CHAPTER I

THE LAWS OF THERMODYNAMICS

In this chapter we shall be concerned mainly with the first and the second laws of thermodynamics. In our presentation of the fundamental principles of thermodynamics we shall follow Carathéodory's axiomatic point of view. This axiomatic presentation of the laws of thermodynamics has the advantage of reducing the number of new undefinables to a minimum and achieves at the same time the maximum logical simplicity. Since a proper appreciation of the meaning and content of the laws of thermodynamics is necessary for the developments in the succeeding chapters, we shall accordingly develop the fundamental ideas *ab initio*.

1. We shall consider only the simplest of thermodynamical systems, namely, those composed of chemically noninteracting mixtures of gases and liquids. We shall assume that the elementary notions concerning mass, force, pressure, work, and volume are familiar; we shall, however, define accurately the purely thermal notions, such as "temperature," "quantity of heat," etc.

In the purely mechanical discussions of the equilibrium of a body —as, for instance, in hydrodynamics—the inner state of a fluid of known mass is determined when we know its specific volume, V, the volume per unit mass of the fluid. But this is not generally true, as we can alter the pressure exerted by a gas without altering its specific volume, V. For this purpose it is necessary to consider physical processes which are associated with "heating." In thermodynamics such physical situations are realized, and we introduce both the pressure, p, and the volume, V, as independent variables. Thus, V and p specify completely the inner state of a system.

We assume that individual systems can be isolated from the outside world by means of inclosures, or that two parts of a given system can be separated by walls. Though we shall not include these inclosures or walls as a part of the thermodynamical system, we shall yet have to make certain specific ideal requirements for these partitions. We shall have to consider two types of such partitions.

a) *Adiabatic inclosures.*—If a body is inclosed in an adiabatic inclosure and if it is in equilibrium, then, in the absence of external fields of forces, the only way in which we can change the inner state of the body is by means of actual displacements of at least some finite part of the walls of the inclosure. If we assume the notion of heat, this means that the only way in which we can change the inner state of a body in an adiabatic inclosure is by doing external work, and that, furthermore, the walls of the inclosure are opaque to the communication of heat.

b) *Diathermic partitions.*—If two bodies are inclosed in an adiabatic inclosure but are mutually separated by a diathermic wall, then a certain definite relation between the four parameters p_1, V_1; p_2, V_2 (defining the state of the two bodies, respectively) must exist in order that there may be equilibrium; the relation depends on the nature of the two bodies only. Thus, we must have

$$F(p_1,\ V_1,\ p_2,\ V_2) = 0\,. \tag{1}$$

We shall say that two bodies are in "thermal contact" if they are both inclosed in the same adiabatic inclosure but are separated by a diathermic wall. Equation (1) then expresses the condition for thermal equilibrium.

Thus, it is empirically found that, if two perfect gases are in thermal contact, we always have

$$p_1 V_1 - p_2 V_2 = 0\,.$$

2. *Empirical temperature.*—Experience shows the following characteristic of thermal equilibrium. If (p_1, V_1), (p_2, V_2), $(\bar{p}_1, \overline{V}_1)$, and $(\bar{p}_2, \overline{V}_2)$ define two distinct states of two different systems (not necessarily those of two different bodies) and if both (p_1, V_1) and (p_2, V_2) are in thermal equilibrium with $(\bar{p}_1, \overline{V}_1)$, and if, further, (p_1, V_1) is in thermal equilibrium with $(\bar{p}_2, \overline{V}_2)$, then it is always true that (p_2, V_2) will be in thermal equilibrium with $(\bar{p}_2, \overline{V}_2)$. This simply means that, if two bodies are separately in thermal equilibrium with a third body, then the two original bodies, if brought into thermal contact, would also be in thermal equilibrium. By equation (1),

which specifies the condition for thermal equilibrium, the foregoing means that the equations

$$F(p_1, V_1, \bar{p}_1, \overline{V}_1) = 0 , \qquad F(p_2, V_2, \bar{p}_1, \overline{V}_1) = 0 , \left.\begin{array}{c}\\\\\end{array}\right\} \quad (2)$$
$$F(p_1, V_1, \bar{p}_2, \overline{V}_2) = 0 ,$$

imply the validity of

$$F(p_2, V_2, \bar{p}_2, \overline{V}_2) = 0 . \tag{3}$$

But this is then, and only then, possible if the relation $F(p, V, \bar{p}, \overline{V})$ $= 0$ has the form

$$t(p, V) - \bar{t}(\bar{p}, \overline{V}) = 0 . \tag{4}$$

In (4) t and $\bar{t}$ are not uniquely determined, for the condition of equilibrium, (4), can also be written as

$$T[t(p, V)] = T[\bar{t}(\bar{p}, \overline{V})] , \tag{4'}$$

where $T(x)$ can be any arbitrary function in x.

Of all the possible forms which the condition of equilibrium can take, let us choose arbitrarily one particular form and write it in the form (4). The values $t(p, V)$ and $\bar{t}(\bar{p}, \overline{V})$ define on an arbitrary scale the *empirical temperature* of the two bodies; if the two bodies are in thermal contact and are in equilibrium, then we should always have the equality of the empirical temperatures. If

$$t = t(p, V), \qquad \bar{t} = \bar{t}(\bar{p}, \overline{V}) , \tag{5}$$

then in equilibrium

$$t = \bar{t} . \tag{6}$$

The equations (5) define in the (p, V) and in the $(\bar{p}, \overline{V})$ planes, respectively, a one-parametric family of curves which are called "isothermals." The equations (5) are called the "equations of state."

If the empirical temperature scale is once selected and defined, then we can always choose any two of the three variables p, V, and t as the independent variables defining the state of a system. In the

same way two arbitrary functions of the physical variables p, V, and t would also suffice to specify a state of the system.

3. *The First Law of Thermodynamics.*—The experiments of Joule establish the following circumstance:

In order to bring a body (or a system of bodies) from a prescribed initial state to another prescribed final state adiabatically, then the same constant amount of mechanical work (or an equivalent electrical work), which is independent of how the change is carried out and which depends only on the prescribed initial and final states, has to be done.

