law be expressed except mathematically? Every form of energy we have discussed is known *only* as a function of other variables, and I have been careful to say internal energy *function*, potential energy *function*, etc. Functions are *pencil-and-paper* constructs. I can't show you a function that has any other substance, and that is why I can't show you a chunk of energy or why I can't define it or tell you what it is. It is just mathematical or abstract or just a group of numbers. Thus we have no energy meters, no device we can stick into a system which will record its energy. The whole thing is man-made.

What we have is a scheme with a set of rules. The scheme involves only changes in the energy functions. It is set up this way because we have no way to calculate absolute values of our energy functions. The remarkable thing about this scheme is its enormous generality. It applies equally to the very small and to the very large; it applies over any time interval, short or long; it applies to living matter as well as to dead. It applies in the quantum-mechanical and relativistic realm as well as in the classical. It just plain works. We can never be absolutely sure that it will always work, but we are sufficiently confident so that with it we make all sorts of predictions, and that is its use.

2 The Concept of Reversibility

In Chap. 1 I talked about energy and its conservation from a very general point of view. I tried to show how we go about the business of accounting for energy. We ended with a scheme and a set of rules—a *formalism*. Now this formalism is something we have created to serve our own ends, but it has built-in limitations which derive from the fact that energy is not a thing, like a sugar cube or a jelly bean. My point is that this particular formalism may not be appropriate for just any old system we might select in applications of the law of conservation of energy. The law itself is, of course, always right, but the particular formalism used to express it may present difficulties if the system is not selected with care.

For example, consider a block of steel acted upon by a force F so that it slides at uniform velocity over another piece of steel, as shown in Fig. 2-1. Let us apply our formal-

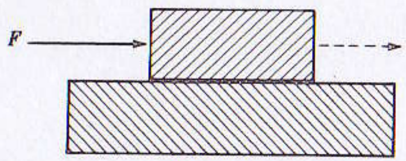

Figure 2-1

ism to the first block taken as the system. This block is shown in Fig. 2-2 along with the forces that act on it along

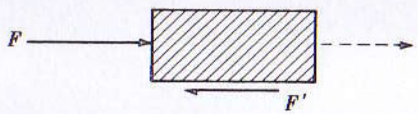

Figure 2-2

the line of its motion. Since the velocity of the block is uniform, the frictional force F' must be equal and opposite to the applied force F. Thus

$$F - F' = 0$$

and there is no net force on the block. Since the work done on the block is equal to the net force times the distance through which it moves, we conclude that the net work done on the block is zero. The First Law of Thermodynamics as we have expressed it may be written for the block as

$$\Delta U = Q - W$$

where ΔU is the internal energy change of the block, Q is the heat added to the block, and W is the net work done by the block. But $W = 0$, and therefore

$$\Delta U = Q$$

This result says that the internal energy change of the block is equal to the heat transferred to the block from the surroundings. Remember that Q is a term which is included to account for energy changes in the surroundings. However, we call it *heat* because it is energy transferred across the boundary of the system as a result of a temperature difference. Now we know from experience that the temperature of the sliding block increases, and this increases its internal energy. According to our equation this implies a transfer of heat to the block from the surroundings, which would then necessarily be at a higher temperature than the block. But there is no mechanism by which the temperature of the surroundings is raised above that of the system (the moving block). Thus if Q has the significance we have attached to it, the equation must be wrong, and if the equation is correct, we must redefine Q. The formalism we have developed simply does not apply to the *particular* system chosen in this example. Our choice was such as to make the system boundary the site of a transformation of energy. The mechanism is friction, and the friction occurs at the boundary separating the system from the surroundings. This always leads to embarrassment.

