Kelvin and Caratheodory—A Reconciliation

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(Received 28 December 1965)

In conventional thermodynamics, the two most important consequences of the second law of thermodynamics, namely, the existence of an absolute temperature scale and the existence of an entropy function are deduced from the Kelvin–Planck statement or its equivalent, the Clausius statement, with the aid of the Carnot engine and Carnot refrigerator. In the Caratheodory method, a new statement of the second law is made; the Carnot cycle is dispensed with and purely analytical methods are used to derive the absolute temperature and the entropy. It is shown in this paper how the analytic methods of Caratheodory may be used without replacing the traditional statements of the second law by a new axiom. Both the Caratheodory statement of the second law and the Caratheodory theorem on Pfaffian differential forms are unnecessary.

INTRODUCTION

IN the conventional treatment of that part of classical thermodynamics dealing with the second law and its consequences, engineering experiences with heat engines and refrigerators are generalized into the Kelvin–Planck and Clausius statements of the second law: (Kelvin–Planck) *No process is possible whose sole result is the conversion of heat completely into work.* (Clausius) *No process is possible whose sole result is the transfer of heat from a colder to a hotter body.*

These statements are then shown to be equivalent. Using either statement, Carnot's theorem and its corollary are proved: (Theorem) *No engine operating between two reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.* (Corollary) *All Carnot engines operating between the same two reservoirs are equally efficient.*

The fact that the efficiency of a Carnot engine is independent of the nature of the substance undergoing the cycle leads to the definition of the Kelvin scale $Q_1/T_1=Q_2/T_2$.

It is possible then to prove, for any reversible cycle, the Clausius theorem

$$\oint_R \frac{dQ}{T}=0,$$

and the concept of entropy then follows directly

$$dS=dQ_R/T.$$

Among the many good reasons why this conventional treatment has been popular with engineers, physicists, and chemists for so many years should be mentioned (1) the second law is a generalization from simple kinds of experience that everyone can understand and (2) the mathematical manipulations needed to prove the various theorems and to derive the necessary equations are very simple. The fact that all of the proofs require the operation of one or more Carnot engines is not much more of a strain on one's imagination than what is evoked in mechanics, —e.g., point masses, frictionless and massless pulleys, inextensible strings, etc.

Nevertheless, an entirely different and purely axiomatic treatment of the second law and its consequencies has existed almost sixty years. Christian Caratheodory,[1] a mathematician of Greek origin, studying and working in Germany and stimulated by the physicist, Max Born, formulated an axiom in 1908 *to replace* the Kelvin–Planck or Clausius statements of the second law. The Caratheodory axiom was not based directly on any experience or experiments but could be used in conjunction with a purely mathematical theorem (also due to Caratheodory) to derive all of the consequences of the conventional method. The axiom is

In the neighborhood (however close) of any equilibrium state of a system of any number of independent coordinates, there exist other equilibrium states which are inaccessible by means of reversible adiabatic processes.

The mathematical theorem that Caratheodory proved was concerned with the conditions of integrability of Pfaffian differential equations. It may be stated thus:

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[1] C. Caratheodory, Math. Ann. 67, 355 (1909) (German).

Given an expression of the type $Pdx+Qdy+Rdz+\cdots$, *where* P, Q, R, $\cdots$ *are functions of* x, y, z, $\cdots$. *If, in the neighborhood of a point, there are other points which cannot be reached along solution curves of the equation* $Pdx+Qdy+Rdz+\cdots=0$, *then there exist functions* Λ and Σ *of* x, y, z, $\cdots$ *such that* $Pdx+Qdy+Rdz+\cdots=\Lambda d\Sigma$.

Using this theorem, in conjunction with Caratheodory's axiom, it is possible to show that the small amount of heat dQ_R absorbed reversibly by any system at a temperature t (on any scale) may be written

$$dQ_R=\varphi(t)f(\sigma)d\sigma,$$

where σ is an undetermined function of the independent coordinates of the system. The Kelvin temperature T can then be associated with $\varphi(t)$ and the entropy change dS with $f(\sigma)d\sigma$.

Due to the fact that Caratheodory's axiom was not based directly on experience and that the proof of his theorem was longwinded and difficult, most physicists and textbook writers ignored the Caratheodory treatment, in spite of the efforts of Born, Landé, Chandrasekhar,[2] and Buchdahl[3] to promote it. In the last few years, due mainly to the work of Turner,[4] Sears,[5] and Landsberg,[6] it has been found possible to clear away some of the unnecessary mathematical obstacles, and to arrive at the worthwhile results of Caratheodory in a simpler manner.

Turner first showed how to go from the Caratheodory axiom to the existence of reversible adiabatic surfaces by invoking a simple geometrical argument, discarding completely the Caratheodory mathematical theorem. Once the set of nonintersecting reversible adiabatic surfaces was shown to exist, ordinary mathematical methods could be used to infer the existence of an absolute temperature and an entropy function.