Let the initial state be specified by p_0, V_0, ... , and the final state by p_1, V_1, ... Let the work done to carry out the change of state adiabatically be W. Then, according to the first law, if we keep the initial state fixed, W depends only on the final state. We can therefore write

$$W = U - U_0 , \tag{7}$$

where U is a function of the parameters determining the state of the system—p and V, if there is only one body—and U_0 is its value in the initial state. U, thus defined, is called the "internal energy" of the system.

If we define our unit of heat as the mechanical work (expressed in ergs) required to change the (empirical) temperature, t, of water of unit volume (at constant volume) between two definite values, then we obtain the so called "mechanical equivalent of heat."

4. *Quantity of heat.*—Suppose that we know the internal energy as a function of the physical parameters from a series of calorimetric experiments, as, for instance, Joule's experiments. Suppose, now, that in some given arbitrary nonadiabatic process the internal energy of a system changes by $(U - U_0)$; further, let W be the amount of work done on the system. Then we say that a quantity Q of heat, where

$$Q = (U - U_0) - W , \tag{8}$$

has been supplied to the system.

We see that the notion of the quantity of heat has no independent meaning apart from the First Law of Thermodynamics. $(U - U_0)$

is a physical quantity which can be determined experimentally, while the notion of Q is a derived one.

5. *The internal energy of a system of bodies.*—If two or more bodies are isolated from each other adiabatically, then by definition the energy of the system is equal to the sum of the energies of the individual bodies:

$$U = U_1 + U_2. \tag{9}$$

In general, when the two bodies are brought into contact, the energy is not additive; it is easy to see, however, that the deviation must be proportional to the common surface area of the bodies, and hence, for large volumes the deviations from the additive law can be neglected.

6. *Stationary and quasi-statical processes.*—In the formulation of the first law we assumed that the work done can in principle be measured. But to evaluate the work done during a given process we need an apparatus to register continuously the forces exerted on, and the displacements of, the walls of the inclosure, for the work done is simply the integral over the product of the force and the displacement. In practice this limits us to only two essentially distinct procedures for which we can measure the work done. These are:

a) Stationary processes.—For example, as in Joule's experiments, there is a stirrer which rotates in the fluid at a constant rate. This would give rise to a stationary system of currents in which the stirrer experiences a constant friction. If we neglect the relatively small acceleration in the beginning and the end of the interval during which the stirrer rotates, then the work done is simply the product of the torque times the rate of working of the stirrer.

b) Quasi-statical processes.—We conduct the process infinitely slowly, so that we can regard the state of the system at any given moment as one of equilibrium. We refer to such processes as "quasi-statical processes." They are generally referred to as "reversible processes" because, in general, quasi-statical processes can be conducted in the reverse sense. We shall refer to a process as "nonstatical" if it is not quasi-statical.

7. *Infinitesimal quasi-statical adiabatic changes.*—If we have a body inclosed in an adiabatic inclosure, and if we do an infinitesimal amount of mechanical work, dW (by displacing the walls of the in-

closure), carried out quasi-statically, then we say that we have carried out an "infinitesimal quasi-statical adiabatic change." If during such an infinitesimal quasi-statical adiabatic change the change in volume amounts to dV, then clearly

$$dW = -pdV,\tag{10}$$

where p is the equilibrium pressure. Then, according to the first law,

$$dQ = dU + pdV = 0.\tag{11}$$

For a system of two bodies which are both inclosed in the same adiabatic inclosure but which are separated from one another by means of a diathermic wall, we have, since both Q and U are additive,

$$\begin{aligned} dQ &= dQ_1 + dQ_2, \\ &= dU_1 + dU_2 + p_1 dV_1 + p_2 dV_2 = 0. \end{aligned}\tag{12}$$

Finite quasi-statical adiabatic changes are simply continuous sequences of equilibrium states and therefore are curves in the phase-space (i.e., the p, V plane for a single body) which satisfy at each point equations of the form (11) or (12). Equations (11) and (12) are called the "equations of the adiabatics."

If we consider U as a function of V and t, then

$$dU = \left(\frac{\partial U}{\partial V}\right) dV + \left(\frac{\partial U}{\partial t}\right) dt.\tag{13}$$

Hence (11) takes the form

$$dQ = \left(\frac{\partial U}{\partial V} + p\right) dV + \frac{\partial U}{\partial t} dt = 0.\tag{14}$$

Equation (12) has interest only when the two bodies are in thermal contact. The system then can be described by three independent variables, V_1, V_2, and t, the common empirical temperature:

$$t(p_1, V_1) = t(p_2, V_2) = t.\tag{15}$$

Equation (12) can then be written as

$$dQ = \left(\frac{\partial U_1}{\partial V_1} + p_1\right) dV_1 + \left(\frac{\partial U_2}{\partial V_2} + p_2\right) dV_2 \left.\begin{array}{c} \\ + \left(\frac{\partial U_1}{\partial t} + \frac{\partial U_2}{\partial t}\right) dt = 0 \, . \end{array}\right\} \quad (16)$$

Equations (14) and (16) are the equations of the adiabatics. Equations of the form (14) and (16) are called "Pfaffian differential equations." We must now study some mathematical properties of these differential equations.

8. *Mathematical theorems on Pfaffian differential equations.*—We shall consider first a Pfaffian differential expression in two variables x and y:

$$dQ = X(x, y)dx + Y(x, y)dy \, , \quad (17)$$

which has the same form as equation (14). The integral of dQ between two points 1 and 2 depends in general on the path of the integration. Hence $\int_1^2 dQ$ cannot in general be written as $Q(x_2, y_2) - Q(x_1, y_1)$, which means that dQ is not "integrable." This in turn means that dQ in general is not a perfect differential of the function $Q(x, y)$. If dQ were a perfect differential, we should have $dQ = d\sigma$, where σ is a function of x and $y;$ we should have further

$$d\sigma = \frac{\partial \sigma}{\partial x} dx + \frac{\partial \sigma}{\partial y} dy \, . \quad (18)$$

Comparing (17) and (18), we have

$$X(x, y) = \frac{\partial \sigma}{\partial x} \, ; \qquad Y(x, y) = \frac{\partial \sigma}{\partial y} \, , \quad (19)$$

or

$$\frac{\partial X}{\partial y} = \frac{\partial^2 \sigma}{\partial x \partial y} = \frac{\partial Y}{\partial x} \, . \quad (20)$$

Condition (20) between the coefficients in the Pfaffian expression need not, of course, be true.

