first law of thermodynamics, the conservation of energy, was not known. Carnot's arguments were so carefully drawn, however, that they are valid even though the first law was not known in his time! Some time afterwards, Clausius made a simpler derivation that could be understood more easily than Carnot's very subtle reasoning. But it turned out that Clausius assumed, not the conserva-

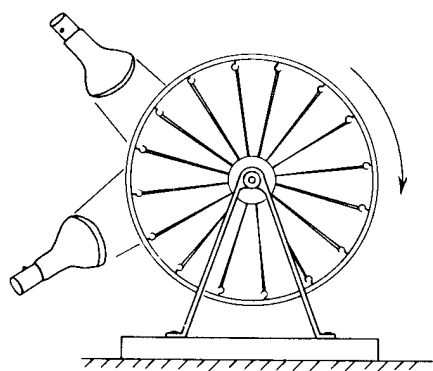


Fig. 44-2. The rubber-band heat engine.

tion of energy in general, but that *heat* was conserved according to the caloric theory, which was later shown to be false. So it has often been said that Carnot's logic was wrong. But his logic was quite correct. Only Clausius' simplified version, that everybody read, was incorrect.

The so-called second law of thermodynamics was thus discovered by Carnot before the first law! It would be interesting to give Carnot's argument that did not use the first law, but we shall not do so because we want to learn physics, not history. We shall use the first law from the start, in spite of the fact that a great deal can be done without it.

Let us begin by stating the first law, the conservation of energy: if one has a system and puts heat into it, and does work on it, then its energy is increased by the heat put in and the work done. We can write this as follows: The heat Q put into the system, plus the work W done on the system, is the increase in the energy U of the system; the latter energy is sometimes called the internal energy:

$$\text{Change in } U = Q + W. \quad (44.1)$$

The change in U can be represented as adding a little heat ΔQ and adding a little work ΔW :

$$\Delta U = \Delta Q + \Delta W, \quad (44.2)$$

which is a differential form of the same law. We know that very well, from an earlier chapter.

44-2 The second law

Now, what about the second law of thermodynamics? We know that if we do work against friction, say, the work lost to us is equal to the heat produced. If we do work in a room at temperature T , and we do the work slowly enough, the room temperature does not change much, and we have converted work into heat at a given temperature. What about the reverse possibility? Is it possible to convert the heat back into work at a given temperature? The second law of thermodynamics asserts that it is not. It would be very convenient to be able to convert heat into work merely by reversing a process like friction. If we consider only the conservation of energy, we might think that heat energy, such as that in the vibrational motions of molecules, might provide a goodly supply of useful energy. But Carnot assumed that it is impossible to extract the energy of heat at a single temperature. In other words, if the whole world were at the same temperature, one could not convert any of its heat energy into work: while the process of making work go into heat can take place at a given temperature, one cannot reverse it to get the work back again. Specifically, Carnot assumed that heat cannot be taken in at a certain temperature and converted into work *with no other change* in the system or the surroundings.

That last phrase is very important. Suppose we have a can of compressed air at a certain temperature, and we let the air expand. It can do work; it can make hammers go, for example. It cools off a little in the expansion, but if we had a big sea, like the ocean, at a given temperature—a heat reservoir—we could warm it up again. So we have taken the heat out of the sea, and we have done work with the compressed air. But Carnot was not wrong, because *we did not leave everything as it was*. If we recompress the air that we let expand, we will find we are doing extra work, and when we are finished we will discover that we not only got no work out of the system at temperature T , but we actually put some in. We must talk only about situations in which the *net result* of the whole process is to take heat away and convert it into work, just as the net result of the process of doing work against friction is to take work and convert it into heat. If we move in a circle, we can bring the system back precisely to its starting point, with the net result that we did work against friction and produced heat. Can we reverse the process? Turn a switch, so that everything goes backwards, so the friction does work against us, and cools the sea? According to Carnot: no! So let us suppose that this is impossible.

If it were possible it would mean, among other things, that we could take heat out of a cold body and put it into a hot body at no cost, as it were. Now we know it is natural that a hot thing can warm up a cool thing; if we simply put a hot body and a cold one together, and change nothing else, our experience assures us that it is not going to happen that the hot one gets hotter, and the cold one gets colder! But if we could obtain work by extracting the heat out of the ocean, say, or from anything else at a single temperature, then that work could be converted back into heat by friction at some other temperature. For instance, the other arm of a working machine could be rubbing something that is already hot. The net result would be to take heat from a “cold” body, the ocean, and to put it into a hot body. Now, the hypothesis of Carnot, the second law of thermodynamics, is sometimes stated as follows: heat cannot, of itself, flow from a cold to a hot object. But, as we have just seen, these two statements are equivalent: first, that one cannot devise a process whose only result is to convert heat to work at a single temperature, and second, that one cannot make heat flow by itself from a cold to a hot place. We shall mostly use the first form.

Carnot’s analysis of heat engines is quite similar to the argument that we gave about weight-lifting engines in our discussion of the conservation of energy in Chapter 4. In fact, that argument was patterned after Carnot’s argument about heat engines, and so the present treatment will sound very much the same.

