

## 8-6 Conditions for Reversibility

Most processes that occur in nature are included among the general types of process listed in the preceding articles. Living processes, such as cell division, tissue growth, etc., are no exception. If one takes into account all the interactions that accompany living processes, such processes are irreversible. It is a direct consequence of the second law of thermodynamics that *all natural spontaneous processes are irreversible*.

A careful inspection of the various types of natural process shows that all involve one or both of the following features:

- 1 The conditions for mechanical, thermal, or chemical equilibrium, i.e., thermodynamic equilibrium, are not satisfied.
- 2 Dissipative effects, such as viscosity, friction, inelasticity, electric resistance, and magnetic hysteresis, are present.

For a process to be reversible, it must not possess these features. If a process is performed quasi-statically, the system passes through states of thermodynamic equilibrium, which may be traversed just as well in one direction as in the opposite direction. If there are no dissipative effects, all the work done by the system during the performance of a process in one direction can be returned to the system during the reverse process. We are led, therefore, to the conclusion that a process will be reversible when (1) it is performed quasi-statically and (2) it is not accompanied by any dissipative effects.

Since it is impossible to satisfy these two conditions perfectly, it is obvious that a reversible process is purely an ideal abstraction, extremely useful for theoretical calculations (as we shall see) but quite devoid of reality. In this sense, the assumption of a reversible process in thermodynamics resembles the assumptions made so often in mechanics, such as those which refer to weightless strings, frictionless pulleys, and point masses.

A heat reservoir was defined as a body of very large mass capable of absorbing or rejecting an unlimited supply of heat without suffering appreciable changes in its thermodynamic coordinates. The changes that do take place are so very slow and so minute that dissipative actions never develop. *Therefore, when heat enters or leaves a reservoir, the changes that take place in the reservoir are the same as those which would take place if the same quantity of heat were transferred reversibly.*

It is possible in the laboratory to approximate the conditions necessary for the performance of reversible processes. For example, if a gas is confined in a cylinder equipped with a well-lubricated piston and is allowed to expand very slowly against an opposing force provided either by an object suspended from a frictionless pulley or by an elastic spring, the gas undergoes an approxi-

mately reversible process. Similar considerations apply to a wire and to a surface film.

A reversible transfer of electricity through an electric cell may be imagined as follows: Suppose that a motor whose coils have a negligible resistance is caused to rotate until its back emf is only slightly different from the emf of the cell. Suppose further that the motor is coupled either to an object suspended from a frictionless pulley or to an elastic spring. If neither the cell itself nor the connecting wires to the motor have appreciable resistance, a reversible transfer of electricity takes place.

In order to arrive at conclusions concerning the equilibrium states of thermodynamic systems, it is often necessary to invoke some sort of process in which the system passes through these states. To assume the process to be quasi-static only, often is not sufficient, for if dissipative processes are present there may be heat flows or internal energy changes of neighboring systems (envelopes, containers, surroundings) that may limit the validity of the argument. In order to ensure that equilibrium states of the system *only* are considered—without having to take account of the effect of dissipated work in the system itself or in some other neighboring body—it is useful to invoke the concept of a *reversible process*, even though this assumption may at times seem a bit drastic.

## 8-7 Existence of Reversible Adiabatic Surfaces

Up to this point, the only consequence of the second law of thermodynamics that has been drawn is the irreversibility of natural, spontaneous processes. To develop further consequences, it has been customary to proceed along either of two lines: the engineering method, due to Carnot, Kelvin, and Clausius; and the axiomatic method, due to the Greek mathematician C. Caratheodory.<sup>†</sup> The engineering method is based upon the Kelvin-Planck formulation of the second law or its equivalent, the Clausius statement. One starts first by defining a particularly simple reversible cycle called the *Carnot cycle* and then proving that an engine operating in this cycle between reservoirs at two different temperatures is more efficient than any other engine operating between the same two reservoirs. After proving that all Carnot engines operating between the same two reservoirs have the same efficiency, regardless of the substance undergoing the cycle, the Kelvin temperature scale is defined so as to be independent of the properties of any particular kind of thermometer. A theorem called the *Clausius theorem* is then derived, and from it the existence of the entropy function. The engineering method of developing the consequences of the Kelvin-Planck or Clausius statements of

<sup>†</sup> C. Caratheodory, *Math. Ann.*, 67:355 (1909) (in German).



the second law is rigorous and general. If one is interested in the design and manufacture of engines and refrigerators, it is essential to employ principles that hold regardless of the nature of the materials involved. If, however, one is interested in the behavior of systems, their coordinates, their equations of state, their properties, their processes, etc., *apart* from their use in the cylinders of engines and refrigerators, then it is desirable to adopt a method more closely associated with the coordinates and equations of actual systems.

