Entropy

8.1
REVERSIBLE PART OF THE SECOND LAW

Work diagrams in which a generalized force such as P, $\mathcal{F}$, γ, $\mathcal{E}$, or $\mu_0\mathcal{H}$ is plotted against the corresponding generalized displacement V, L, A, Z, or $\mathcal{M}$ have been used to indicate processes of various systems. An isothermal process or an adiabatic process is represented by a different curve on each diagram. In this chapter, it is desired to formulate general principles that apply to all systems. If we let the symbol Y denote any generalized force and the symbol X its corresponding generalized displacement, a generalized work diagram in which Y is plotted against X may be used to depict processes common to all systems and will thus be suitable for general discussions.

Consider a reversible process represented by the smooth curve $i \rightarrow f$ on the generalized work diagram shown in Fig. 8-1. The nature of the system is not essential. The dashed curves through i and f, respectively, represent portions of adiabatic processes. Let us draw a curve $a \rightarrow b$, representing an isothermal process, in such a way that the area under the smooth curve if is equal to the area under the zigzag sequence of processes, path $iabf$. Then, the work done in traversing both paths is the same, or

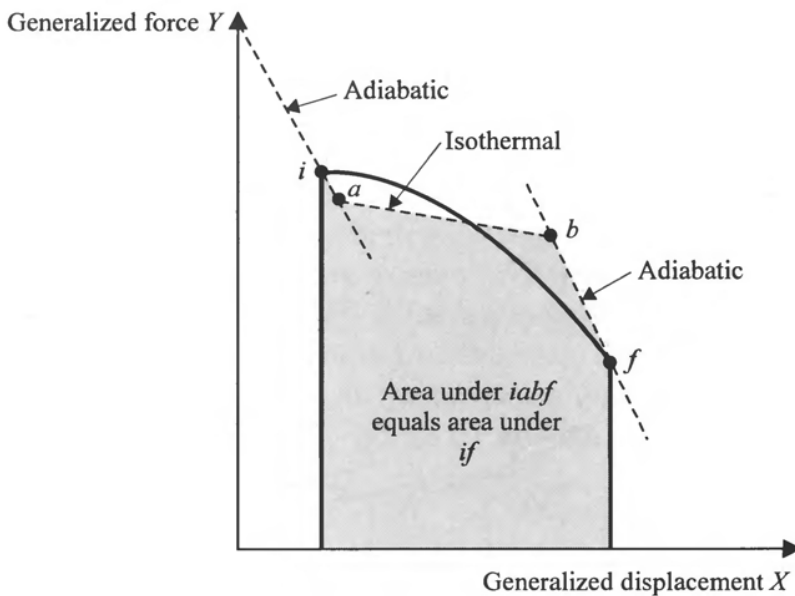$$W_{if} = W_{iabf}.$$

From the first law,

$$Q_{if} = U_f - U_i - W_{if},$$

and

$$Q_{iabf} = U_f - U_i - W_{iabf}.$$

Therefore,

$$Q_{if} = Q_{iabf}.$$

FIGURE 8-1
Generalized work diagram, where $i \to f$ is any reversible process; $i \to a$ is a reversible adiabatic process; $a \to b$ is a reversible isothermal process; and $b \to f$ is a reversible adiabatic process.

But, since no heat is transferred in the two adiabatic processes *ia* and *bf*, we have

$$Q_{if} = Q_{ab}. \tag{8.1}$$

If we are given, therefore, a reversible process in which the temperature may change in any manner, it is always possible to find a reversible zigzag path between the same two states, consisting of an adiabatic process followed by an isothermal process followed by an adiabatic process, such that the heat transferred during the isothermal segment is the same as that transferred during the original process.