Suppose we build a heat engine that has a “boiler” somewhere at a temperature T_1 . A certain heat Q_1 is taken from the boiler, the steam engine does some work W , and it then delivers some heat Q_2 into a “condenser” at another temperature T_2 (Fig. 44-3). Carnot did not say how much heat, because he did not know the first law, and he did not use the law that Q_2 was equal to Q_1 because he did not believe it. Although everybody thought that, according to the caloric theory, the heats Q_1 and Q_2 would have to be the same, Carnot did not say they were the same—that is part of the cleverness of his argument. If we do use the first law, we find that the heat delivered, Q_2 , is the heat Q_1 that was put in minus the work W that was done:

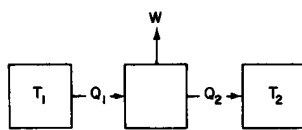


Fig. 44-3. Heat engine.

$$Q_2 = Q_1 - W. \quad (44.3)$$

(If we have some kind of cyclic process where water is pumped back into the boiler after it is condensed, we will say that we have heat Q_1 absorbed and work W done, during each cycle, for a certain amount of water that goes around the cycle.)

Now we shall build another engine, and see if we cannot get more work from the same amount of heat being delivered at the temperature T_1 , with the condenser still at the temperature T_2 . We shall use the same amount of heat Q_1 from the boiler, and we shall try to get more work than we did out of the steam engine, perhaps by using another fluid, such as alcohol.

44-3 Reversible engines

Now we must analyze our engines. One thing is clear: we will lose something if the engines contain devices in which there is friction. The best engine will be a frictionless engine. We assume, then, the same idealization that we did when we studied the conservation of energy; that is, a perfectly frictionless engine.

We must also consider the analog of frictionless motion, “frictionless” heat transfer. If we put a hot object at a high temperature against a cold object, so that the heat flows, then it is not possible to make that heat flow in a reverse direction by a very small change in the temperature of either object. But when we have a practically frictionless machine, if we push it with a little force one way, it goes that way, and if we push it with a little force the other way, it goes the other way. We need to find the analog of frictionless motion: heat transfer whose direction we can reverse with only a tiny change. If the difference in temperature is finite, that is impossible, but if one makes sure that heat flows always between two things at essentially the same temperature, with just an infinitesimal difference to make it flow in the desired direction, the flow is said to be reversible (Fig. 44-4). If we heat

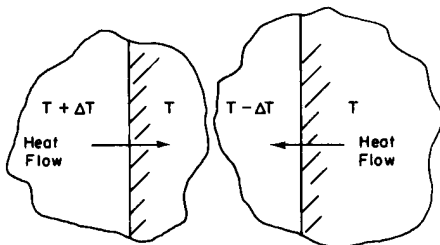


Fig. 44-4. Reversible heat transfer.

the object on the left a little, heat will flow to the right; if we cool it a little, heat will flow to the left. So we find that the ideal engine is a so-called *reversible* engine, in which every process is reversible in the sense that, by minor changes, infinitesimal changes, we can make the engine go in the opposite direction. That means that nowhere in the machine must there be any appreciable friction, and nowhere in the machine must there be any place where the heat of the reservoirs, or the flame of the boiler, is in direct contact with something definitely cooler or warmer.

Let us now consider an idealized engine in which all the processes are reversible. To show that such a thing is possible in principle, we will give an example of an engine cycle which may or may not be practical, but which is at least reversible, in the sense of Carnot's idea. Suppose that we have a gas in a cylinder equipped with a frictionless piston. The gas is not necessarily a perfect gas. The fluid does not even have to be a gas, but to be specific let us say we do have a perfect gas. Also, suppose that we have two heat pads, T_1 and T_2 —great big things that have definite temperatures, T_1 and T_2 . We will suppose in this case that T_1 is higher than T_2 . Let us first heat the gas and at the same time expand it, while it is in contact with the heat pad at T_1 . As we do this, pulling the piston out very slowly as the heat flows into the gas, we will make sure that the temperature of the gas never gets very far from T_1 . If we pull the piston out too fast, the temperature of the gas will fall too much below T_1 and then the process will not be quite reversible, but if we pull it out slowly enough, the temperature of the gas will never depart much from T_1 . On the other hand, if we push the piston back slowly, the temperature would be only infinitesimally higher than T_1 , and the heat would pour back. We see that such an isothermal (constant-temperature) expansion, done slowly and gently enough, is a reversible process.

To understand what we are doing, we shall use a plot (Fig. 44-6) of the pressure of the gas against its volume. As the gas expands, the pressure falls. The curve marked (1) tells us how the pressure and volume change if the temperature is kept fixed at the value T_1 . For an ideal gas this curve would be $PV = NkT_1$. During an isothermal expansion the pressure falls as the volume increases until we stop at the point b . At the same time, a certain heat Q_1 must flow into the gas from the reservoir, for if the gas were expanded without being in contact with the reservoir it would cool off, as we already know. Having completed the isothermal expansion, stopping at the point b , let us take the cylinder away from the reservoir and continue the expansion. This time we permit no heat to enter the cylinder. Again we perform the expansion slowly, so there is no reason why we cannot reverse it, and we again assume there is no friction. The gas continues to expand and the temperature falls, since there is no longer any heat entering the cylinder.

