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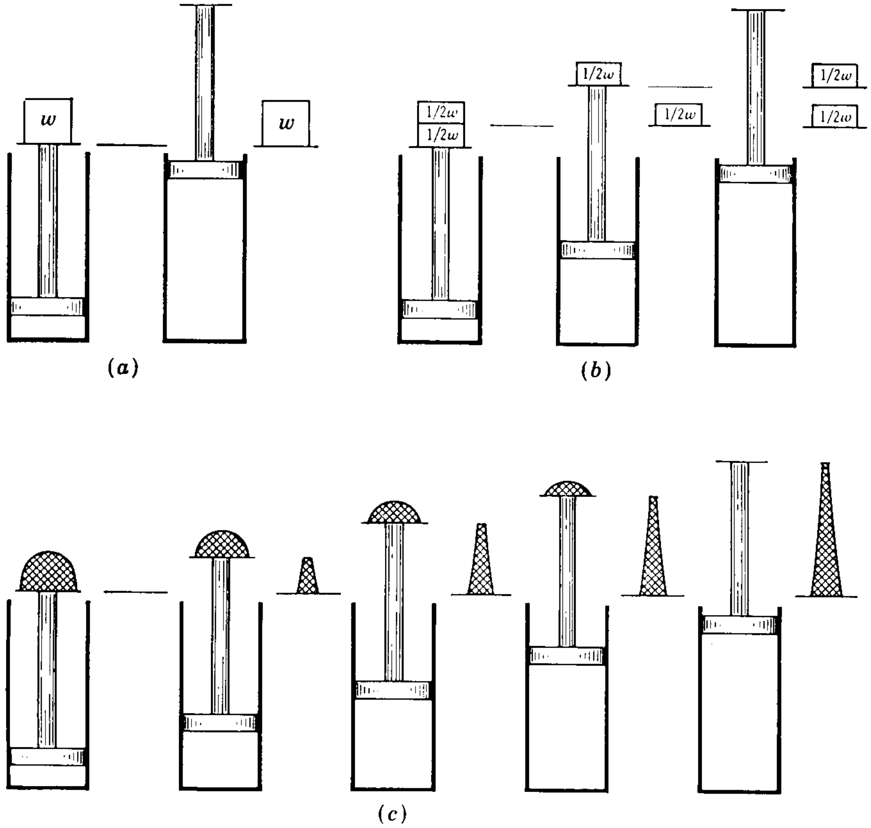
2-9. The Reversible Process. Important thermodynamic features of a process are revealed by considering how the process can be carried out to yield the maximum work. This problem will be studied in terms of a gas expanding against a piston. Suppose a pair of simplifying assumptions are made in order to focus attention on the problem at hand:

1. The cylinder and piston will neither absorb nor transmit heat, so that the effects of heat transfer need not be considered.



(a) (b)

(c)

FIG. 2-3. Irreversible and reversible expansion processes.

2. The piston moves within the cylinder without friction, so that the possibility of mechanical inefficiencies is removed.

The apparatus is shown in Fig. 2-3. The system will be chosen so as to include only the gas. All else constitutes the surroundings. The object is to allow the process to take place in such a way as to raise a weight, thereby accomplishing useful work in the surroundings.

Consider first Fig. 2-3a. The piston is shown inserted far into the cylinder where it confines a gas at a pressure just sufficient to balance the weight of the piston, the atmosphere, and the weight *w*. This is a condition of equilibrium, for the system has no tendency to change. The weight must be removed if the piston is to rise. Imagine in this first alternative that the weight is suddenly slid from the piston to a shelf that is placed close by and at the same level. The piston rises and eventually reaches a new condition of equilibrium such that the pressure exerted by the gas is just sufficient to balance the weight of the piston and atmosphere. The system has undergone a change; the pressure of the gas is lower, and the piston has been elevated. However, no useful work has been accomplished for the weight is still at the same level as before. Work has been done in elevating the piston and in pushing back the atmosphere, but this is hardly useful.

In an improved process shown in Fig. 2-3*b* the weight *w* is divided into two parts. Initially the piston is depressed as before, but this time only half of the weight is slid over to the shelf. The piston rises roughly half the distance and eventually assumes an equilibrium position. The second half of the weight is then slid from the piston to another conveniently located shelf as shown, and the piston completes its stroke. This process is an improvement over the first one since part of the weight has been raised roughly half the distance of the piston's travel, and useful work has been accomplished.