Now, consider the smooth closed curve on the generalized work diagram shown in Fig. 8-2. Since no two adiabatic lines can intersect (see Prob. 6.13), a number of adiabatic lines may be drawn, dividing the cycle into a number of adjacent strips. A zigzag closed path may now be drawn, consisting of alternate adia-batic and isothermal portions, such that the heat transferred during all the isothermal portions is equal to the heat transferred in the original cycle. Consider the two isothermal processes *ab* at the temperature T_1, during which heat Q_1 is absorbed, and *cd* at the temperature T_2, during which heat Q_2 is rejected. Since *ab* and *cd* are bounded by the same adiabatic curves, *abcd* is a Carnot cycle, and we may write Eq. (7.6) as

$$\frac{|Q_1|}{T_1} = \frac{|Q_2|}{T_2}.$$

For the sake of clearness and simplicity, we have been considering only the absolute values of heat entering or leaving a system, thus ignoring the sign
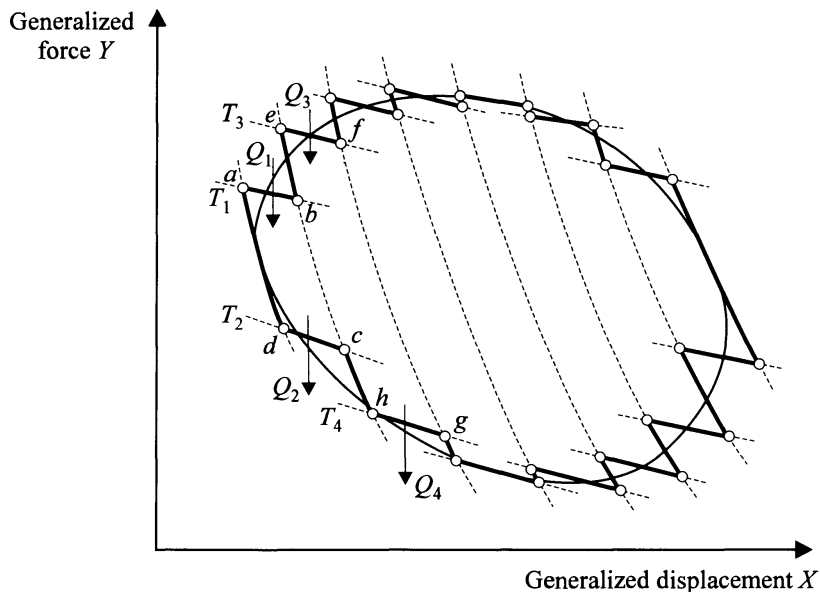
FIGURE 8-2
Generalized work diagram, where the smooth closed curve is a reversible cycle and the zigzag closed path is made up of alternating reversible isothermal and reversible adiabatic processes.

convention introduced in Chap. 4. Let us now return to the sign convention and regard any Q as an algebraic symbol, positive for heat absorbed by a system and negative for heat rejected from a system. We may then write the equation cited above as

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0,$$

where Q_1 is a positive number and Q_2 is a negative number. Since the isothermal curves ef and gh are bounded by the same two adiabatic curves, $efgh$ is also a Carnot cycle, and

$$\frac{Q_3}{T_3} + \frac{Q_4}{T_4} = 0.$$

If a similar equation is written for each pair of isothermal curves bounded by the same two adiabatic curves and if all the equations are added, then the result obtained is that

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \frac{Q_4}{T_4} + \cdots = 0.$$

Since no heat is transferred during the adiabatic portions of the zigzag cycle, we may write

$$\sum_j \frac{Q_j}{T_j} = 0, \tag{8.2}$$

where the summation is taken over the entire zigzag cycle consisting of Carnot cycles, j in number.

Now, imagine the cycle divided into a very large number of strips by drawing a large number of adiabatic curves close together. If we connect these adiabatic curves with small isothermal curves, in the manner already described, then a zigzag path may be traced that can be made to approximate the original cycle as closely as we please. When these isothermal processes become infinitesimal, the ratio $đQ/T$ for an infinitesimal isothermal between two adjacent adiabatic curves is equal to the ratio $đQ/T$ for the infinitesimal piece of the original cycle bounded by the same two adiabatic curves. In the limit, therefore, we may write for Eq. (8.2) any reversible cycle,

$$\oint_R \frac{đQ}{T} = 0.$$

(8.3)

The circle through the integral sign signifies that the integration takes place over the complete cycle, and the letter R emphasizes the fact that the equation is true only for a reversible cycle. This result, known as *Clausius' theorem*, is one part of Clausius' mathematical statement of the second law. The other part applicable to irreversible cycles will be presented in Sec. 8.8.