We let the gas expand, following the curve marked (2), until the temperature falls to T_2 , at the point marked c . This kind of expansion, made without adding heat, is called an *adiabatic* expansion. For an ideal gas, we already know that curve (2) has the form $PV^\gamma = \text{constant}$, where γ is a constant greater than 1, so that the adiabatic curve has a more negative slope than the isothermal curve. The gas cylinder has now reached the temperature T_2 , so that if we put it on the heat pad at temperature T_2 there will be no irreversible changes. Now we slowly compress the gas while it is in contact with the reservoir at T_2 , following the curve marked (3) (Fig. 44-5, Step 2). Because the cylinder is in contact with the reservoir, the temperature does not rise, but heat Q_2 flows from the cylinder into the reservoir at the temperature T_2 . Having compressed the gas isothermally along curve (3) to the point d , we remove the cylinder from the heat pad at temperature T_2 and compress it still further, without letting any heat flow out. The temperature will rise, and the pressure will follow the curve marked (4). If we carry out each step properly, we can return to the point a at temperature T_1 where we started, and repeat the cycle.

We see that on this diagram we have carried the gas around a complete cycle, and during one cycle we have put Q_1 in at temperature T_1 , and have removed Q_2 at temperature T_2 . Now the point is that this cycle is reversible, so that we could represent all the steps the other way around. We could have gone backwards instead of forwards: we could have started at point a , at temperature T_1 , expanded

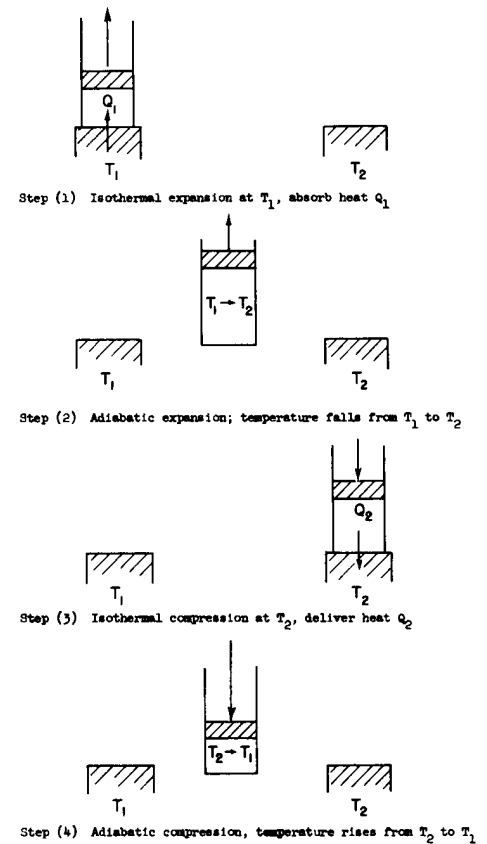


Fig. 44-5. Steps in Carnot cycle.

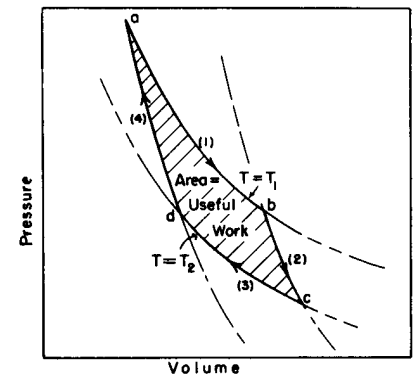


Fig. 44-6. The Carnot cycle.

along the curve (4), expanded further at the temperature T_2^* , absorbing heat Q_2 , and so on, going around the cycle backward. If we go around the cycle in one direction, we must do work on the gas; if we go in the other direction, the gas does work on us.

Incidentally, it is easy to find out what the total amount of work is, because the work during any expansion is the pressure times the change in volume, $\int P dV$. On this particular diagram, we have plotted P vertically and V horizontally. So if we call the vertical distance y and the horizontal distance x , this is $\int y dx$ —in other words, the area under the curve. So the area under each of the numbered curves is a measure of the work done by or on the gas in the corresponding step. It is easy to see that the net work done is the shaded area of the picture.