Corresponding to (17), the Pfaffian equation in two variables is

$$dQ = Xdx + Ydy = 0 ,\qquad (21)$$

or

$$\frac{dy}{dx} = -\frac{X}{Y} . \qquad (22)$$

The right-hand side of equation (22) is a known function of x and y, and hence the Pfaffian equation (21) defines a definite direction at each point in the (x, y) plane. The solving of the equation simply consists of drawing a system of curves in the (x, y) plane such that at any point the tangent to the curve (at that point) has the same direction as that specified by (21). Hence, the solution of the equation (21) defines a one-parametric family of curves in the (x, y) plane. The solution can therefore be written as $\sigma(x, y) = c = $ constant. Then

$$\frac{\partial \sigma}{\partial x} + \frac{\partial \sigma}{\partial y}\frac{dy}{dx} = 0 . \qquad (23)$$

From (22) and (23) we easily find, that

$$Y\frac{\partial \sigma}{\partial x} = X\frac{\partial \sigma}{\partial y} = \frac{XY}{\tau} , \qquad (24)$$

where $\tau(x, y)$ is a factor depending on x and y. Equation (24) can also be written as

$$X = \tau\frac{\partial \sigma}{\partial x} ; \qquad Y = \tau\frac{\partial \sigma}{\partial y} . \qquad (25)$$

Inserting (25) into (17), we have

$$dQ = \tau\left(\frac{\partial \sigma}{\partial x} dx + \frac{\partial \sigma}{\partial y} dy\right) = \tau d\sigma , \qquad (26)$$

or

$$\frac{dQ}{\tau} = d\sigma ; \qquad (27)$$

i.e., if we divide the Pfaffian expression (17) by τ, we obtain a perfect differential. A factor, τ, which has this property is called

an "integrating denominator." A Pfaffian differential expression, then, in two variables always admits of an integrating denominator.

If we replace σ by another function of σ, say $S[\sigma(x, y)]$, then $S = c =$ constant will again represent the solutions of the differential equation. In that case

$$dS = \frac{dS}{d\sigma} d\sigma = \frac{dS}{d\sigma} \frac{dQ}{\tau} , \qquad (28)$$

$$= \frac{1}{T(x, y)} dQ , \qquad (29)$$

where

$$T(x, y) = \tau(x, y) \frac{d\sigma}{dS} . \qquad (30)$$

Therefore, T is also an integrating denominator. Hence, if a Pfaffian expression admits of one integrating denominator, it must admit of an infinity of them. This result is easily seen to be true for a Pfaffian expression in any number of variables.

We shall now proceed to consider a Pfaffian expression in three variables. (The generalization to more than three variables is immediate.) Consider the Pfaffian expression

$$dQ = Xdx + Ydy + Zdz , \qquad (31)$$

where X, Y, and Z are functions of the variables x, y, and z. Our thermodynamical equation (16) is of this form. The ratio $dx:dy:dz$ defines a definite direction in the (x, y, z) space. The equation $dQ = 0$, corresponding to (31), specifies that dx, dy, and dz must satisfy a linear equation at each point in the space, and hence specifies a certain tangential plane at each point in the (x, y, z) space. A solution of a Pfaffian equation, $dQ = 0$, passing through a given point, (x, y, z), must lie in the tangential plane through that point; but its direction in the tangential plane is arbitrary.

Now, dQ in general will not be a perfect differential. If it were, $dQ = d\sigma$, where σ is some function of x, y, z, so that

$$dQ = d\sigma(x, y, z) = \frac{\partial \sigma}{\partial x} dx + \frac{\partial \sigma}{\partial y} dy + \frac{\partial \sigma}{\partial z} dz .$$

Hence, by comparison with (31),

$$X = \frac{\partial \sigma}{\partial x} ; \qquad Y = \frac{\partial \sigma}{\partial y} ; \qquad Z = \frac{\partial \sigma}{\partial z} , \tag{32}$$

or

$$\frac{\partial Y}{\partial z} = \frac{\partial Z}{\partial y} ; \qquad \frac{\partial Z}{\partial x} = \frac{\partial X}{\partial z} ; \qquad \frac{\partial X}{\partial y} = \frac{\partial Y}{\partial x} . \tag{33}$$

The relations (33) need not be valid for arbitrary functions X, Y, Z.

But we can ask: Does the Pfaffian expression admit of an integrating denominator? In other words, can we determine a function, τ, of x, y, and z such that

$$\frac{dQ}{\tau(x, y, z)} = d\sigma = \frac{\partial \sigma}{\partial x} dx + \frac{\partial \sigma}{\partial y} dy + \frac{\partial \sigma}{\partial z} dz \quad ? \tag{34}$$

If we can determine an integrating denominator $\tau(x, y, z)$, then every solution of the differential equation $dQ = 0$ would also be a solution of $d\sigma = 0$; or the solution can be written in the form $\sigma(x, y, z) = c = $ constant; i.e., the solutions can be any arbitrary curve lying on any one of the one-parametric family of surfaces $\sigma(x, y, z) = c$. It is, however, important to realize that we cannot, in general, find integrating denominators for Pfaffian expressions in more than two variables. This can be verified by the following example. Consider the equation

$$dQ = -ydx + xdy + kdz = 0 , \tag{35}$$

where k is a constant. If the Pfaffian expression (35) admitted of an integrating denominator τ, then

$$\frac{dQ}{\tau} = -\frac{y}{\tau} dx + \frac{x}{\tau} dy + \frac{k}{\tau} dz = d\sigma \tag{36}$$

is a perfect differential. Hence, we should have

$$\frac{\partial \sigma}{\partial x} = -\frac{y}{\tau} ; \qquad \frac{\partial \sigma}{\partial y} = \frac{x}{\tau} ; \qquad \frac{\partial \sigma}{\partial z} = \frac{k}{\tau} . \tag{37}$$