8.2
ENTROPY

Let an initial equilibrium state of any thermodynamic system be represented by the point i on any convenient diagram, such as the generalized work diagram of Fig. 8-3. Denote a final equilibrium state by the point f. It is possible to take the system from i to f along any number of different reversible paths, since i and f are equilibrium states. Suppose the system is taken from i to f along the reversible path R_1 and then back to i again along another reversible path R_2. The two paths form a reversible cycle, and from Clausius' theorem we may write

$$\oint_{R_1 R_2} \frac{đQ}{T} = 0.$$

The above integral may be expressed as the sum of two integrals, one for the path R_1 and the other for the path R_2. Then, we have

$$\int_{R_1} \int_i^f \frac{đQ}{T} + \int_{R_2} \int_f^i \frac{đQ}{T} = 0,$$

or

$$\int_{R_1} \int_i^f \frac{đQ}{T} = - \int_{R_2} \int_f^i \frac{đQ}{T}.$$

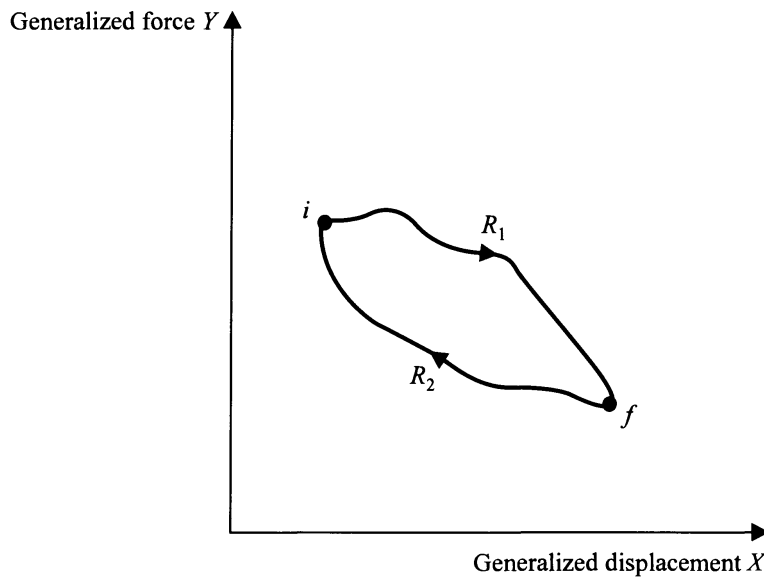Since R_2 is a reversible path,

Generalized displacement X

FIGURE 8-3
Two reversible paths joining two equilibrium states of a system.

$$- {}_{R_2}\int_f^i \frac{dQ}{T} = {}_{R_2}\int_i^f \frac{dQ}{T},$$

and, finally,

$$_{R_1}\int_i^f \frac{dQ}{T} = {}_{R_2}\int_i^f \frac{dQ}{T}. \tag{8.4}$$

Since R_1 and R_2 were chosen at random and represent *any* two reversible paths, the above equation expresses the important fact that $_R\int_i^f dQ/T$ *is independent of the reversible path connecting i and f.* Therefore, it follows from Eq. (8.4) that *there exists a function of the thermodynamic coordinates of a system whose value at the final state minus its value at the initial state equals the integral* $_R\int_i^f dQ/T$. This state function was named the *entropy* by Rudolf Clausius in 1865 and is denoted by S. If S_i is the entropy at the initial state and S_f the entropy at the final state, then we have a finite *change of entropy* $S_f - S_i$ from state i to state f, given by

$$S_f - S_i = {}_R\int_i^f \frac{dQ}{T}, \tag{8.5}$$

where the path from state i to state f is *any* reversible path R. Thus, the entropy change of the system between states i and f is independent of the path. This is a very remarkable result. Although the heat entering the system depends on the path between the states i and f, the entropy change does *not* depend on the path.

The existence of an entropy function S is deduced in the same way as that of the internal-energy function U, that is, by showing that a certain quantity is independent of choice of reversible processes connecting the initial equilibrium

state with the final equilibrium state. Both U and S are state functions, which means that the difference of either function evaluated at the final and initial equilibrium states is independent of the path connecting the two states. In neither function, however, does the defining equation enable us to calculate a single value of the function, only the difference of two values.

If the two equilibrium states i and f are infinitesimally near, then the integral sign may be eliminated and $S_f - S_i$ becomes dS, an *infinitesimal* change of entropy of the system. Equation (8.5) then becomes

$$dS = \frac{đQ_R}{T},$$

(8.6)

where dS is an exact differential, since it is the differential of an actual function and not a small inexact quantity, such as $đQ$ or $đW$. The subscript R to $đQ$ indicates that the preceding equation is true *only* if a small amount of heat $đQ$ is transferred reversibly.