Now that we have given a single example of a reversible machine, we shall suppose that other such engines are also possible. Let us assume that we have a reversible engine A which takes Q_1 at T_1 , does work W , and delivers some heat at T_2 . Now let us assume we have any other engine B , made by man, already designed or not yet invented, made of rubber bands, steam, or whatever, reversible or not, which is designed so that it takes in the same amount of heat Q_1 at T_1 , and rejects the heat at the lower temperature T_2 (Fig. 44-7). Assume that engine B does some work, W' . Now we shall show that W' is not greater than W —that no engine can do more work than a reversible one. Why? Suppose that, indeed, W' were bigger than W . Then we could take the heat Q_1 out of the reservoir at T_1 , and with engine B we could do work W' and deliver some heat to the reservoir at T_2 ; we do not care how much. That done, we could save some of the work W' , which is supposed to be greater than W ; we could use a part of it, W , and save the remainder, $W' - W$, for useful work. With the work W we could run engine A backwards *because it is a reversible engine*. It will absorb some heat from the reservoir at T_2 and deliver Q_1 back to the reservoir at T_1 . After this double cycle, the net result would be that we would have put everything back the way it was before, and we would have done some excess work, namely $W' - W$, and *all* we would have done would be to extract energy from the reservoir at T_2 ! We were careful to restore the heat Q_1 to the reservoir at T_1 . So that reservoir can be small and “inside” our combined machine $A + B$, whose net effect is therefore to extract a net heat $W' - W$ from the reservoir at T_2 and convert it into work. But to obtain useful work from a reservoir at a single temperature *with no other changes* is impossible according to Carnot’s postulate; it cannot be done. Therefore no engine which absorbs a given amount of heat from a higher temperature T_1 and delivers it at the temperature T_2 can do more work than a reversible engine operating under the same temperature conditions.

Now suppose that engine B is also reversible. Then, of course, not only must W' be not greater than W , but now we can reverse the argument and show that W cannot be greater than W' . So, if both engines are reversible they must both do the same amount of work, and we thus come to Carnot’s brilliant conclusion: that if an engine is reversible, it makes no difference how it is designed, because the amount of work one will obtain if the engine absorbs a given amount of heat at temperature T_1 and delivers heat at some other temperature T_2 *does not depend on the design of the engine*. It is a property of the world, not a property of a particular engine.

If we could find out what the law is that determines how much work we obtain when we absorb the heat Q_1 at T_1 and deliver heat at T_2 , this quantity would be a universal thing, independent of the substance. Of course if we knew the properties of a particular substance, we could work it out and then say that all other substances must give the same amount of work in a reversible engine. That is the key idea, the clue by which we can find the relationship between how much, for instance, a rubber band contracts when we heat it, and how much it cools when we let it contract. Imagine that we put that rubber band in a reversible machine, and that we make it go around a reversible cycle. The net result, the total amount of work done, is that universal function, that great function which is independent of substance. So we see that a substance’s properties must be limited in a certain way; one

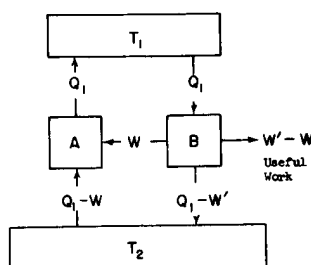


Fig. 44-7. Reversible engine A being driven backwards by engine B .

cannot make up anything he wants, or he would be able to invent a substance which he could use to produce more than the maximum allowable work when he carried it around a reversible cycle. This principle, this limitation, is the only real rule that comes out of the thermodynamics.

44-4 The efficiency of an ideal engine

Now we shall try to find the law which determines the work W as a function of Q_1 , T_1 , and T_2 . It is clear that W is proportional to Q_1 , for if we consider two reversible engines in parallel, both working together and both double engines, the combination is also a reversible engine. If each one absorbed heat Q_1 , the two together absorb $2Q_1$ and the work done is $2W$, and so on. So it is not unreasonable that W is proportional to Q_1 .

Now the next important step is to find this universal law. We can, and will, do so by studying a reversible engine with the one particular substance whose laws we know, a perfect gas. It is also possible to obtain the rule by a purely logical argument, using no particular substance at all. This is one of the very beautiful pieces of reasoning in physics and we are reluctant not to show it to you, so for those who would like to see it we shall discuss it in just a moment. But first we shall use the much less abstract and simpler method of direct calculation for a perfect gas.

We need only obtain formulas for Q_1 and Q_2 (for W is just $Q_1 - Q_2$), the heats exchanged with the reservoirs during the isothermal expansion or contraction. For example, how much heat Q_1 is absorbed from the reservoir at temperature T_1 during the isothermal expansion [marked (1) in Fig. 44-6] from point a , at pressure p_a , volume V_a , temperature T_1 , to point b with pressure p_b , volume V_b , and the same temperature T_1 ? For a perfect gas each molecule has an energy that depends only on the temperature, and since the temperature and the number of molecules are the same at a and at b , the internal energy is the same. *There is no change in U* ; all the work done by the gas,

$$W = \int_a^b p dV,$$

during the expansion is energy Q_1 taken from the reservoir. During the expansion, $pV = NkT_1$, or

$$p = \frac{NkT_1}{V}$$

or

$$Q_1 = \int_a^b p dV = \int_a^b NkT_1 \frac{dV}{V} \quad (44.4)$$

or

$$Q_1 = NkT_1 \ln \frac{V_b}{V_a}$$

is the heat taken from the reservoir at T_1 . In the same way, for the compression at T_2 [curve (3) of Fig. 44-6] the heat delivered to the reservoir at T_2 is