We have

$$\frac{\partial}{\partial y}\left(-\frac{y}{\tau}\right) = -\frac{1}{\tau} + \frac{y}{\tau^2} \frac{\partial \tau}{\partial y} = \frac{\partial}{\partial x}\left(\frac{x}{\tau}\right) = \frac{1}{\tau} - \frac{x}{\tau^2} \frac{\partial \tau}{\partial x} , \tag{38}$$

or

$$2\tau = x\frac{\partial \tau}{\partial x} + y\frac{\partial \tau}{\partial y}. \tag{39}$$

Again

$$\frac{\partial}{\partial z}\left(-\frac{y}{\tau}\right) = \frac{y}{\tau^2}\frac{\partial \tau}{\partial z} = \frac{\partial}{\partial x}\left(\frac{k}{\tau}\right) = -\frac{k}{\tau^2}\frac{\partial \tau}{\partial x}, \tag{40}$$

or

$$\frac{\partial \tau}{\partial x} = -\frac{y}{k}\frac{\partial \tau}{\partial z}. \tag{41}$$

Similarly,

$$\frac{\partial}{\partial y}\left(\frac{k}{\tau}\right) = -\frac{k}{\tau^2}\frac{\partial \tau}{\partial y} = \frac{\partial}{\partial z}\left(\frac{x}{\tau}\right) = -\frac{x}{\tau^2}\frac{\partial \tau}{\partial z}, \tag{42}$$

or

$$\frac{\partial \tau}{\partial y} = \frac{x}{k}\frac{\partial \tau}{\partial z}. \tag{43}$$

From (39), (41), and (43) we have $\tau \equiv 0$, thus leading to a contradiction.

By means of such examples we realize that Pfaffian expressions in three (or more) variables will not in general admit of integrating denominators except under very special circumstances. It is necessary to appreciate this, for precisely such special circumstances obtain in thermodynamics.

We have seen that the Pfaffian differential expressions fall into two classes, those which admit of integrating denominators and those which do not. We must look for a less abstract characteristic of this difference. Consider a Pfaffian equation in two variables. Then through every point in the (x, y) plane there passes just one curve of the family $\sigma(x, y) = c$. Hence from any given point in the plane we cannot certainly reach all the neighboring points by means of curves which satisfy the Pfaffian equation. We shall refer to this circumstance by the statement that not all the neighboring points are *accessible* from a given point.

Now consider a Pfaffian expression in three variables. If it admits of an integrating denominator, the situation is the same as in

the plane; all the solutions lie on one or other of the family of surfaces $\sigma(x, y, z) = c$, so that we cannot reach all points in the neighborhood of a given point. Only those points will be accessible which are on the surface belonging to the family $\sigma(x, y, z) = c$, which passes through the point under consideration.

We now ask the converse question: If in the neighborhood of a point (however near) there are points which are inaccessible to it along curves which are solutions of the Pfaffian equation, then does the Pfaffian expression admit of an integrating denominator? Caratheodory has shown that the answer to the foregoing question is in the affirmative. The proof is as follows:

All those points which are accessible to a given point, P_0 (accessible along curves which are solutions of the Pfaffian equation), and which are in its immediate neighborhood, must form, together with P_0, a continuous domain of points; hence we have three possibilities: all the accessible points in the immediate neighborhood of P_0 either fill a certain volume element containing P_0, or a surface element containing P_0, or a line element passing through P_0. The first possibility is excluded because all points in a sufficiently close neighborhood of P_0 would then be accessible to P_0; this contradicts our hypothesis that in the neighborhood of a point, however near, there are always points inaccessible to it. Again, the last possibility is also excluded because $dQ = 0 = Xdx + Ydy + Zdz$ already defines an infinitesimal surface element containing only points accessible to P_0. Hence, the points which are accessible to P_0 and which are in its neighborhood must form a surface element, dF_0. If we now consider the boundary points P' of dF_0, we can again define surface elements dF' containing all the points accessible to the points P' on the boundary of dF_0. These surface elements dF' must overlap dF_0; at the same time the elements dF' cannot form surface elements lying above or below dF_0, for then along paths going from P_0 to a point P' on the boundary of dF_0, and thence from P' along a curve lying in an appropriate element dF', we should be able to reach all the points in an immediate spatial neighborhood of P_0; this would again contradict our hypothesis. Thus, the element dF_0, together with the elements dF', must form a continuous set of surface elements. By this process of continuation, only points

lying on a definite surface passing through P_0 are obtained, and hence all the points accessible to P_0 must lie on a definite surface F_0. If we now start at a point P_1 not on F_0, we must obtain in the same way another surface F_1 which cannot either intersect or touch the surface F_0. In this way we can construct a whole family of noninter-secting surfaces F_0, F_1, F_2, ... , continuously filling the whole (x, y, z) space, such that only points on any given surface are accessible to points on the surface itself. These surfaces then form a one-parametric family of surfaces, $\sigma(x, y, z) =$ constant, such that $d\sigma = 0$ implies $dQ = 0$. Hence, we must have

$$dQ = \tau(x, y, z)d\sigma(x, y, z) , \qquad (44)$$

where

$$\tau = \frac{X}{\dfrac{\partial \sigma}{\partial x}} = \frac{Y}{\dfrac{\partial \sigma}{\partial y}} = \frac{Z}{\dfrac{\partial \sigma}{\partial z}} . \qquad (45)$$

We have thus proved Carathéodory's theorem:
If a Pfaffian expression

$$dQ = Xdx + Ydy + Zdz$$

has the property that in every arbitrarily close neighborhood of a point P *there are inaccessible points, i.e., points which cannot be connected to* P *along curves which satisfy the equation* $dQ = 0$, *then the Pfaffian expression must admit of an integrating denominator.*

It is easily seen that the foregoing theorem must also be true for Pfaffian expressions in more than three variables. Further, it is clear that, if a Pfaffian expression admits of one integrating denominator, it must admit of infinitely many integrating denominators.