In the first decade of the twentieth century Caratheodory, to replace the Kelvin-Planck and Clausius statements of the second law, presented this axiom: *In the neighborhood (however close) of any equilibrium state of a system of any number of thermodynamic coordinates, there exist states that cannot be reached (are inaccessible) by reversible adiabatic processes.* He showed how to derive the Kelvin temperature scale from this axiom and how to derive every other consequence of the engineering method. Physicists (Born, Ehrenfest, Landé) recognized the importance of Caratheodory's work, but since the mathematics needed to deal with Caratheodory's axiom presented much more difficulty than the simple manipulations involving outputs and inputs of engines and refrigerators, other physicists were slow in adopting his methods. In recent years, mainly because of the activities of Pippard, Turner, Landsberg, and Sears,<sup>†</sup> the mathematical machinery of the Caratheodory method has been considerably simplified, and now it appears that *the axiom itself can be dispensed with entirely.* All the consequences of the Caratheodory axiom follow directly from the Kelvin-Planck statement of the second law.

Consider a system described with the aid of five thermodynamic coordinates: the empiric temperature  $t$ , measured on *any* scale whatsoever; two generalized forces  $Y$  and  $Y'$ ; and two corresponding generalized displacements  $X$  and  $X'$ . For such a system, the first law for a reversible process is

$$dQ = dU + Y dX + Y' dX',$$

and because of the existence of two equations of state, only three of the coordinates are independent. At first, let us choose these coordinates to be  $U$ ,  $X$ , and  $X'$ . A system of three independent variables is chosen for two reasons: (1) it enables us to use simple three-dimensional graphs, and (2) all conclusions concerning the mathematical properties of the differential  $dQ$  will hold equally well for all systems with *more or fewer* than three independent variables.

In Fig. 8-3, the three independent variables  $U$ ,  $X$ , and  $X'$  are plotted along three rectangular axes, and an arbitrarily chosen equilibrium state  $i$  is indi-

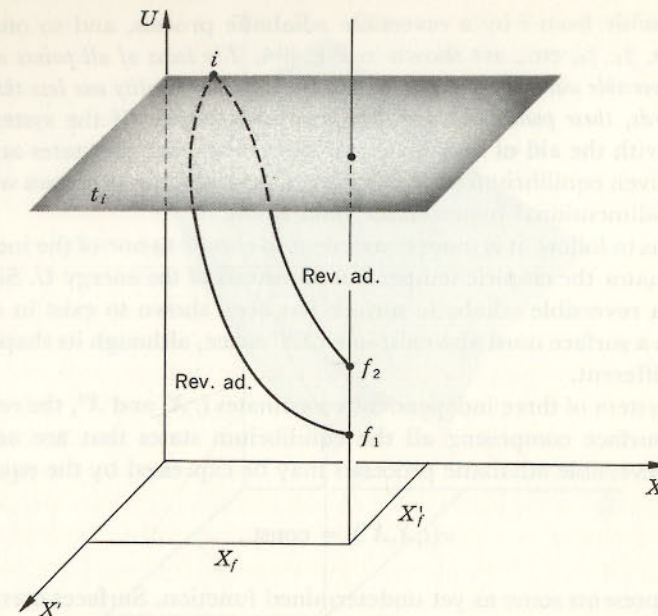


Fig. 8-3 Both  $f_1$  and  $f_2$ , lying on a line of constant  $X$  and  $X'$ , cannot be reached by reversible adiabatic processes from  $i$ .

cated. Let  $f_1$  be an equilibrium state that the system can reach by means of a reversible adiabatic process. Through  $f_1$  draw a vertical line for which the values of  $X$  and  $X'$  are constant at every point. Let  $f_2$  be any other equilibrium state on this vertical line. We now proceed to prove that *both states  $f_1$  and  $f_2$  cannot be reached by reversible adiabatic processes from  $i$ .* Assume that it is possible for the system to proceed along either of the two reversible adiabatic paths  $i \rightarrow f_1$  or  $i \rightarrow f_2$ . Let the system start at  $i$ , proceed to  $f_1$ , then to  $f_2$ , and then back to  $i$  along  $f_2 \rightarrow i$ , which, being a reversible path, can be traversed in either direction. Since  $f_2$  lies above  $f_1$ , the system undergoes an *increase* of energy at constant  $X$  and  $X'$ , during which process no work is done. It follows from the first law that *heat  $Q$  must be absorbed* in the process  $f_1 \rightarrow f_2$ . In the reversible adiabatic processes, however, no heat is transferred but *work  $W$  is done*. In the entire cycle  $if_1f_2i$ , there is no energy change, and therefore  $Q = W$ . The system has thus performed a cycle in which the sole effect is the absorption of heat and the conversion of this heat completely into work. Since this violates the Kelvin-Planck statement of the second law, it follows that *both  $f_1$  and  $f_2$  cannot be reached by reversible adiabatic processes. Only one point on the line of constant  $X$  and  $X'$  can be reached by a reversible adiabatic process from  $i$ .*

For a different line (different  $X_f$  and  $X'_f$ ), there would be another single

<sup>†</sup> A. B. Pippard, "Elements of Classical Thermodynamics," Cambridge University Press, New York, 1957, p. 38; L. A. Turner, *Am. J. Phys.*, **28**:781 (1960); P. T. Landsberg, *Nature*, **201**:485 (1964); F. W. Sears, *Am. J. Phys.*, **31**:747 (1963).



point accessible from  $i$  by a reversible adiabatic process, and so on. A few such points,  $f_1, f_2$ , etc., are shown in Fig. 8-4. The locus of all points accessible from  $i$  by reversible adiabatic processes is a space of dimensionality one less than three; in other words, these points lie on a two-dimensional surface. If the system were described with the aid of four independent coordinates, the states accessible from any given equilibrium state  $i$  by reversible adiabatic processes would lie on a three-dimensional hypersurface, and so on.