$$Q_2 = NkT_2 \ln \frac{V_c}{V_d}. \quad (44.5)$$

To finish our analysis we need only find a relation between V_c/V_d and V_b/V_a . This we do by noting that (2) is an adiabatic expansion from b to c , during which pV^γ is a constant. Since $pV = NkT$, we can write this as $(pV)V^{\gamma-1} = \text{const}$ or, in terms of T and V , as $TV^{\gamma-1} = \text{const}$, or

$$T_1V_b^{\gamma-1} = T_2V_c^{\gamma-1}. \quad (44.6)$$

Likewise, since (4), the expansion from d to a , is also adiabatic, we find

$$T_1V_a^{\gamma-1} = T_2V_d^{\gamma-1}. \quad (44.6a)$$

If we divide this equation by the previous one, we find that V_b/V_a must equal V_c/V_d , so the ln's in (44.4) and (44.5) are equal, and that

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}. \quad (44.7)$$

This is the relation we were seeking. Although proved for a perfect gas engine, we know it must be true *for any reversible engine at all*.

Now we shall see how this universal law could also be obtained by logical argument, without knowing the properties of any specific substances, as follows. Suppose that we have three engines and three temperatures, let us say T_1 , T_2 , and T_3 . Let one engine absorb heat Q_1 from the temperature T_1 and do a certain amount of work W_{13} , and let it deliver heat Q_3 to the temperature T_3 (Fig. 44-8). Let another engine run backwards between T_2 and T_3 . Suppose that we let the second engine be of such a size that it will absorb the same heat Q_3 , and deliver the heat Q_2 . We will have to put a certain amount of work, W_{32} , into it—negative because the engine is running backwards. When the first machine goes through a cycle, it absorbs heat Q_1 and delivers Q_3 at the temperature T_3 ; then the second machine takes the same heat Q_3 out of the reservoir at the temperature T_3 and delivers it into the reservoir at temperature T_2 . Therefore the net result of the two machines in tandem is to take the heat Q_1 from T_1 , and deliver Q_2 at T_2 . The two machines are thus equivalent to a third one, which absorbs Q_1 at T_1 , does work W_{12} , and delivers heat Q_2 at T_2 , because $W_{12} = W_{13} - W_{32}$, as one can immediately show from the first law, as follows:

$$W_{13} - W_{32} = (Q_1 - Q_3) - (Q_2 - Q_3) = Q_1 - Q_2 = W_{12}. \quad (44.8)$$

We can now obtain the laws which relate the efficiencies of the engines, because there clearly must be some kind of relationship between the efficiencies of engines running between the temperatures T_1 and T_3 , and between T_2 and T_3 , and between T_1 and T_2 .

We can make the argument very clear in the following way: We have just seen that we can always relate the heat absorbed at T_1 to the heat delivered at T_2 by finding the heat delivered at some other temperature T_3 . Therefore we can get all the engines' properties if we introduce a standard temperature, analyzing everything with that standard temperature. In other words, if we knew the efficiency of an engine running between a certain temperature T and a certain arbitrary standard temperature, then we could work out the efficiency for any other difference in temperature. Because we assume we are using only reversible engines, we can work from the initial temperature down to the standard temperature and back up to the final temperature again. We shall define the standard temperature arbitrarily as *one degree*. We shall also adopt a special symbol for the heat which is delivered at this standard temperature: we shall call it Q_s . In other words, when a reversible engine absorbs the heat Q at temperature T , it will deliver, at the unit temperature, a heat Q_s . *If one engine, absorbing heat Q_1 at T_1 , delivers the heat Q_s at one degree, and if an engine absorbing heat Q_2 at temperature T_2 will also deliver the same heat Q_s at one degree, then it follows that an engine which absorbs heat Q_1 at the temperature T_1 will deliver heat Q_2 if it runs between T_1 and T_2 , as we have already proved by considering engines running between three temperatures. So all we really have to do is to find how much heat Q_1 we need to put in at the temperature T_1 in order to deliver a certain amount of heat Q_s at the unit temperature. If we discover that, we have everything. The heat Q , of course, is a function of the temperature T . It is easy to see that the heat must increase as the temperature increases, for we know that it takes work to run an engine backwards and deliver heat at a higher temperature. It is also easy to see that the heat Q_1 must be proportional to Q_s . So the great law is something like this: for a given amount of heat Q_s delivered at one degree from an engine running at temperature T degrees, the heat Q absorbed must be that amount Q_s times some increasing function of the temperature:*

$$Q = Q_s f(T). \quad (44.9)$$

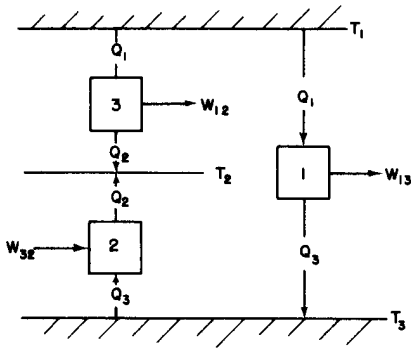


Fig. 44-8. Engines 1 and 2 together are equivalent to engine 3.