For the family of surfaces, $\sigma(x, y, z) =$ constant can also be written as $S[\sigma(x, y, z) =]$ constant, where $S(\sigma)$ is an arbitrary function in σ. Then we have

$$dS = \frac{dS}{d\sigma} d\sigma = \frac{dS}{d\sigma} \frac{dQ}{\tau} , \qquad (46)$$

or

$$dQ = T(x, y, z)dS , \qquad (47)$$

where

$$T = \tau \frac{d\sigma}{dS} = \frac{X}{\dfrac{\partial S}{\partial x}} = \frac{Y}{\dfrac{\partial S}{\partial y}} = \frac{Z}{\dfrac{\partial S}{\partial z}}. \tag{48}$$

Carathéodory's theorem, which expresses the mathematical equivalence of the inaccessibility along curves $dQ = 0$ with the existence of an integrating denominator $\tau(x, y, z)$ to Q, contains, as we shall see, the essence of the Second Law of Thermodynamics.

9. *The Second Law of Thermodynamics.*—The physical basis for the second law is the realization that certain processes are not physically realizable. The most sweeping statement of this character is that without "compensation" it is not possible to transfer heat from a colder to a hotter body; more precisely, the law is included in Kelvin's principle, which states: *In a cycle of processes it is impossible to transfer heat from a heat reservoir and convert it all into work, without at the same time transferring a certain amount of heat from a hotter to a colder body.* The second law is sometimes also stated in the form: *It is impossible that, at the end of a cycle of changes, heat has been transferred from a colder to a hotter body without at the same time converting a certain amount of work into heat.* This latter statement of the second law is due to Clausius. However, the essential point of Carathéodory's theory is that it formulates the facts of experience in a very much more general way, enabling us at the same time to obtain all the mathematical consequences of the second law without any further physical discussion. In fact, in order to obtain the full mathematical content of the second law, it is sufficient that there exist certain processes that are not physically realizable. Carathéodory states his principle in the following form: *Arbitrarily near to any given state there exist states which cannot be reached from an initial state by means of adiabatic processes.*

From Carathéodory's principle it follows in particular that there exist states neighboring a given one which cannot be reached by means of quasi-static adiabatic processes.

In the first instance we shall only apply Carathéodory's principle to quasi-static adiabatic processes. Later (§ 10), we shall have occasion to use the principle in its wider form, namely, that there exist

states neighboring a given one which are inaccessible to it along nonstatic adiabatic processes.

From the restricted form of Carathéodory's principle, it follows that there are states neighboring a given one which cannot be reached along adiabatics (Eqs. [14] and [16]); hence, by Carathéodory's theorem the Pfaffian differential expression for dQ must admit of an integrating denominator:

$$dQ = \tau d\sigma . \tag{49}$$

For one single substance whose state is characterized by the two parameters V and t, Carathéodory's principle does not lead to anything new, because a Pfaffian expression in two variables always admits of an integrating denominator.

When, however, we consider a system composed of two bodies adiabatically inclosed and in thermal contact, Carathéodory's principle asserts something new in so far as we can now assert that $dQ = dQ_1 + dQ_2$ can always be written in the form

$$dQ = dQ_1 + dQ_2 = \tau(V_1, V_2, t)d\sigma(V_1, V_2, t) . \tag{50}$$

On the other hand, we have for each of the two bodies

$$dQ_1 = \tau_1(V_1, t_1)d\sigma_1(V_1, t_1) , \tag{51}$$

$$dQ_2 = \tau_2(V_2, t_2)d\sigma_2(V_2, t_1) . \tag{52}$$

If the two bodies are in thermal contact, we have

$$t_1 = t_2 = t . \tag{53}$$

Hence,

$$\tau d\sigma = \tau_1 d\sigma_1 + \tau_2 d\sigma_2 . . \tag{54}$$

If we now choose σ_1, σ_2 and t as the independent variables, instead of V_1, V_2, and t, we can regard τ and σ as functions of σ_1, σ_2 and t; from (54) we then have

$$\frac{\partial \sigma}{\partial \sigma_1} = \frac{\tau_1(\sigma_1, t)}{\tau(\sigma_1, \sigma_2, t)} ; \qquad \frac{\partial \sigma}{\partial \sigma_2} = \frac{\tau_2(\sigma_2, t)}{\tau(\sigma_1, \sigma_2, t)} ; \qquad \frac{\partial \sigma}{\partial t} = 0 . \tag{55}$$

From the last equation it follows that σ is independent of t; hence, σ depends only on σ_1 and σ_2, or

$$\sigma = \sigma(\sigma_1, \sigma_2) . \qquad (56)$$

From the first two equations in (55) it follows that τ_1/τ and τ_2/τ are also functions independent of t. Hence,

$$\frac{\partial}{\partial t}\left(\frac{\tau_1}{\tau}\right) = 0 \; ; \qquad \frac{\partial}{\partial t}\left(\frac{\tau_2}{\tau}\right) = 0 , \qquad (57)$$

or

$$\frac{1}{\tau_1}\frac{\partial \tau_1}{\partial t} = \frac{1}{\tau_2}\frac{\partial \tau_2}{\partial t} = \frac{1}{\tau}\frac{\partial \tau}{\partial t} . \qquad (58)$$

Now τ_1 is a function only of σ_1 and t, and τ_2 is a function only of σ_2 and t. Hence, the first equality in (58) can be valid only if the two quantities are functions of t only. We can therefore write (58) as

$$\frac{\partial \log \tau_1}{\partial t} = \frac{\partial \log \tau_2}{\partial t} = \frac{\partial \log \tau}{\partial t} = g(t) , \qquad (59)$$

where $g(t)$ must be a universal function, because it has the same value for two arbitrary systems and also for the "combined" system. We are thus led to a universal function of the empirical temperature, t.