In what is to follow, it is more convenient to choose as one of the independent coordinates the empiric temperature  $t$  instead of the energy  $U$ . Since, for a given  $i$ , a reversible adiabatic surface has been shown to exist in a  $UXX'$  space, such a surface must also exist in a  $tXX'$  space, although its shape might be quite different.

With a system of three independent coordinates  $t, X$ , and  $X'$ , the reversible adiabatic surface comprising all the equilibrium states that are accessible from  $i$  by reversible adiabatic processes may be expressed by the equation

$$\sigma(t, X, X') = \text{const.}, \quad (8-1)$$

where  $\sigma$  represents some as yet undetermined function. Surfaces correspond-

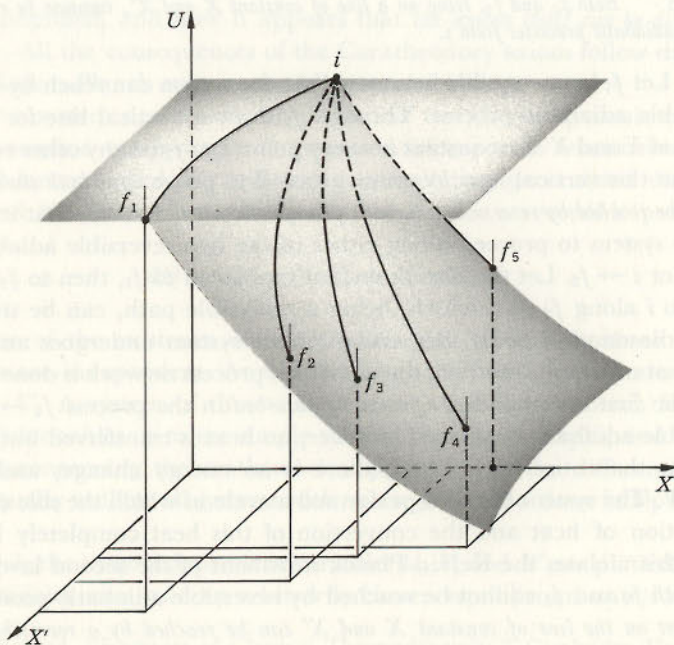


Fig. 8-4 All states that can be reached by reversible adiabatic processes starting at  $i$  lie on a surface.

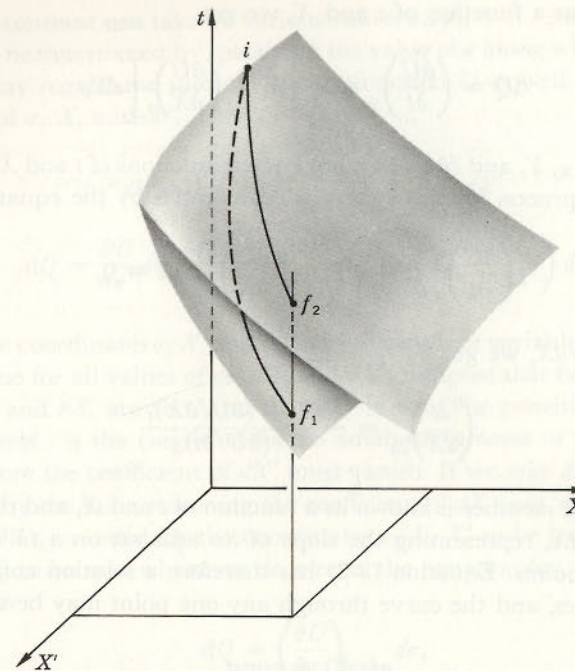


Fig. 8-5 If two reversible adiabatic surfaces could intersect, it would be possible to violate the second law by performing the cycle  $if_1f_2i$ .

ing to other initial states would be represented by different values of the constant.

Reversible adiabatic surfaces cannot intersect, for if they did it would be possible, as shown in Fig. 8-5, to proceed from an initial equilibrium state  $i$  on the curve of intersection to two different final states  $f_1$  and  $f_2$ , having the same  $X_f$  and  $X'_f$ , along reversible adiabatic paths. We have just shown that this is impossible.

## 8-8 Integrability of $dQ$

It has been emphasized that  $dW$  and  $dQ$  are inexact differentials; there are no functions  $W$  and  $Q$  representing, respectively, the work and heat of a body. When a system can be described with the aid of two independent thermodynamic coordinates, say, a temperature  $t$  (on any scale) and a generalized displacement  $X$ , then if  $Y$  is the generalized force,

$$dQ = dU + Y dX.$$



Regarding  $U$  as a function of  $t$  and  $X$ , we get

$$dQ = \left( \frac{\partial U}{\partial t} \right)_X dt + \left[ Y + \left( \frac{\partial U}{\partial X} \right)_t \right] dX,$$

where  $(\partial U/\partial t)_X$ ,  $Y$ , and  $(\partial U/\partial X)_t$  are known functions of  $t$  and  $X$ . A reversible adiabatic process for this system is represented by the equation

$$\left( \frac{\partial U}{\partial t} \right)_X dt + \left[ Y + \left( \frac{\partial U}{\partial X} \right)_t \right] dX = 0, \quad (8-2)$$