44-5 The thermodynamic temperature

At this stage we are not going to try to find the formula for the above increasing function of the temperature in terms of our familiar mercury temperature scale, but instead *we shall define temperature by a new scale*. At one time "the temperature" was defined arbitrarily by dividing the expansion of water into even degrees of a certain size. But when one then measures temperature with a mercury thermometer, one finds that the degrees are no longer even. But *now we can make a definition of temperature which is independent of any particular substance*. We can use that function $f(T)$, which does not depend on what device we use, because the efficiency of these reversible engines is independent of their working substances. Since the function we found is rising with temperature, we will define the *function itself* as the temperature, measured in units of the standard one-degree temperature, as follows:

$$Q = ST, \quad (44.10)$$

where

$$Q_s = S \cdot 1^\circ. \quad (44.11)$$

This means that we can tell how hot an object is by finding out how much heat is absorbed by a reversible engine working between the temperature of the object and the unit temperature (Fig. 44-9). If seven times more heat is taken out of a boiler than is delivered at a one-degree condenser, the temperature of the boiler will be called seven degrees, and so forth. So, by measuring how much heat is absorbed at different temperatures, we determine the temperature. The temperature defined in this way is called the *absolute thermodynamic temperature*, and it is independent of the substance. We shall use this definition exclusively from now on.*

Now we see that when we have two engines, one working between T_1 and one degree, the other working between T_2 and one degree, delivering the same heat at unit temperature, then the heats absorbed must be related by

$$\frac{Q_1}{T_1} = S = \frac{Q_2}{T_2}. \quad (44.12)$$

But that means that if we have a single engine running between T_1 and T_2 , then the result of the whole analysis, the grand finale, is that Q_1 is to T_1 as Q_2 is to T_2 , if the engine absorbs energy Q_1 at temperature T_1 and delivers heat Q_2 at temperature T_2 . Whenever the engine is reversible, this relationship between the heats must follow. That is all there is to it: that is the center of the universe of thermodynamics.

If this is all there is to thermodynamics, why is it considered such a difficult subject? In doing a problem involving a given mass of some substance, the condition of the substance at any moment can be described by telling what its temperature is and what its volume is. If we know the temperature and volume of a substance, and that the pressure is some function of the temperature and volume, then we know the internal energy. One could say, "I do not want to do it that way. Tell me the temperature and the pressure, and I will tell you the volume. I can think of the volume as a function of temperature and pressure, and the internal energy as a function of temperature and pressure, and so on." That is why thermodynamics is hard, because everyone uses a different approach. If we could only sit down once and decide on our variables, and stick to them, it would be fairly easy.

Now we start to make deductions. Just as $F \Rightarrow ma$ is the center of the universe in mechanics, and it goes on and on and on after that, in the same way the principle just found is all there is to thermodynamics. But can one make conclusions out of it?

* We have previously defined our scale of temperature in a different way, namely by stating that the mean kinetic energy of a molecule in a perfect gas is proportional to the temperature, or that the perfect gas law says pV is proportional to T . Is this new definition equivalent? Yes, since the final result (44.7) derived from the gas law is the same as that derived here. We shall discuss this point again in the next chapter.

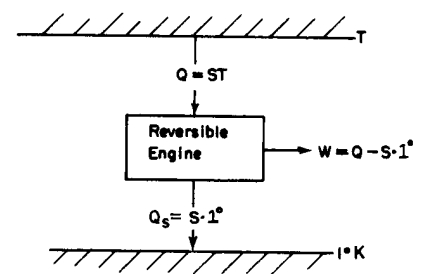


Fig. 44-9. Absolute thermodynamic temperature.

We begin. To obtain our first conclusion, we shall combine both laws, the law of conservation of energy and this law which relates the heats Q_2 and Q_1 , and we can easily obtain *the efficiency of a reversible engine*. From the first law, we have $W = Q_1 - Q_2$. According to our new principle,

$$Q_2 = \frac{T_2}{T_1} Q_1,$$

so the work becomes

$$W = Q_1 \left(1 - \frac{T_2}{T_1}\right) = Q_1 \frac{T_1 - T_2}{T_1}, \quad (44.13)$$

which tells us the efficiency of the engine—how much work we get out of so much heat. The efficiency of an engine is proportional to the difference in the temperatures between which the engine runs, divided by the higher temperature:

$$\text{Efficiency} = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1}. \quad (44.14)$$

The efficiency cannot be greater than unity and the absolute temperature cannot be less than zero, absolute zero. So, since T_2 must be positive, the efficiency is always less than unity. That is our first conclusion.

44-6 Entropy

Equation (44.7) or (44.12) can be interpreted in a special way. Working always with reversible engines, a heat Q_1 at temperature T_1 is “equivalent” to Q_2 at T_2 if $Q_1/T_1 = Q_2/T_2$, in the sense that as one is absorbed the other is delivered. This suggests that if we call Q/T something, we can say: in a reversible process as much Q/T is absorbed as is liberated; there is no gain or loss of Q/T . This Q/T is called *entropy*, and we say “there is no net change in entropy in a reversible cycle.” If T is 1° , then the entropy is $Q/1^\circ$ or, as we symbolized it, $Q_S/1^\circ = S$. Actually, S is the letter usually used for entropy, and it is numerically equal to the heat (which we have called Q_S) delivered to a 1° -reservoir (entropy is not itself a heat, it is heat divided by a temperature, hence it is measured in *joules per degree*).

