

Understanding Thermodynamics

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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

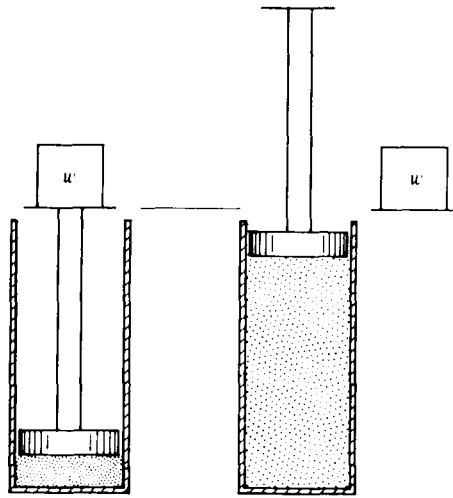


Figure 2-5

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,

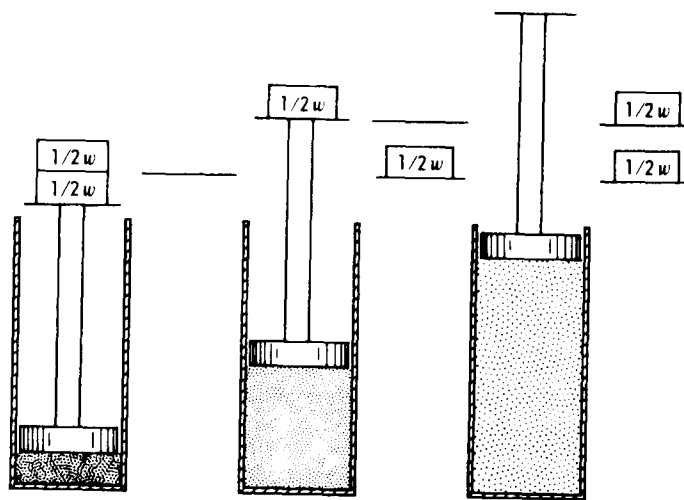


Figure 2-6

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

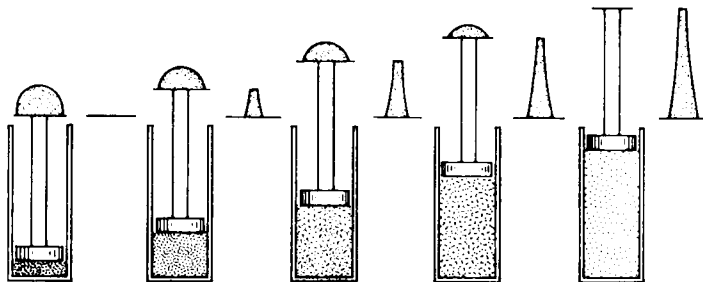


Figure 2-7

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 maxi-

mum 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 infi-

tesimal. 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.