Solving for  $dt/dX$ , we get

$$\left( \frac{dt}{dX} \right)_{\text{ad}} = - \frac{Y + (\partial U/\partial X)_t}{(\partial U/\partial t)_X}.$$

The right-hand member is known as a function of  $t$  and  $X$ , and therefore the derivative  $dt/dX$ , representing the slope of an adiabat on a  $tX$  diagram, is known at all points. Equation (8-2) has therefore a solution consisting of a family of curves, and the curve through any one point may be written

$$\sigma(t, X) = \text{const.}$$

A set of curves is obtained when different values are assigned to the constant. *The existence of the family of curves  $\sigma(t, X) = \text{const.}$ , representing reversible adiabatic processes, follows from the fact that there are only two independent coordinates, and not from any law of physics.*

When three or more independent coordinates are needed to describe a system, the situation is quite different. The second law of thermodynamics is needed to enable us to conclude that:

*Through any arbitrary initial-state point, all reversible adiabatic processes lie on a surface, and reversible adiabatics through other initial states determine a family of nonintersecting surfaces.*

Consider a system whose coordinates are the empiric temperature  $t$ , two generalized forces  $Y$  and  $Y'$ , and two generalized displacements  $X$  and  $X'$ . The first law for a reversible process is expressed by the equation

$$dQ = dU + Y dX + Y' dX', \quad (8-3)$$

where  $U$ ,  $Y$ , and  $Y'$  are functions of  $t$ ,  $X$ , and  $X'$ . Since the  $t, X, X'$  space is subdivided into a family of nonintersecting reversible adiabatic surfaces,

$$\sigma(t, X, X') = \text{const.},$$

where the constant can take on various values  $\sigma_1, \sigma_2, \dots$ , any point in this space may be determined by specifying the value of  $\sigma$  along with  $X$  and  $X'$ , so that we may regard the internal energy function  $U$  as well as  $Y$  and  $Y'$  as functions of  $\sigma$ ,  $X$ , and  $X'$ . Then,

$$dU = \frac{\partial U}{\partial \sigma} d\sigma + \frac{\partial U}{\partial X} dX + \frac{\partial U}{\partial X'} dX',$$

$$\text{and} \quad dQ = \frac{\partial U}{\partial \sigma} d\sigma + \left( Y + \frac{\partial U}{\partial X} \right) dX + \left( Y' + \frac{\partial U}{\partial X'} \right) dX'. \quad (8-4)$$

Since the coordinates  $\sigma$ ,  $X$ , and  $X'$  are independent variables, this equation must be true for all values of  $d\sigma$ ,  $dX$ , and  $dX'$ . Suppose that two of the differentials,  $d\sigma$  and  $dX$ , are zero and that  $dX'$  is not. The provision that  $d\sigma = 0$  (or  $\sigma = \text{const.}$ ) is the condition for an adiabatic process in which  $dQ = 0$ , and therefore the coefficient of  $dX'$  must vanish. If we take  $d\sigma$  and  $dX'$  to be zero, then by the same reasoning the coefficient of  $dX$  must vanish. It follows therefore that, in order for the coordinates  $\sigma$ ,  $X$ ,  $X'$  to be independent, and also for  $dQ$  to be zero whenever  $d\sigma$  is zero, the equation for  $dQ$  must reduce to the form

$$dQ = \left( \frac{\partial U}{\partial \sigma} \right)_{X, X'} d\sigma, \quad (8-5)$$

If we define a function  $\lambda$  by the equation

$$\lambda = \left( \frac{\partial U}{\partial \sigma} \right)_{X, X'}, \quad (8-6)$$

we get the result

$$dQ = \lambda d\sigma. \quad (8-7)$$

According to its definition, given in Eq. (8-6),  $\lambda$  is a function of  $\sigma$ ,  $X$ , and  $X'$ . Since  $\sigma$  is a function of  $t$ ,  $X$ , and  $X'$ , however, we may imagine  $X'$  to be eliminated, with the result that  $\lambda$  is a function of  $t$ ,  $\sigma$ , and  $X$ .

It is seen from Eq. (8-7) that the function  $1/\lambda$  is an integrating factor, such that when  $dQ$  is multiplied by  $1/\lambda$  the result is an exact differential  $d\sigma$ . Now, an infinitesimal of the type

$$P dx + Q dy + R dz + \dots,$$

known as a *linear differential form* or a *Pfaffian expression*, when it involves three or more independent variables, does not admit, in general, of an integrating factor. *It is only because of the existence of the second law that the differential form for*



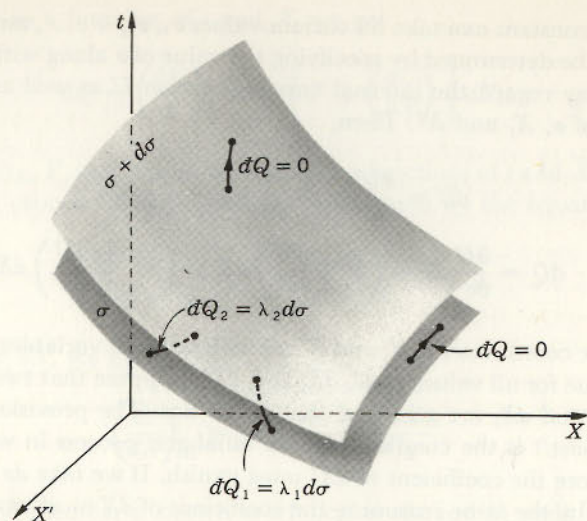


Fig. 8-6 Two reversible adiabatic surfaces, infinitesimally close. When the process is represented by a curve connecting the two surfaces, heat  $dQ = \lambda d\sigma$  is transferred.