We can either abandon the formalism or select a new system. Usually, we take the latter course and pick a different system. In this case we may take both blocks as the system. This serves to put the friction *inside* the system. Figure 2-3 shows our new system and the force F acting on it. Both block 1 and block 2 experience changes in internal

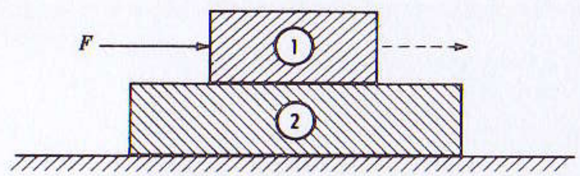

Figure 2-3

energy, and we write our First Law equation as

$$\Delta U_1 + \Delta U_2 = Q - W$$

The work W is simply the work done by the force F as it moves a distance Δs. This work is negative (done on the system); thus we write $W = -F\,\Delta s$. Therefore,

$$\Delta U_1 + \Delta U_2 = Q + F\,\Delta s$$

In this equation Q is not heat transfer between the blocks, but heat transfer from both blocks to their surroundings. We now have an entirely proper equation and have avoided any embarrassment. On the other hand, we cannot by thermodynamics alone evaluate ΔU_1, ΔU_2, or Q. Thermodynamics just tells us what terms we need to take into account, and it gives us an equation relating the terms.

With this illustration I've tried to make two major points. First, we must use judgment in the selection of a system if we expect to use the formalism by which the First Law is normally expressed. Second, many problems cannot be solved by thermodynamics alone.

Another apparently simple device encountered endlessly in thermodynamics is the piston-and-cylinder combination, as shown in Fig. 2-4 (we usually consider a gas to be trapped in the cylinder). If embarrassments of the kind encountered with the sliding block are to be avoided here, we must assume that the piston moves in the cylinder without fric-

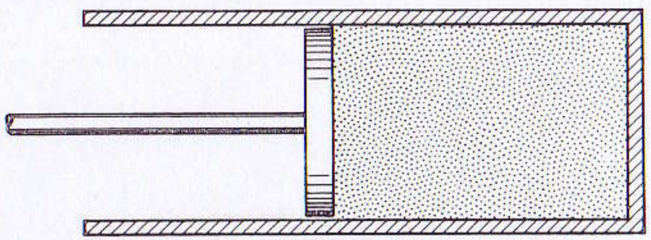

Figure 2-4

tion. This is good for all sorts of trivial applications of thermodynamics, but it can also be used to illustrate a number of very important concepts; we will use it extensively for this purpose.

Imagine that we have such a piston-and-cylinder combination and that a weight w is placed on the piston to hold a gas under compression in the cylinder. This initial state of the system is shown on the left in Fig. 2-5. We will

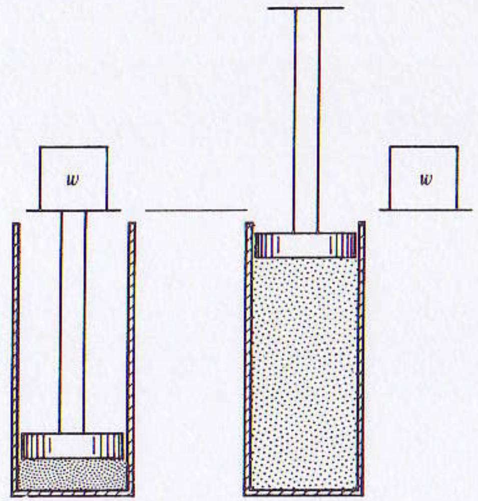

Figure 2-5

assume that the piston is so perfectly lubricated that it can move without friction in the cylinder. In addition, we will assume that the piston and cylinder are constructed of a special material that is a perfect heat insulator. Thus there can be no heat transfer between the gas and its surroundings. Any such process is said to be *adiabatic.*

We wish to use the compressed gas in the cylinder to accomplish useful work, and the question is how to carry out a process so that we may obtain the maximum possible useful work. Raising the weight w will be considered the object of the process and will thus constitute the performance of useful work. Since the initial state as shown in Fig. 2-5 is one of equilibrium, it is clear that the piston will not move unless the weight w is removed from the piston. Imagine that the weight is struck from the side so as to cause it to slide suddenly to an adjacent shelf. The piston, of course, shoots upward and after a period of up-and-down oscillation settles into a final equilibrium position, as shown on the right in Fig. 2-5. On the other hand, the weight w has not been raised, and no purpose has been served by the process. We must do things differently.