As the removal of the weight in two parts effected an improvement in the process, it is only logical to assume that a further division of the weight into parts would result in even greater improvement. The ultimate extension of this idea would require a weight made up of differential elements. A close approach to this is to imagine the weight to be replaced by a pile of fine sand. This situation is shown in Fig. 2-3*c*. The grains of sand are removed one at a time and piled in such a way as to remain at the level at which they are removed from the piston. Various stages of the process are represented in the figure. The removal of a grain of sand causes very little change, and equilibrium is restored by only a minute adjustment of the system after each grain is removed. This system is never more than slightly out of balance, never more than slightly removed from equilibrium. As a result, the pile of sand reaches almost the full height of the piston's travel. On the average, all the weight has been raised slightly less than half the distance of the piston's stroke. The only further improvement possible would be obtained if the grains of sand were made infinitesimal in size. It is worthwhile to study the implications of this optimum process, accomplished in differential steps.

The process carried out in this manner yields the maximum possible work that can be obtained under the conditions imposed on the system. In no other way can the process be used to full advantage. This system is always at equilibrium, or at least no more than differentially removed from equilibrium. If the removal of sand from the piston is stopped at any point in the process and sand transferred from the pile to the piston instead, the process would reverse itself and retrace the exact path it had followed up to that point. The piston would be returned to its original position by replacing the sand, grain by grain, taking it always from the pile at the level of the piston. In other words, the system could be restored to its original condition merely by making use of the work it had already accomplished in raising the sand. Not only would the system be restored to its original condition, but so would the surroundings. This kind of process is termed *reversible.*

The two procedures described in Fig. 2-3*a* and *b* are *irreversible.* The first one produced no work; therefore none was available for returning the piston to its original position. This could be accomplished only through the use of *extra* work which would come from the surroundings and which would therefore produce some change in the surroundings. The same thing can be said about the second process, though it was more efficient than the first since it produced some useful work. However, some *extra* work would be required to return the piston to the level of the raised weight where it could be used to force the piston back to its initial position.

The reversible process is an ideal one in that it can be approached but never actually realized. It is of practical importance, nevertheless, for it represents the limit of what may be accomplished by actual processes. In thermodynamics, the calculation of work is usually made for ideal systems, because such systems lend themselves completely to mathematical analysis. Often, the choice is between calculations for an ideal system and no calculations at all. Moreover, the results of calculations obtained for ideal systems may be easily combined with various efficiencies to give good approximations of the work for actual processes. The selection of these efficiencies requires knowledge of a practical nature acquired through experience.

It was shown in Sec. 1-11 that the work of compression or expansion of a gas caused by the movement of a piston in a cylinder can be calculated by the equation

$$W = \int_{V_1}^{V_2} p\,dV \tag{1-5}$$

Even if the integral in this equation could be evaluated for each of the processes described and shown in Fig. 2-3, it would not equal the work appearing in the surroundings except for the case of the reversible expansion. This can be made clear by the following analysis. The work done on the surroundings in each case appears as an increase in the potential energy of the material supported by the gas. By definition, this equals $F\,ds$, where F is the force of gravity on all the material supported by the gas. This includes the piston, the material on it, and the atmosphere. In the case of the reversible process, this force is never more than differentially out of balance with the pressure of the gas. Therefore, it may be described in terms of the internal pressure acting on the piston, that is, $F = pA$, and Eq. (1-5) is then obtained. The situation is different in the case of the irreversible processes. The moment a finite weight is removed from the piston, the force of gravity acting downward is overbalanced by the pressure of the gas by a finite amount, and F does not again equal pA until a new equilibrium position is reached. Thus pA cannot be substituted for F, and Eq. (1-5) does not hold. The conclusion is that W is identical with $\int p\,dV$ only for a reversible process. In other words, the work appearing in the surroundings can be evaluated from the properties of the *system* only for reversible processes. Of course, it may be possible to determine the work from the effects in the *surroundings*.

Attention should be called to other aspects of reversible processes. The removal of sand from the piston in the last process described was accomplished grain by grain, thus requiring a very long time. For the truly reversible process where the weight is removed in differential increments, an infinite time is required. Indeed, this is the case for all reversible processes; they proceed infinitely slowly. That this must be the case should be evident from the fact that only differential driving forces are involved.