$dQ$  referring to a physical system of any number of independent coordinates possesses an integrating factor.

Two infinitesimally neighboring reversible adiabatic surfaces are shown in Fig. 8-6. One surface is characterized by a constant value of the function  $\sigma$ , and the other by a slightly different value  $\sigma + d\sigma$ . In any process represented by a curve on either of the two surfaces  $dQ = 0$ . When a reversible process is represented by a curve connecting the two surfaces, however, heat  $dQ = \lambda d\sigma$  is transferred. All curves joining the two surfaces represent processes with the same  $d\sigma$ , but the values of  $\lambda$  are different.

### 8-9 Physical Significance of $\lambda$

The various infinitesimal processes that may be chosen to connect the two neighboring reversible adiabatic surfaces shown in Fig. 8-6 involve the same change of  $\sigma$  but take place at different values of  $\lambda$ , because  $\lambda$  is a function of  $t$ ,  $\sigma$ , and  $X$ . To find the temperature dependence of  $\lambda$ , we go back to the fundamental concept of temperature as the property of a system determining thermal equilibrium between it and another system. Let us therefore consider two systems, each of three independent coordinates (for mathematical generality), in contact through a diathermic wall, as depicted schematically in Fig. 8-7. The two systems are assumed to be at all times in thermal equilibrium having

a common temperature  $t$ , and together they constitute a composite system with five independent coordinates.

- 1 *Main system.* The three independent coordinates are  $t$ ,  $X$ , and  $X'$ , and the reversible adiabatic surfaces are specified by different values of the function  $\sigma$  of  $t$ ,  $X$ , and  $X'$ . When heat  $dQ$  is transferred,  $\sigma$  changes by  $d\sigma$ , and  $dQ = \lambda d\sigma$  where  $\lambda$  is a function of  $t$ ,  $\sigma$ , and  $X$ .
- 2 *Reference system.*<sup>†</sup> The three independent coordinates are  $t$ ,  $\hat{X}$ , and  $\hat{X}'$ , and the reversible adiabatic surfaces are specified by different values of the function  $\hat{\sigma}$  of  $t$ ,  $\hat{X}$ , and  $\hat{X}'$ . When heat  $d\hat{Q}$  is transferred,  $\hat{\sigma}$  changes by  $d\hat{\sigma}$ , and  $d\hat{Q} = \hat{\lambda} d\hat{\sigma}$  where  $\hat{\lambda}$  is a function of  $t$ ,  $\hat{\sigma}$ , and  $\hat{X}$ .
- 3 *Composite system.* The five independent coordinates are  $t$ ,  $X$ ,  $X'$ ,  $\hat{X}$ , and  $\hat{X}'$ , and the reversible adiabatic hypersurfaces are specified by different values of the function  $\sigma$  of these independent variables.

Using the equation for  $\sigma$  of the main system, we may express  $X'$  in terms of  $t$ ,  $\sigma$ , and  $X$ . Similarly, using the equation for  $\hat{\sigma}$  of the reference system,  $\hat{X}'$

<sup>†</sup> The diacritical mark or accent over the symbols referring to the reference system is called a *circumflex*.

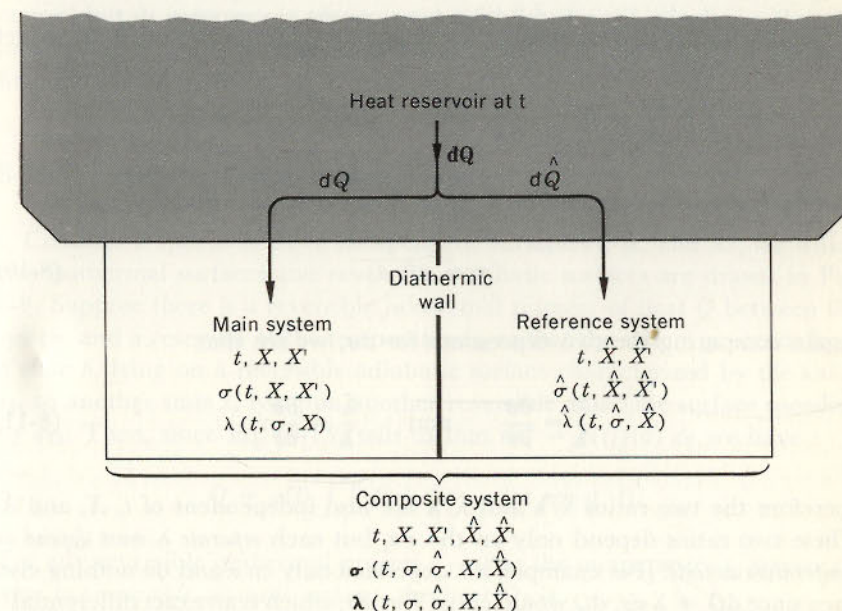


Fig. 8-7 Two systems in thermal equilibrium, constituting a composite system receiving heat from a reservoir.