From (59) we have, on integration,

$$\log \tau = \int g(t)dt + \log \Sigma(\sigma_1, \sigma_2) , \qquad (60)$$

$$\log \tau_i = \int g(t)dt + \log \Sigma_i(\sigma_i) , \qquad (i = 1, 2) , \quad (61)$$

where the constants of integration Σ and Σ_i are independent of t and are functions only of the other physical variables characterizing the system. Equations (60) and (61) can also be written as

$$\tau = \Sigma(\sigma_1, \sigma_2) \cdot e^{\int g(t)dt} ; \qquad \tau_i = \Sigma_i(\sigma_i) \cdot e^{\int g(t)dt} . \qquad (62)$$

Thus, for any thermodynamical system the integrating denominator consists of two factors, one factor which depends on the tempera-

ture (and which is the same for all substances) and another factor which depends on the remaining variables characterizing the system. We therefore introduce the *absolute temperature*, T, defined by

$$T = Ce^{\int g(t)dt}, \tag{63}$$

where C is an arbitrary constant (instead of which we can also introduce an arbitrary lower limit to the integral in the exponent in [63]), and which is determined in such a way that two fixed points (e.g., the freezing- and the boiling-point of water) differ by 100 on the absolute scale. It should be noticed that T does not contain any additive constant—in other words, the zero of the absolute scale of temperature is physically determined. From (49), (62), and (63) we have

$$dQ = \tau d\sigma = T \frac{\Sigma}{C} d\sigma, \qquad dQ_i = \tau_i d\sigma_i = T \frac{\Sigma_i}{C} d\sigma_i. \tag{64}$$

If we are dealing with a single homogeneous body the state of which is defined by the independent variables t and σ_1, then Σ_1 depends only on σ_1, so that we can introduce the function S_1, which is defined as

$$S_1 = \frac{1}{C} \int \Sigma_1(\sigma_1) d\sigma_1 + \text{constant}. \tag{65}$$

The function S_1 depends only on σ_1 and is determined apart from an arbitrary additive constant. Furthermore, S_1 is constant along an adiabatic. The function S_1, so defined, is called the "entropy." One can now write

$$dQ_1 = TdS_1. \tag{66}$$

If we now consider a system composed of two bodies in thermal contact, we have for the two bodies separately

$$dQ_1 = \tau_1 d\sigma_1 = T \frac{\Sigma_1(\sigma_1)}{C} d\sigma_1 = TdS_1, \tag{67}$$

$$dQ_2 = \tau_2 d\sigma_2 = T \frac{\Sigma_2(\sigma_2)}{C} d\sigma_2 = TdS_2, \tag{68}$$

and for the combined system

$$dQ = \tau d\sigma = T \frac{\Sigma(\sigma_1, \sigma_2)}{C} d\sigma(\sigma_1, \sigma_2) , \tag{69}$$

$$= dQ_1 + dQ_2 = T \frac{\Sigma_1(\sigma_1)}{C} d\sigma_1 + T \frac{\Sigma_2(\sigma_2)}{C} d\sigma_2 . \tag{69'}$$

Hence,

$$\Sigma(\sigma_1, \sigma_2)d\sigma = \Sigma_1(\sigma_1)d\sigma_1 + \Sigma_2(\sigma_2)d\sigma_2 . \tag{70}$$

From (70) it follows that

$$\Sigma(\sigma_1, \sigma_2) \frac{\partial \sigma}{\partial \sigma_1} = \Sigma_1(\sigma_1) ; \qquad \Sigma(\sigma_1, \sigma_2) \frac{\partial \sigma}{\partial \sigma_2} = \Sigma_2(\sigma_2) . \tag{71}$$

Hence,

$$\frac{\partial \Sigma_1}{\partial \sigma_2} = \frac{\partial \Sigma}{\partial \sigma_2} \frac{\partial \sigma}{\partial \sigma_1} + \Sigma \frac{\partial^2 \sigma}{\partial \sigma_1 \partial \sigma_2} = 0 , \tag{72}$$

$$\frac{\partial \Sigma_2}{\partial \sigma_1} = \frac{\partial \Sigma}{\partial \sigma_1} \frac{\partial \sigma}{\partial \sigma_2} + \Sigma \frac{\partial^2 \sigma}{\partial \sigma_1 \partial \sigma_2} = 0 . \tag{73}$$

From (72) and (73) it follows that the functional determinant

$$\frac{\partial \Sigma}{\partial \sigma_1} \frac{\partial \sigma}{\partial \sigma_2} - \frac{\partial \Sigma}{\partial \sigma_2} \frac{\partial \sigma}{\partial \sigma_1} = \frac{\partial(\Sigma, \sigma)}{\partial(\sigma_1, \sigma_2)} \tag{74}$$

is zero, and consequently $\Sigma(\sigma_1, \sigma_2)$ contains the variables σ_1 and σ_2 only in the combination $\sigma(\sigma_1, \sigma_2)$. We can therefore write

$$\Sigma(\sigma_1, \sigma_2) = \Sigma(\sigma) . \tag{75}$$

Equation (69) can be written as

$$dQ = \tau d\sigma = T dS , \tag{76}$$

where

$$dS = \frac{\Sigma(\sigma)}{C} d\sigma , \tag{77}$$

or

$$S = \frac{1}{C} \int \Sigma(\sigma)d\sigma + \text{constant} , \tag{78}$$

where S is now the "total" entropy of the system. From (67), (68), and (76) we further have that

$$dS = dS_1 + dS_2 = d(S_1 + S_2) , \qquad (79)$$

or, in words: the change of entropy of a system composed of two bodies in thermal contact, during a quasi-statical process, is the sum of the entropy changes in the two bodies separately.

By a suitable choice of the additive constant entering into our definition of entropy we can arrange so that

$$S = S_1 + S_2 , \qquad (80)$$

or: the entropy of a system is the sum of the entropies of its different parts.

Equation (76) contains the mathematical statement of the Second Law of Thermodynamics, which follows as a purely mathematical consequence of the Carathéodory principle: *The differential of the heat,* dQ, *for an infinitesimal quasi-statical change, when divided by the absolute temperature* T, *is a perfect differential,* dS, *of the entropy function.*

The essential differences between (47) and (76) should be noted. In (47) T and S (and τ and σ) are functions of *all* the physical variables; while in (76), τ and T depend only on the empirical temperature, t, which is the same for the different parts of the system; furthermore, σ and S depend only on the variables (σ_1 and σ_2) which do not alter their values for adiabatic changes; finally, T is a universal function of t, and S is a function only of $\sigma(\sigma_1, \sigma_2)$.