We decide to divide the weight into two parts so that we need not remove all of it from the piston at once. Again we start with the piston held in position by the weight w, as shown in Fig. 2-6. This time we slide only $\frac{1}{2}w$ off the piston to an adjacent shelf. The piston again shoots upward and eventually comes to rest in a new equilibrium position,

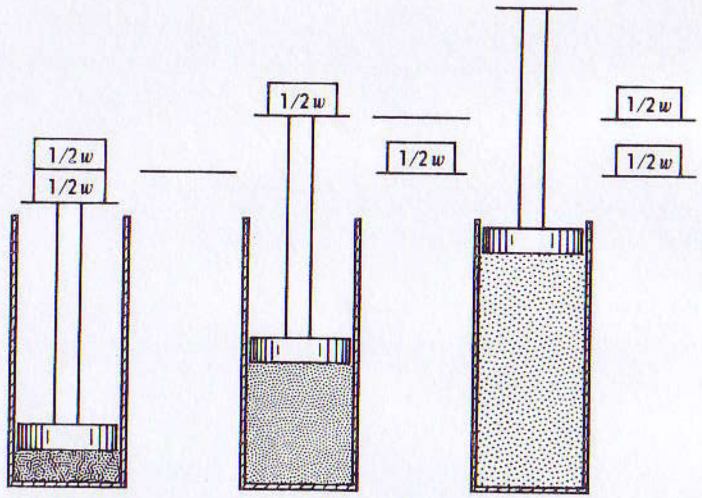

Figure 2-6

but this time it has carried half the weight w with it. This $\frac{1}{2}w$ may now be pushed off to another shelf, and the piston is again free to find a new final position. All three stages of this process are shown in Fig. 2-6. Clearly, a weight has been raised; the process has been of some use. Half of the weight w has been raised somewhere near half the distance of the piston stroke. But is this the best we can do? What if we divide up the weight into much smaller bits and use, for example, a pile of sand? We might imagine flicking grains of sand off the pile one by one and having them stick to a sheet of flypaper. Various stages of this process are depicted in Fig. 2-7. The removal of each grain of sand

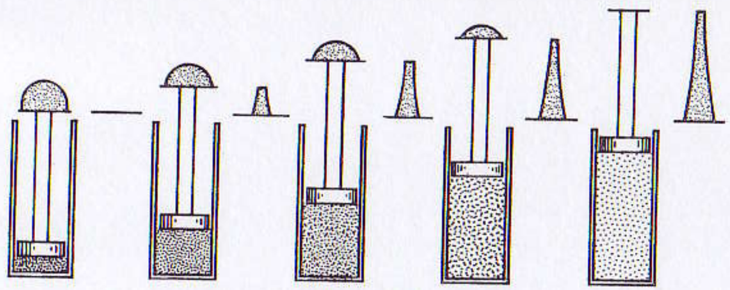

Figure 2-7

from the piston causes very little change in the system. The piston moves but a very small distance at a time, and there is but the slightest oscillation of the piston as it finds a new equilibrium position only a hair above its previous position. Clearly the final grain of sand is carried with the piston almost to the end of its stroke, and in the end we have raised all the weight w (the sand) an average distance of something like half the stroke of the piston.

All we can do to improve on this last process is to use a finer sand and in the limit to make the grains infinitesimal or vanishingly small in size. Then the process is carried out in differential steps, and we can only imagine it. Such an imaginary process would improve but slightly upon the one just described. But it does represent the limit of what can be done by way of improving the process and thus providing the maximum possible work, and as such it is worthy of our close attention.

This imaginary process is called *reversible* because at any point it could be turned around and made to go the other way simply by replacing the infinitesimal grains of sand on the piston. Only one *additional* infinitesimal grain of sand would be needed to start the reverse process. Then the particles previously removed from the piston could be placed back on the piston at exactly the same level they had on the flypaper. In other words, only a differential change in conditions would be required to reverse the process, and then the reverse process would carry the system back to its initial state, leaving only a minute or differential change in the surroundings.