may be expressed in terms of  $t$ ,  $\sigma$ , and  $\hat{X}$ . The primed quantities  $X'$  and  $\hat{X}'$  may therefore be eliminated from the expression for  $\sigma$  of the composite system, and  $\sigma$  may be regarded as a function of  $t$ ,  $\sigma$ ,  $\hat{\sigma}$ ,  $X$ , and  $\hat{X}$ . For an infinitesimal process between two neighboring reversible adiabatic hypersurfaces specified by  $\sigma$  and  $\sigma + d\sigma$ , the heat transferred is  $dQ = \lambda d\sigma$ , where  $\lambda$  is also a function of  $t$ ,  $\sigma$ ,  $\hat{\sigma}$ ,  $X$ , and  $\hat{X}$ . We have

$$d\sigma = \frac{\partial \sigma}{\partial t} dt + \frac{\partial \sigma}{\partial \sigma} d\sigma + \frac{\partial \sigma}{\partial \hat{\sigma}} d\hat{\sigma} + \frac{\partial \sigma}{\partial X} dX + \frac{\partial \sigma}{\partial \hat{X}} d\hat{X}. \quad (8-8)$$

Now suppose that, in a reversible process, there is a transfer of heat  $dQ$  between the composite system and an external reservoir, as shown in Fig. 8-7, with heats  $dQ$  and  $d\hat{Q}$  being transferred, respectively, to the main and to the reference systems. Then,

$$\begin{aligned} dQ &= dQ + d\hat{Q}, \\ \text{and} \quad \lambda d\sigma &= \lambda d\sigma + \hat{\lambda} d\hat{\sigma}, \\ \text{or} \quad d\sigma &= \frac{\lambda}{\hat{\lambda}} d\sigma + \frac{\hat{\lambda}}{\lambda} d\hat{\sigma}. \end{aligned} \quad (8-9)$$

Comparing the two expressions for  $d\sigma$  given by Eqs. (8-8) and (8-9), we get

$$\frac{\partial \sigma}{\partial t} = 0, \quad \frac{\partial \sigma}{\partial X} = 0, \quad \text{and} \quad \frac{\partial \sigma}{\partial \hat{X}} = 0;$$

therefore  $\sigma$  does *not* depend on  $t$ ,  $X$ , or  $\hat{X}$  but only on  $\sigma$  and  $\hat{\sigma}$ . That is,

$$\sigma = \sigma(\sigma, \hat{\sigma}). \quad (8-10)$$

Again comparing the two expressions for  $d\sigma$ , we see that

$$\frac{\lambda}{\hat{\lambda}} = \frac{\partial \sigma}{\partial \sigma} \quad \text{and} \quad \frac{\hat{\lambda}}{\lambda} = \frac{\partial \sigma}{\partial \hat{\sigma}}; \quad (8-11)$$

therefore the two ratios  $\lambda/\hat{\lambda}$  and  $\hat{\lambda}/\lambda$  are also independent of  $t$ ,  $X$ , and  $\hat{X}$ . These two ratios depend only on the  $\sigma$ 's, but each *separate*  $\lambda$  must depend on temperature as well. [For example, if  $\lambda$  depended only on  $\sigma$  and on nothing else, then since  $dQ = \lambda d\sigma$ ,  $dQ$  would equal  $f(\sigma) d\sigma$ , which is an exact differential!] In order, therefore, for each  $\lambda$  to depend on temperature, and at the same time for the ratios of the  $\lambda$ 's to depend only on the  $\sigma$ 's, the  $\lambda$ 's must have the

following structure:

$$\begin{aligned} \lambda &= \varphi(t)f(\sigma), \\ \hat{\lambda} &= \varphi(t)\hat{f}(\hat{\sigma}), \end{aligned} \quad (8-12)$$

and

$$\lambda = \varphi(t)g(\sigma, \hat{\sigma}).$$

(The quantity  $\lambda$  cannot contain  $X$ , nor can  $\hat{\lambda}$  contain  $\hat{X}$ , since  $\lambda/\hat{\lambda}$  and  $\hat{\lambda}/\lambda$  must be functions of the  $\sigma$ 's only.)

Referring now only to our main system as representative of any system of any number of independent coordinates, we have, from the top line of Eq. (8-12),

$$dQ = \varphi(t)f(\sigma) d\sigma. \quad (8-13)$$

Since  $f(\sigma) d\sigma$  is an exact differential, the quantity  $1/\varphi(t)$  is an integrating factor for  $dQ$ . It is an extraordinary circumstance that not only does an integrating factor exist for the  $dQ$  of any system, but *this integrating factor is a function of temperature only and is the same function for all systems!* This universal character of  $\varphi(t)$  enables us to define an *absolute temperature*.

The fact that a system of *two* independent variables has a  $dQ$  which always admits an integrating factor regardless of the second law is interesting, of course; but *its importance in physics* is not established until it is shown that the integrating factor is a function of temperature *only* and that it is the *same* function for all systems.