When Eq. (8.6) is written in the form $đQ_R = T\,dS$, it is seen that the difficulty of dealing with the inexact differential of heat is eliminated by substituting the product of the temperature and exact differential of the entropy. This is a major advancement in the formalism of thermodynamics, comparable to replacing $đW$ with $-P\,dV$ in a hydrostatic system. Entropy S joins P, V, and T as a thermodynamic variable to be used in the development of the formalism and mathematical methods of thermodynamics.

It is instructive to calculate a unit of entropy, a joule per kelvin, in order to gain a feeling for this new variable. Consider the Joule paddle wheel apparatus shown in Fig. 8-4. The system is a kilogram of water at room temperature T. The surroundings are the adiabatic cylindrical wall and top, the
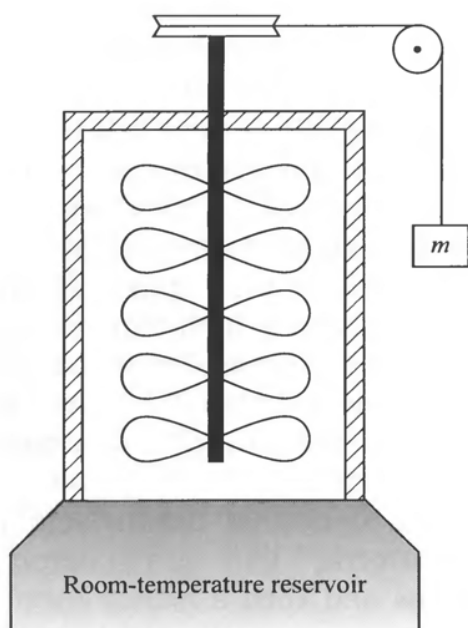

FIGURE 8-4
Joule paddle wheel apparatus, an "entropy generator."

Room-temperature reservoir

diathermic bottom in contact with a heat reservoir, also at temperature T, and the paddle wheels. A slowly falling mass m causes the paddle wheels to turn, so the portion of the boundary formed by the paddle wheels moves. The falling mass does work on the system, which tends to experience an increase in the temperature of the water. However, the diathermic bottom prevents the temperature from rising by removing energy from the system in the form of heat.

The change of entropy of the reservoir ΔS is given by

$$\Delta S = \int \frac{dQ_R}{T} = \frac{Q}{T},$$

which is also the total change of entropy for the composite system of liquid plus reservoir, since the state of the water in the apparatus is unchanged at the end of the process. Furthermore, since the temperature of the water and the volume of the water are both unchanged, the internal energy is unchanged. Thus, the work done by the falling mass equals the heat that enters the reservoir. If the paddle wheel is driven by a mass of 29.9 kg (approximately 66 lb) that falls 1 m, then the change of entropy is given by

$$\Delta S = \frac{W}{T} = \frac{(29.9 \, \text{kg})(9.8 \, \text{N/kg})(1 \, \text{m})}{293 \, \text{K}}$$
$$= 1.00 \, \text{J/K}.$$

The entropy of the mass turning the paddle wheels is not changed during the process, because no heat enters or leaves the mass. Rather, the entropy is generated by the conversion of work (done by the mass) into heat (entering the reservoir). Thus, the paddle wheel apparatus serves as an entropy generator.

8.3
PRINCIPLE OF CARATHÉODORY

We have arrived at the mathematical formulation of the second law by the historical method initiated by the engineer Carnot and elaborated by the physicists Kelvin and Clausius. They thought in terms of practical engines, ideal engines, and physical models. Starting with a statement expressing the impossibility of converting heat completely into work, or the impossibility of spontaneous heat flow from a low-temperature body to a high-temperature body, they conceived of the ideal Carnot engine having maximum thermal efficiency. With the aid of this ideal engine, an absolute thermodynamic temperature scale was defined, and the Clausius theorem was proved. On the basis of Clausius' theorem, the existence of an entropy function was deduced. From a mathematical point of view, this procedure is somewhat unsatisfactory. Mathematicians often prefer an "axiomatic treatment," that is, a statement of the minimum number of fundamental axioms and then a purely formal mathematical deduction from these axioms.