The reversible process is unique, and as such occupies a position of essential importance in thermodynamics. The reason for this is that it represents the *limit* of what is possible in the real world. We cannot even imagine anything better. Moreover, it lends itself to exact mathematical analysis, and this is not true of any other process. Our choice in thermodynamics often is to do calculations for reversible processes or to do no calculations at all. The reason for this is that reversible processes are those for which the forces causing change are almost exactly in balance. Thus the states through which the system passes during a reversible process are for all practical purposes equilibrium states, or more precisely are never removed more than differentially from equilibrium states. The importance of this observation is demonstrated by the following considerations. The work done in raising a weight is given by $\int F\,ds$, where F is the force of gravity on the weight and s is the elevation of the weight above some arbitrary

but fixed datum level. Now if we wish to calculate the work done *by the gas* in any of the processes described earlier, the force F must be the gravitational force acting downward on all of the mass supported by the gas at pressure P. This mass includes that of the piston, the piston rod, the pan, the weight w, and the atmosphere above the piston. In the case of the reversible process this force F is never more than minutely out of balance with the force exerted upward on the piston face by the gas and given by the product of pressure and the piston area. Thus, for all practical purposes, $F = PA$ for the reversible process. In addition, the volume change of the gas (the system) is always given by $dV = A\,ds$. Thus $ds = dV/A$, and the work done by the gas is

$$W = \int F\,ds = \int PA\,\frac{dV}{A} = \int P\,dV$$

Thus if we can substitute PA for F, we can calculate the work from knowledge of the system without knowing anything about what happens in the surroundings. This substitution is possible only for reversible processes where the forces are never more than differentially out of balance.

For irreversible processes this substitution is not possible. When a finite weight is removed from the piston in the processes described, the force of gravity acting downward is overbalanced by the gas pressure acting upward by a finite amount, and F does not equal PA again until a new equilibrium position of the piston is reached. Thus PA cannot be substituted in the integral $\int F\,ds$, and it is not possible to calculate the work from a knowledge of the properties of the system. Thus we have the important result that the work done by the system (the gas) is given by $\int P\,dV$ only when the process is reversible; that is,

$$W_{\text{rev}} = \int_{V_1}^{V_2} P\,dV$$

Moreover, this work for an expansion process is the maximum work which the system can produce. If we were to consider the compression of a gas by a piston in a cylinder, we would obtain the same results except that the reversible work would be the minimum work required for compression of the gas. The difference is, of course, that a compression process is carried out by work done *on* the system, whereas an expansion process results in work done *by* the system. In either case the reversible work is a limiting value, i.e., the maximum obtainable when work is produced and the minimum required when work is expended.

If we were to sit down to flick grains of sand one by one off a piston, we would have to be very patient indeed in order to wait out any appreciable change in our system. If the grains of sand were made infinitesimal, any finite process would require an infinite time. This is characteristic of all reversible processes; we must imagine them to proceed infinitely slowly. This is consistent with the fact that they are imagined to be driven by an infinitesimal imbalance of forces.

We assumed our piston-and-cylinder processes to occur without friction for a very good reason. Without this assumption we could not even imagine a reversible process. If there were friction between the piston and the cylinder, the piston would stick, and we would always have to remove a finite amount of sand from the piston before it would move at all. Then it would move in jumps, and the condition of virtual balance of forces which allows us to substitute PA for F would be violated.

The other assumption we made was that the process was adiabatic, i.e., that there was no heat transfer. This assumption was made merely for convenience, so that we could concern ourselves with just the mechanical aspects of the process. It is entirely possible to imagine reversible heat transfer. The driving force for heat transfer is a temperature difference, and for reversible heat transfer we need only imagine that this temperature difference becomes infinitesimal. Thus heat is transferred reversibly when it flows from an object (or a system) at temperature T to another object (or the surroundings) at temperature $T - dT$.

The concept of reversibility is essential to the subject of thermodynamics. Its abstract nature in no way destroys its practical utility, as I hope to demonstrate in the next chapter.