It will be recalled that the processes considered were assumed to take place without friction. Without this assumption, it would not have been possible to devise a reversible process. Assume for a moment that the piston is not frictionless. The removal of a finite amount of sand would be required before the piston could move, for friction would cause the piston to stick. Thus the equilibrium condition necessary for a reversible process could not be maintained.

An irreversible process does not produce the maximum work. One may well ask what happens to the potentially available but unobtained work and how it is "lost." A complete answer must await the development of the second law of thermodynamics, but some indication of the answer can be given here. The common phenomenon of friction, which accompanies an irreversible process, is a mechanism for transforming mechanical energy into internal energy. Some of this energy must eventually be transferred, as heat, to the surroundings. It is in this sense that work is lost. Energy is not lost, but simply appears in a form other than mechanical energy in the system and surroundings. In the case of irreversible expansions with frictionless pistons, work is lost, not by mechanical rubbing, but by the stirring of the gas. This stirring or mixing is caused by the rapid expansion of the gas after the sudden removal of a weight and by the oscillations of the free piston as it settles down to its new equilibrium position. This effect, called *turbulence*, decreases the work produced, for stirring always requires work just as it did in Joule's experiments.

The discussion of reversible processes has centered around a single type of process: the expansion of a gas in a cylinder, where the potentials or driving forces involved are fluid pressures and mechanical forces. The reverse process, compression of a gas in a cylinder, is much the same. However, in this case work is done *on* the system rather than *by* the system, and the ideal or reversible process is the one that requires a *minimum* expenditure of work rather than the one that yields a *maximum*. In both cases, it is the reversible work that is given by the integral $\int_{V_1}^{V_2} p\,dV$.

There are many processes which occur under the impulse of potentials other than pressure or mechanical forces. For example, heat flow occurs when a temperature difference exists; electricity flows under the influence of electromotive force; and chemical reactions occur because a chemical potential exists. In general, a process is reversible when the net force driving it is only differential in size. Thus heat is transferred reversibly when it flows from an object at temperature T to another object at temperature $T - dT$.

The concept of a reversible chemical reaction may be illustrated by the decomposition of calcium carbonate. If this substance is heated, it decomposes to form calcium oxide and carbon dioxide gas. At equilibrium, this system consists of three phases, two solid and one gas phase, and two components. Application of the phase rule shows that there is but one degree of freedom. Thus fixing the temperature fixes the pressure also, just so long as all three phases remain. This means that for every temperature calcium carbonate exerts a definite decomposition pressure of CO_2 and that, when the pressure tends to fall below this value, $CaCO_3$ will decompose. Assume now that a cylinder is fitted with a frictionless piston and contains an equilibrium mixture of $CaCO_3$, CaO, and CO_2. It is immersed in a constant-temperature bath as shown in Fig. 2-4, with the temperature adjusted to a value such that the dissociation pressure of $CaCO_3$ is just sufficient to balance the weight on the piston. The piston is in balance, the temperature of the reaction mixture is equal to that of the bath, and the chemical reaction is held in balance

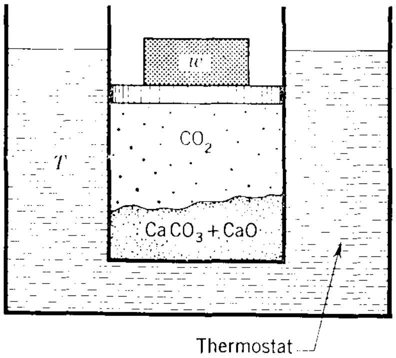


FIG. 2-4. Reversibility of a chemical reaction.

by the pressure of the CO_2. Any alteration of conditions, however slight, will upset the equilibrium and cause the reaction to proceed in one direction or the other. If the weight is differentially increased, the CO_2 pressure will be raised differentially, and CO_2 will combine with CaO to form $CaCO_3$, allowing the weight to fall slowly. The heat given off by this reaction will tend to raise the temperature in the cylinder, and heat will flow to the bath. Decreasing the weight differentially sets off the opposite chain of events. The same results are obtained by raising or lowering the temperature of the bath. If the temperature of the bath is raised differentially, heat flows into the cylinder, where it decomposes calcium carbonate. The CO_2 generated causes the pressure to rise differentially, which in turn raises the piston and weight. This will continue until the $CaCO_3$ has been completely decomposed. The process is reversible, for the system is never more than differentially displaced from equilibrium, and only a differential lowering of the temperature of the bath will cause the system to return to its initial state. Since p is constant, the work done equals $p \, \Delta V$.