Now it is interesting that besides the pressure, which is a function of the temperature and the volume, and the internal energy, which is a function of temperature and volume, we have found another quantity which is a function of the condition, i.e., the entropy of the substance. Let us try to explain how we compute it, and what we mean when we call it a “function of the condition.” Consider the system in two different conditions, much as we had in the experiment where we did the adiabatic and isothermal expansions. (Incidentally, there is no need that a heat engine have only two reservoirs, it could have three or four different temperatures at which it takes in and delivers heats, and so on.) We can move around on a pV diagram all over the place, and go from one condition to another. In other words, we could say the gas is in a certain condition a , and then it goes over to some other condition, b , and we will require that this transition, made from a to b , be reversible. Now suppose that all along the path from a to b we have little reservoirs at different temperatures, so that the heat dQ removed from the substance at each little step is delivered to each reservoir at the temperature corresponding to that point on the path. Then let us connect all these reservoirs, by reversible heat engines, to a single reservoir at the unit temperature. When we are finished carrying the substance from a to b , we shall bring all the reservoirs back to their original condition. Any heat dQ that has been absorbed from the substance at temperature T has now been converted by a reversible machine, and a certain amount of entropy dS has been delivered at the unit temperature as follows:

$$dS = dQ/T. \quad (44.15)$$

Let us compute the total amount of entropy which has been delivered. The entropy difference, or the entropy needed to go from a to b by this particular

reversible transformation, is the total entropy, the total of the entropy taken out of the little reservoirs, and delivered at the unit temperature:

$$S_b - S_a = \int_a^b \frac{dQ}{T}. \quad (44.16)$$

The question is, does the entropy difference depend upon the path taken? There is more than one way to go from a to b . Remember that in the Carnot cycle we could go from a to c in Fig. 44-6 by first expanding isothermally and then adiabatically; or we could first expand adiabatically and then isothermally. So the question is whether the entropy change which occurs when we go from a to b in Fig. 44-10 is the same on one route as it is on another. *It must be the same*, because if we went all the way around the cycle, going forward on one path and backward on another, we would have a reversible engine, and there would be no loss of heat to the reservoir at unit temperature. In a totally reversible cycle, no heat must be taken from the reservoir at the unit temperature, so the entropy needed to go from a to b is the same over one path as it is over another. It is *independent of path*, and depends only on the endpoints. We can, therefore, say that there is a certain function, which we call the entropy of the substance, that depends only on the condition, i.e., only on the volume and temperature.

We can find a function $S(V, T)$ which has the property that if we compute the change in entropy, as the substance is moved along any reversible path, in terms of the heat rejected at unit temperature, then

$$\Delta S = \int \frac{dQ}{T}, \quad (44.17)$$

where dQ is the heat removed from the substance at temperature T . This total entropy change is the difference between the entropy calculated at the initial and final points:

$$\Delta S = S(V_b, T_b) - S(V_a, T_a) = \int_a^b \frac{dQ}{T}. \quad (44.18)$$

This expression does not completely define the entropy, but rather only the *difference* of entropy between two different conditions. Only if we can evaluate the entropy for one special condition can we really define S absolutely.

For a long time it was believed that absolute entropy meant nothing—that only differences could be defined—but finally Nernst proposed what he called the *heat theorem*, which is also called the third law of thermodynamics. It is very simple. We will say what it is, but we will not explain why it is true. Nernst's postulate states simply that the entropy of any object at absolute zero is zero. We know of one case of T and V , namely $T = 0$, where S is zero; and so we can get the entropy at any other point.

To give an illustration of these ideas, let us calculate the entropy of a perfect gas. In an isothermal (and therefore reversible) expansion, $\int dQ/T$ is Q/T , since T is constant. Therefore (from 44.4) the change in entropy is

$$S(V_a, T) - S(V_b, T) = Nk \ln \frac{V_a}{V_b},$$

so $S(V, T) = Nk \ln V$ plus some function of T only. How does S depend on T ? We know that for a reversible adiabatic expansion, *no heat is exchanged*. Thus the entropy does not change even though V changes, provided that T changes also, such that $TV^{\gamma-1} = \text{constant}$. Can you see that this implies that

$$S(V, T) = Nk \left[\ln V + \frac{1}{\gamma - 1} \ln T \right] + a,$$

where a is some constant independent of *both* V and T ? [a is called the chemical constant. It depends on the gas in question, and may be determined experimentally from the Nernst theorem by measuring the heat liberated in cooling and condensing

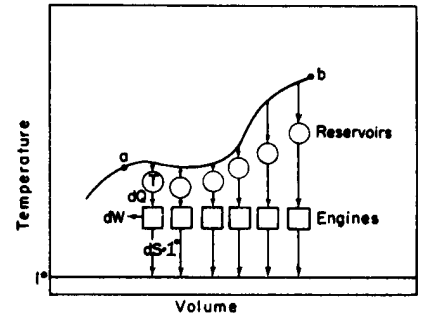


Fig. 44-10. Change in entropy during a reversible transformation.