## 8-10 Kelvin Temperature Scale

Consider a system of three independent variables  $t$ ,  $X$ , and  $X'$ , for which two isothermal surfaces and reversible adiabatic surfaces are drawn in Fig. 8-8. Suppose there is a reversible isothermal transfer of heat  $Q$  between the system and a reservoir at the temperature  $t$ , so that the system proceeds from a state  $b$ , lying on a reversible adiabatic surface characterized by the value  $\sigma_I$ , to another state  $c$ , lying on another reversible adiabatic surface specified by  $\sigma_{II}$ . Then, since Eq. (8-13) tells us that  $dQ = \varphi(t)f(\sigma) d\sigma$  we have

$$Q = \varphi(t) \int_{\sigma_I}^{\sigma_{II}} f(\sigma) d\sigma \quad (\text{at const. } t).$$

For any reversible isothermal process  $a \rightarrow d$  at the temperature  $t_3$  between the same two reversible adiabatic surfaces, the heat  $Q_3$  is

$$Q_3 = \varphi(t_3) \int_{\sigma_I}^{\sigma_{II}} f(\sigma) d\sigma \quad (\text{at const. } t_3).$$



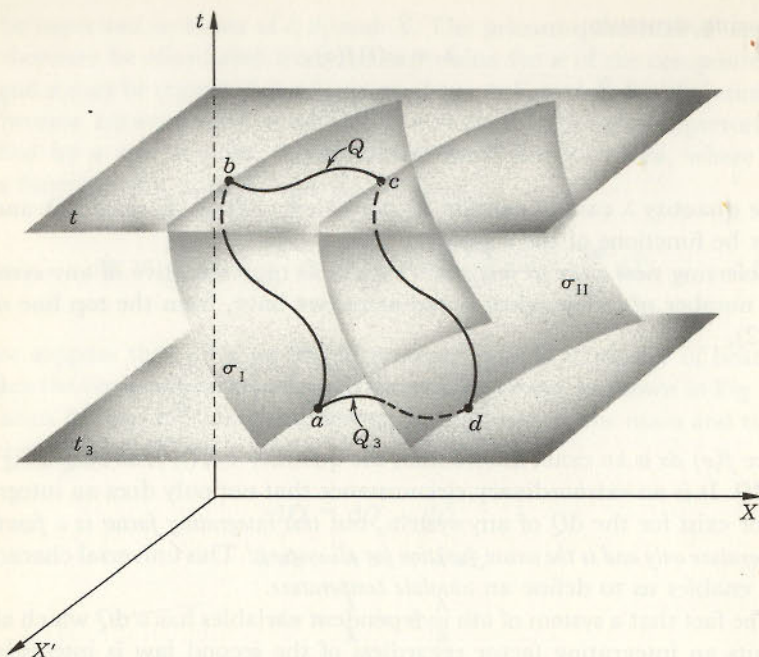


Fig. 8-8 Two isothermal heat transfers,  $Q$  at  $t$  from  $b$  to  $c$  and  $Q_3$  at  $t_3$  from  $a$  to  $d$ , between the same two reversible adiabatic surfaces  $\sigma_I$  and  $\sigma_{II}$ . The cycle  $abcd$  is a Carnot cycle.

Taking the ratio of  $Q$  to  $Q_3$ , we get

$$\frac{Q}{Q_3} = \frac{\varphi(t)}{\varphi(t_3)} = \frac{\text{a function of the temp. at which } Q \text{ is transferred}}{\text{the same function of temp. at which } Q_3 \text{ is transferred}};$$

therefore we define the ratio of two Kelvin temperatures  $T/T_3$  by the relation

$$\frac{Q \text{ (between } \sigma_I \text{ and } \sigma_{II} \text{ at } T)}{Q_3 \text{ (between } \sigma_I \text{ and } \sigma_{II} \text{ at } T_3)} = \frac{T}{T_3}. \quad (8-14)$$

Thus, two temperatures on the Kelvin scale are to each other as the heats transferred between the same two reversible adiabatic surfaces at these two temperatures. It is seen that the Kelvin temperature scale is independent of the peculiar characteristics of any particular substance. It therefore supplies exactly what is lacking in the ideal-gas scale.

If the temperature  $T_3$  is taken arbitrarily to be the triple point of water (the standard fixed point) and  $T_3$  is chosen to have the value  $273.16^\circ\text{K}$ , then

the Kelvin temperature is defined to be

$$T = 273.16^\circ\text{K} \frac{Q}{Q_3} \quad (\text{between the same two reversible adiabatic surfaces}). \quad (8-15)$$

To measure a Kelvin temperature, we must therefore measure or calculate the heats transferred at the unknown temperature and at the triple point of water during reversible isothermal processes between the same two reversible adiabatic surfaces. Comparing this equation with the corresponding equation for the ideal-gas temperature

$$\theta = 273.16^\circ \frac{\lim (PV)}{\lim (PV)_3},$$

it is seen that, in the Kelvin scale,  $Q$  plays the role of a "thermometric property." This does not have the objection attached to a coordinate of an arbitrarily chosen thermometer, however, inasmuch as  $Q/Q_3$  is independent of the nature of the system.