We shall now show that the gas-thermometer scale, $pV = t$, defines a temperature scale proportional to the absolute temperature. It should be emphasized that the usual assumption that $pV = t$ defines, apart from a constant factor, the absolute temperature scale is logically unsound. To assume beforehand that the absolute temperature scale should be precisely $pV = t$ and not any other monotonic function, $t = f(pV)$, is to beg the question. We shall see that we cannot identify $pV \propto T$ without an appeal to the Second Law of Thermodynamics. To do this logically, we need to know the internal energy, U, as a function of the state of the gas. The experi-

mental basis is the idealized Joule-Kelvin experiment, which shows
that, when a gas expands adiabatically without doing any external
work, the product pV (i.e., the gas temperature, $t = f[pV]$) does not
change. (It should be noticed that an appeal is made here to an ir-
reversible process. As Carathéodory has pointed out, it is necessary
at some stage to appeal to an irreversible process to fix the zero-
point of the absolute temperature scale.) It follows, then, from the
Joule-Kelvin experiment that U is independent of V. Hence, we can
write

$$U = U(t) ; \qquad pV = F(t) , \tag{81}$$

where t is the empirical temperature. For the differential of the heat
for a quasi-statical change, we have

$$dQ = dU + pdV = \frac{dU}{dt} dt + F(t) \frac{dV}{V}$$

$$= F(t) \left[\frac{1}{F(t)} \frac{dU}{dt} dt + d \log V \right] . \tag{82}$$

Define a quantity, χ, by the equation

$$\log \chi = \int \frac{1}{F(t)} \frac{dU}{dt} dt + \text{constant} . \tag{83}$$

Equation (82) can be re-written as

$$dQ = F(t)d \log \chi V . \tag{84}$$

Hence, we can choose $F(t)$ as the integrating denominator

$$\tau = F(t) ; \qquad \sigma = \log \chi V . \tag{85}$$

Equation (84) now takes the standard form

$$dQ = \tau d\sigma . \tag{86}$$

We can, of course, choose the integrating factor in many other
ways. If

$$\sigma^* = \sigma^*(\sigma) ; \qquad \tau^* = F(t) \frac{d\sigma}{d\sigma^*} , \tag{85'}$$

equation (86) can be written as

$$dQ = \tau^* d\sigma^* . \tag{86'}$$

Hence, there is no a priori reason to choose $\tau = F(t) = pV$ as the integrating denominator. But we have shown that

$$g(t) = \frac{\partial \log \tau}{\partial t} \tag{87}$$

is a universal function which is the same in whatever way we may choose to define the integrating denominator. $g(t)$, defined by (87), is invariant to the transformations (85'). From our definition of the absolute temperature (Eq. [63]) we have

$$T = Ce^{\int g(t)dt} = CF(t) = CpV . \tag{88}$$

Thus the absolute temperature scale agrees with the temperature on the gas-thermometer scale.

From $dQ = TdS$, we find that

$$dS = \frac{1}{C} \, d \log \chi V , \tag{89}$$

or

$$S = \frac{1}{C} \log \chi V + \text{constant} . \tag{90}$$

If we write $U = c_V T$ and consider c_V as a constant, and further define $R = 1/C$, we have

$$\log \chi = \int \frac{c_V}{RT} \, dT = \frac{c_V}{R} \log T + \text{constant} . \tag{91}$$

Hence, finally,

$$S = S_0 + c_V \log T + R \log V , \tag{92}$$

where S_0 is a constant.

10. *The principle of the increase of entropy.*—So far we have considered only quasi-statical changes of state, though at one point

(§ 9) we had to consider a nonstatical process when we appealed to an idealized Joule-Kelvin experiment. We shall now discuss nonstatical processes more generally.

We shall consider, as we have done so far, an adiabatically inclosed system composed of two bodies in thermal contact. The equilibrium state of such a system can be characterized by three independent variables, such as V_1, V_2, t (the variables we have used so far). We shall now choose V_1, V_2, and S as the independent variables. Let V_1^0, V_2^0, and S^0 be the values of the physical variables in an initial state and V_1, V_2, and S in a final state. We now assert that S is either always greater than S^0 or always less than S^0.

To show this, we consider the final state as being reached in two steps:

a) We alter the volumes V_1^0 and V_2^0 by means of a quasi-statical and adiabatical process such that the volumes at the end are V_1 and V_2. In this way we keep the entropy constant and equal to S^0.

b) We then alter the state of the system, keeping the volumes fixed, but change the entropy by means of adiabatical but nonstatical processes (such as stirring, rubbing, etc., in which $dQ = 0$ but $dQ \neq TdS$) such that the entropy changes from S^0 to S.

If, now, S were greater than S^0 in some processes and less than S^0 in others, then it should be possible to reach every close neighboring state, (V_1, V_2, S), of the initial state, (V_1^0, V_2^0, S^0), by means of adiabatic processes. (After reaching the state (V_1, V_2, S), we can reach all the states, (V_1', V_2', S), by means of processes [*a*]). This contradicts Carathéodory's principle in its more general form, which postulates that in any arbitrarily near neighborhood of a state, (V_1^0, V_2^0, S), there exist adiabatically inaccessible states even when we allow nonstatical processes. Consequently, by means of the processes (*b*), and therefore also by means of the processes (*a*) and (*b*), the entropy S^0 of the system can either only increase or only decrease. Since this is true for every initial state, we see that, because of the continuity of the impossibility of "increase" or "decrease," the entropy of the system we have considered must either never increase or never decrease. The same must also be true for two independent systems because of the additive nature of entropy. We have thus proved: *For all the possible changes (quasi-statical or otherwise)*

that an adiabatically inclosed system can undergo, the entropy, S, *must either never increase or never decrease.*