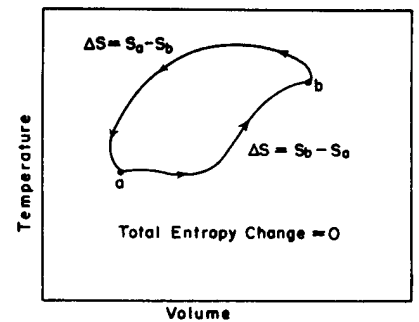


Fig. 44-11. Change in entropy in a completely reversible cycle.

the gas until it is brought to a solid (or for helium, a liquid) at 0° , by integrating $\int dQ/T$. It can also be determined theoretically by means of Planck's constant and quantum mechanics, but we shall not study it in this course.]

Now we shall remark on some of the properties of the entropy of things. We first remember that if we go along a reversible cycle from a to b , then the entropy of the substance will change by $S_b - S_a$. And we remember that as we go along the path, the entropy—the heat delivered at unit temperature—increases according to the rule $dS = dQ/T$, where dQ is the heat we remove from the substance when its temperature is T .

We already know that if we have a reversible *cycle*, the total entropy of everything is not changed, because the heat Q_1 absorbed at T_1 and the heat Q_2 delivered at T_2 correspond to equal and opposite changes in entropy, so that the net change in the entropy is zero. So for a reversible cycle there is no change in the entropy of anything, including the reservoirs. This rule may look like the conservation of energy again, but it is not; it applies only to reversible cycles. If we include irreversible cycles there is no law of conservation of entropy.

We shall give two examples. First, suppose that we do irreversible work on an object by friction, generating a heat Q on some object at temperature T . The entropy is increased by Q/T . The heat Q is equal to the work, and thus when we do a certain amount of work by friction against an object whose temperature is T , the entropy of the whole world increases by W/T .

Another example of irreversibility is this: If we put together two objects that are at different temperatures, say T_1 and T_2 , a certain amount of heat will flow from one to the other by itself. Suppose, for instance, we put a hot stone in cold water. Then when a certain heat ΔQ is transferred from T_1 to T_2 , how much does the entropy of the hot stone change? It decreases by $\Delta Q/T_1$. How much does the water entropy change? It increases by $\Delta Q/T_2$. The heat will, of course, flow only from the higher temperature T_1 to the lower temperature T_2 , so that ΔQ is positive if T_1 is greater than T_2 . So the change in entropy of the whole world is positive, and it is the difference of the two fractions:

$$\Delta S = \frac{\Delta Q}{T_2} - \frac{\Delta Q}{T_1}. \quad (44.19)$$

So the following proposition is true: in any process that is irreversible, the entropy of the whole world is increased. Only in reversible processes does the entropy remain constant. Since no process is absolutely reversible, there is always at least a small gain in the entropy; a reversible process is an idealization in which we have made the gain of entropy minimal.

Unfortunately, we are not going to enter into the field of thermodynamics very far. Our purpose is only to illustrate the principal ideas involved and the reasons why it is possible to make such arguments, but we will not use thermodynamics very much in this course. Thermodynamics is used very often by engineers and, particularly, by chemists. So we must learn our thermodynamics in practice in chemistry or engineering. Because it is not worth while duplicating everything, we shall just give some discussion of the origin of the theory, rather than much detail for special applications.

The two laws of thermodynamics are often stated this way:

First law: the energy of the universe is always constant.

Second law: the entropy of the universe is always increasing.

That is not a very good statement of the second law; it does not say, for example, that in a reversible cycle the entropy stays the same, and it does not say exactly what the entropy is. It is just a clever way of remembering the two laws, but it does not really tell us exactly where we stand. We have summarized the laws discussed in this chapter in Table 44-1. In the next chapter we shall apply these laws to discover the relationship between the heat generated in the expansion of a rubber band, and the extra tension when it is heated.

Table 44-1

Summary of the laws of thermodynamics

First law:

Heat put into a system + Work done on a system = Increase in internal energy of the system:

$$dQ + dW = dU.$$

Second law:

A process whose *only* net result is to take heat from a reservoir and convert it to work is impossible.

No heat engine taking heat Q_1 from T_1 and delivering heat Q_2 at T_2 can do more work than a reversible engine, for which

$$W = Q_1 - Q_2 = Q_1 \left(\frac{T_1 - T_2}{T_1} \right).$$

The entropy of a system is defined this way:

(a) If heat ΔQ is added reversibly to a system at temperature T , the increase in entropy of the system is $\Delta S = \Delta Q/T$.

(b) At $T = 0$, $S = 0$ (*third law*).

In a *reversible change*, the total entropy of all parts of the system (including reservoirs) does not change.

In *irreversible change*, the total entropy of the system always increases.