It follows from Eq. (8-15) that the heat transferred isothermally between two given reversible adiabatic surfaces decreases as the temperature decreases. Conversely, the smaller the value of  $Q$ , the lower the corresponding  $T$ . The smallest possible value of  $Q$  is zero, and the corresponding  $T$  is absolute zero. Thus, if a system undergoes a reversible isothermal process between two reversible adiabatic surfaces without transfer of heat, the temperature at which this process takes place is called absolute zero.

It should be noticed that the definition of absolute zero holds for all substances and is therefore independent of the peculiar properties of any one arbitrarily chosen substance. Furthermore, the definition is in terms of purely macroscopic concepts. No reference is made to molecules or to molecular energy. Whether absolute zero may be achieved experimentally is a question that we shall defer until a later chapter.

### 8-11 Equality of Ideal-gas Temperature and Kelvin Temperature

For the sake of generality, systems with three or more independent coordinates have been used in most of the discussions in this chapter. The systems encountered most frequently in practical applications of thermodynamics, however, usually have no more than two independent variables. In such cases, isothermal and reversible adiabatic surfaces degenerate into plane curves such as those shown on the  $\theta V$  diagram of an ideal gas in Fig. 8-9.



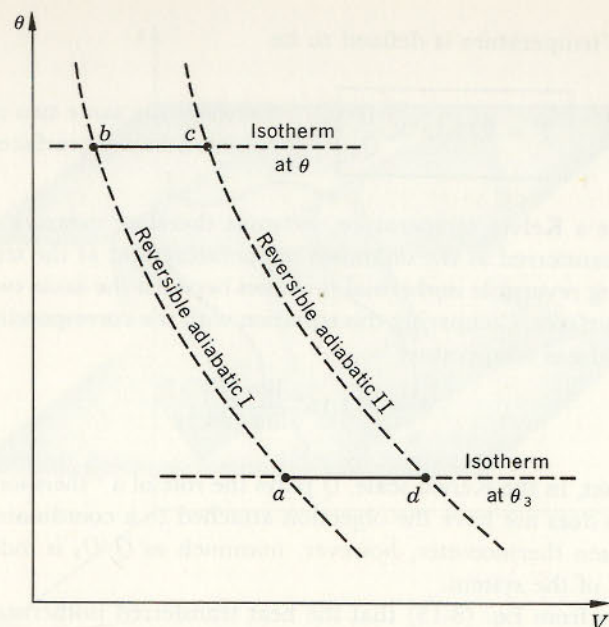


Fig. 8-9 Two isotherms, at  $\theta$  and at  $\theta_3$ , between two reversible adiabats of an ideal gas.  $abcd$  is a Carnot cycle.

For any infinitesimal reversible process of an ideal gas, the first law may be written

$$dQ = C_V d\theta + P dV.$$

When this equation is applied to the isothermal process  $b \rightarrow c$ , the heat transferred is found to be

$$Q = \int_{V_b}^{V_c} P dV = nR\theta \ln \frac{V_c}{V_b}.$$

Similarly, for the isothermal process  $a \rightarrow d$ , the heat transferred is

$$Q_3 = nR\theta_3 \ln \frac{V_d}{V_a}.$$

Therefore,

$$\frac{Q}{Q_3} = \frac{\theta \ln (V_c/V_b)}{\theta_3 \ln (V_d/V_a)}.$$

Since the process  $a \rightarrow b$  is adiabatic, we may write for any infinitesimal portion

$$C_V d\theta = -P dV = -\frac{nR\theta}{V} dV.$$

Integrating from  $a$  to  $b$ , we get

$$\frac{1}{nR} \int_{\theta_3}^{\theta} C_V \frac{d\theta}{\theta} = \ln \frac{V_a}{V_b}.$$

Similarly, for the adiabatic process  $d \rightarrow c$ ,

$$\frac{1}{nR} \int_{\theta}^{\theta_3} C_V \frac{d\theta}{\theta} = \ln \frac{V_d}{V_c}.$$

Therefore,  $\ln \frac{V_a}{V_b} = \ln \frac{V_d}{V_c}$  and  $\ln \frac{V_c}{V_b} = \ln \frac{V_d}{V_a}$ ,

and we get, finally,

$$\frac{Q}{Q_3} = \frac{\theta}{\theta_3}.$$

Since, however, the Kelvin temperature scale is defined by the same sort of equation, we have

$$\frac{\theta}{\theta_3} = \frac{T}{T_3}.$$

If  $\theta$  and  $T$  refer to any temperature and if  $\theta_3$  and  $T_3$  refer to the triple point of water,

$$\theta_3 = T_3 = 273.16^\circ\text{K},$$

and

$$\boxed{\theta = T.} \quad (8-14)$$

The Kelvin temperature is therefore numerically equal to the ideal-gas temperature and, in the proper range, may be measured with a gas thermometer.

## PROBLEMS

**8-1** A gas is contained within a cylinder-piston combination. In the following five sets of conditions, tell (1) whether  $dW = P dV$  or not and (2) whether the process is reversible, quasi-static, or irreversible:

- There is no external pressure on the piston and no friction between the piston and the cylinder wall.
- There is no external pressure, and friction is small.
- The piston is jerked out faster than the average molecular speed.
- The friction is adjusted to allow the gas to expand slowly.