Whether the entropy decreases or increases depends in the first instance on the sign of C introduced in our definition of entropy (78). This is naturally chosen in such a way that the absolute temperature is positive. Then one single experiment is sufficient to determine the sign of the entropy change. By the expansion of an ideal gas, G, into a vacuum, the entropy S_G of the gas increases, as can be seen from equation (92) (V increases and T remains the same). We now consider a system composed of the gas, G, and of another body, K. If we consider such changes of state in which the entropy S_K of the body remains constant and S_G changes, then $S = S_G + S_K$ must increase (since, as we have just seen, S_G always increases); consequently, S can never decrease. Hence, if we consider processes in which the entropy of the gas remains constant, it is clear that, as S can only increase, S_K can only increase; this is true also when K and G are adiabatically separated. Hence, in general we have proved the following important result:

For an adiabatically inclosed system the entropy can never decrease:

$$S > S^0, \quad \text{(nonstatical process)}, \; \left. \right\}$$
$$S = S^0 \quad \text{(statical process)} . \qquad (93)$$

It follows that if in any change of state of an adiabatically inclosed system the entropy becomes different, then no adiabatic change can be realized which will change the system from the final to the initial state. In this sense, therefore, every change of state in which the entropy changes must be irreversible. This can also be stated as follows: For an adiabatically inclosed system the entropy must tend to a maximum.

Still another formulation of the foregoing is

$$\oint \frac{dQ}{T} \leqslant 0, \qquad (94)$$

where the integral is taken over a closed cycle of changes, it being assumed that during the cycle the system can be characterized at

each instant by a unique value for T. To prove this let us consider a cycle of changes in which the working substance is carried through states A and B, and in which, further, the part of the cycle from A to B is carried out adiabatically (but not necessarily statically) while the part of the cycle from B to A is carried out reversibly. For this cycle of changes

$$\oint \frac{dQ}{T} = \int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ}{T}.$$

Since the part of the cycle from A to B has been carried out adiabatically, we have

$$\oint \frac{dQ}{T} = \int_B^A \frac{dQ}{T} = S_A - S_B, \qquad (94')$$

which, according to (93), must be zero or negative. We have thus proved (94) for the special cycle of changes considered. The arguments can be extended to prove (94) quite generally.

We thus see that the full mathematical content of the second law can be deduced from Carathéodory's principle. But the question still remains whether Carathéodory's principle can lead us to Kelvin's formulation of the second law. To answer this, we must supplement Carathéodory's principle with some additional axioms before we can derive Kelvin's or Clausius' formulation of the second law. The arguments necessary to establish this involve some rather delicate considerations, and these go beyond the scope of our present chapter. The interested reader may refer to an illuminating discussion by T. Ehrenfest Afanassjewa quoted in the bibliographical note at the end of the chapter.

11. *The free energy and the thermodynamical potential.*—We have shown in § 10 that

$$\oint \frac{dQ}{T} \leqslant 0, \qquad (95)$$

where the integral is taken over a closed cycle of changes. Let us suppose that the closed cycle of changes carries the working sub-

stance through states A and B, and that, further, the part of the
cycle for B to A is along a reversible path. Then

$$\oint \frac{dQ}{T} = \int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ}{T} , \qquad (96)$$

or, since the path from B to A is reversible, we have, according to
(95) and (96),

$$\int_A^B \frac{dQ}{T} \leqslant S_B - S_A . \qquad (97)$$

Equation (97) is, of course, equivalent to (95).

Let us now consider an isothermal change. Then (97) can be writ-
ten as

$$\int_A^B dQ \leqslant T(S_B - S_A), \qquad (98)$$

where T denotes the constant temperature. By the First Law of
Thermodynamics we now have.

$$U_B - U_A + W_{AB} \leqslant T(S_B - S_A) , \qquad (99)$$

where W_{AB} is the work done by the system. Equation (99) can be
written alternatively in the form

$$F_B - F_A + W_{AB} \leqslant 0 , \qquad (100)$$

where

$$F \equiv U - TS . \qquad (101)$$

The function F, thus introduced, is called the "free energy" of the
system. From (100) it follows that for an isothermal change in which
no work is done the free energy cannot increase.

Another function of importance is the thermodynamical potential,
defined by

$$G = F + pV = U + pV - TS . \qquad (102)$$

It is clear that if the temperature and the external forces are kept
constant G cannot increase.

12. *Some thermodynamical formulae.*—So far we have concerned ourselves only with general principles. We shall conclude this chapter with the derivation of some thermodynamical formulae which are of considerable practical importance.

Let us consider a homogeneous isotropic medium. Then for a quasi-statical change (in Eq. [14] we shall now use the absolute temperature, T, instead of the empirical temperature, t)

$$dQ = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV + \left(\frac{\partial U}{\partial T}\right)_V dT .\qquad (103)$$

Since dQ/T is a perfect differential, we should have

$$\frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial U}{\partial V} + p\right)\right] = \frac{\partial}{\partial V}\left(\frac{1}{T}\frac{\partial U}{\partial T}\right),\qquad (104)$$

or, carrying out the differentiations,

$$-\frac{1}{T^2}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] + \frac{1}{T}\left[\frac{\partial^2 U}{\partial T \partial V} + \left(\frac{\partial p}{\partial T}\right)_V\right] = \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T},\quad (105)$$

or

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p .\qquad (106)$$

Let us next consider the free energy. By definition (Eq. [101])

$$dF = dU - TdS - SdT ,\qquad (107)$$

or, since

$$dQ = TdS = dU + pdV ,\qquad (108)$$

we have

$$dF = - SdT - pdV .\qquad (109)$$

dF is, however, a perfect differential. Hence, we should have

$$\left(\frac{\partial F}{\partial T}\right)_V = -S ; \qquad \left(\frac{\partial F}{\partial V}\right)_T = -p .\qquad (110)$$

Finally, let us consider the thermodynamical potential, G. We have

$$dG = dF + pdV + Vdp , \tag{111}$$

or, using (109),

$$dG = -SdT + Vdp . \tag{112}$$

Hence, we should have

$$\left(\frac{\partial G}{\partial T}\right)_p = - S ; \qquad \left(\frac{\partial G}{\partial p}\right)_T = V . \tag{113}$$

We shall have occasion later to use (106), (110), and (113).

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