The observable results of the chemical potential in the previous example were temperature and pressure driving forces. Consider another reaction system in which the chemical potential is manifested as an electromotive force. Suppose metallic zinc is brought into contact with an aqueous solution of hydrochloric acid at atmospheric pressure in a cylinder equipped with a frictionless piston. As the chemical reaction occurs, the hydrogen evolved pushes the piston against the atmosphere. However, no useful work is accomplished, and the process cannot be reversed with only differential changes in the conditions of the system and surroundings. On the other hand, suppose the apparatus is arranged in the form of an electrolytic cell, with the metallic zinc as one electrode and platinum as the other. The electrodes are connected to an external circuit. When the electrodes are dipped in the acid solution, an emf is produced which can be utilized to accomplish work. The amount of this work depends upon the characteristics of the external circuit. If there is no counter emf to that produced by the cell, no useful work will result and the process is still irreversible. On the other hand, if the counter voltage is only differentially less than that of the cell, a maximum amount of work is produced. The chemical potential of the reaction is balanced by the electrical potential of the external circuit, and the process occurs reversibly. By increasing the counter emf differentially, the reaction will proceed in the reverse direction, taking electrical energy from the surroundings and plating out zinc on the electrode.

In summary, a reversible process is frictionless; it is never more than differentially removed from equilibrium; the driving forces are differential in magnitude; and the process can be reversed, leaving no change in the system or surroundings.

Example 2-8. A horizontal piston-and-cylinder arrangement is placed in contact with a constant-temperature bath. The piston slides in the cylinder with negligible friction, and an external force holds it in place against an initial gas pressure of 200 psia. The initial gas volume is 1 ft³. The external force on the piston is to be reduced gradually, allowing the gas to expand, until its volume doubles. Under these conditions it has been determined that the volume of the gas is related to its pressure in such a way that the product pV is constant. Calculate the work done by the gas in moving the external force.

How much work would be done if the external force were suddenly reduced to half its initial value instead of being gradually reduced?

Solution. The process, carried out as first described, is a reversible one, and

$$W = \int_{V_1}^{V_2} p\,dV$$

Since

$$pV = k \text{ (a constant)} \qquad p = \frac{k}{V}$$

and

$$W = k \int_{V_1}^{V_2} \frac{dV}{V} = k \ln \frac{V_2}{V_1}$$

But

$$k = pV = p_1V_1 = (200)(144)(1) = 28{,}800 \text{ ft-lb}_f$$
$$V_1 = 1 \text{ ft}^3 \qquad \text{and} \qquad V_2 = 2 \text{ ft}^3$$

Therefore

$$W = 28{,}800 \ln 2 = 19{,}930 \text{ ft-lb}_f$$

The final pressure will be

$$p_2 = \frac{k}{V_2} = \frac{28{,}800}{2} = 14{,}400 \text{ lb}_f/\text{sq ft or } 100 \text{ psia}$$

In the second case the force exerted is constant and equivalent to a pressure of 100 psia. After half the initial force has been removed, the gas will undergo a sudden expansion. Eventually the system will return to an equilibrium condition identical with the final state attained in the reversible process. Thus ΔV will be the same as before, and the net work accomplished will equal the equivalent external pressure times the volume change, or

$$W = (100)(144)(2 - 1) = 14{,}400 \text{ ft-lb}_f$$

This process is clearly irreversible, and it demonstrates the fact that an irreversible process accomplishes less work than a reversible process for the same change in state. Compared with the reversible process, the irreversible expansion is said to have an efficiency of

$$\frac{14{,}400}{19{,}930} = 0.723, \text{ or } 72.3 \text{ per cent}$$

Example 2-9. The piston-and-cylinder arrangement shown in the accompanying figure contains nitrogen gas trapped below the piston at a pressure of 100 psia. The piston is held in place by latches as shown. The space behind the piston is evacuated.