Sears elucidated and simplified Turner's exposition. In later work, Sears converted the Caratheodory axiom into an equivalent one in terms of adiabatic work, instead of accessibility of states. Landsberg showed how the Caratheodory axiom could be derived from the Kelvin–Planck statement of the second law. To summarize roughly: Turner showed how one could dispense with the Caratheodory mathematical theorem, and Landsberg showed how one could dispense with the Caratheodory axiom. The purpose of this paper is to dispense with both.

It is the opinion of the author that the body of experience leading to the Kelvin–Planck and the Clausius statements of the second law represents the main strength of thermodynamics, and should not be given up. An axiomatic treatment of a physical theory is very much to be desired, *provided* the fundamental axiom is a generalization of experience like, for example, Newton's laws of motion. It is the author's contention that the analytic methods used by Caratheodory are superior to those of the conventional method because the analytic steps deal directly with the coordinates and equations of systems, instead of being obscured by the working of the all-powerful but mysterious Carnot engine. In short, what is really desirable is to *base the analytical methods of Caratheodory (or a simplification thereof) on the conventional Kelvin–Planck statement of the second law*. This can be done. *The Caratheodory axiom, modified or unmodified, adds little to our understanding of nature and is unnecessary in the derivation of the equations expressing the consequencies of the second law—which law is best stated in its Kelvin–Planck formulation.*

In what is to follow, the existence of reversible adiabatic surfaces is inferred directly from the Kelvin–Planck statement of the second law. Once reversible adiabatic surfaces are shown to exist, everything else follows (more or less) the analytic methods of Caratheodory.

I. EXISTENCE OF REVERSIBLE ADIABATIC SURFACES

The systems most often dealt with in thermodynamics have only three thermodynamic coordinates, the empiric temperature t (measured on any scale), a generalized force such as pressure P, or tension F, or magnetic intensity H, etc., and the corresponding generalized displacement such

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[2] S. Chandrasekhar, *Stellar Structure* (Univ. of Chicago Press, Chicago, Illinois, 1939; Dover Publications, New York, 1957), Chap. 1.

[3] H. A. Buchdahl, Zeit. Phys. **152**, 425 (1958) (in English).

[4] L. A. Turner, Am. J. Phys. **28**, 781 (1960); **29**, 40 (1961); **30**, 506 (1962).

[5] F. W. Sears, Am. J. Phys. **31**, 747 (1963).

[6] P. T. Landsberg, Nature **201**, 485 (1964).

[7] F. W. Sears, Am. J. Phys. **34**, 665 (1966).

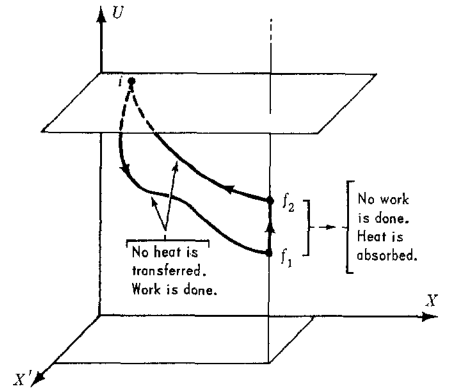

FIG. 1. Both f_1 and f_2 lying on a line of constant X and X' cannot be reached by reversible adiabatic processes from i.

as volume V, length L, total magnetization M. The first law for a simple hydrostatic system undergoing an infinitesimal reversible process is, for example, $dQ_R = dU + PdV$. Since an equation of state exists, both P and U are functions of t and V, and therefore dQ_R may be represented by a differential expression involving the differentials of only two independent variables dt and dV. A system of this sort, however, is not suited for general discussions of thermodynamic theory because *the mathematical properties of differential expressions involving only two independent variables are not shared by those involving more than two.*

One should consider systems of at least three independent coordinates, such as a composite system consisting of two different gases separated by a heat-conducting wall, where the heat transferred in an infinitesimal reversible process is given by $dQ = dU + PdV + P'dV'$, and U, P, and P' are functions of t, V, and V'; or a uniform system such as a paramagnetic gas, where $dQ = dU + PdV - HdM$, and U, P, and H are functions of t, V, and M. Therefore, let us 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 is $dQ = dU + YdX + Y'dX'$, 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_R will hold equally well for systems with *more* or *fewer* independent variables.

In Fig. 1, the three independent variables U, X, and X' are plotted along three rectangular axes and an arbitrarily chosen equilibrium state i is indicated. 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 at every point of which the values of X and X' are constant. 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 two 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 therefore 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 and X') there would be another single 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. 2. *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 sufface has been shown to exist in a U, X, X' space, such a surface must also exist in a t, x, x' 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

$$\sigma(t,X,X')=\text{const}, \tag{1}$$

where σ represents some, as yet, undetermined function. *Surfaces corresponding to other initial states would be represented by different values of the constant.*

Reversible adiabatic surfaces cannot intersect because, if they did, it would be possible, as shown in Fig. 3, 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 and X', along reversible adiabatic paths. We have just shown that this is impossible.

Once the existence of a set of nonintersecting reversible adiabatic surfaces is established, the methods of Caratheodory may be applied to lead to the Kelvin scale and to the concept of entropy. These methods are well-known and are to be found in many books and papers. Since there are slightly different variations in these methods, it was thought best to give, in the following sections the details of the treatment regarded by the author as the simplest. He makes no claim to originality.

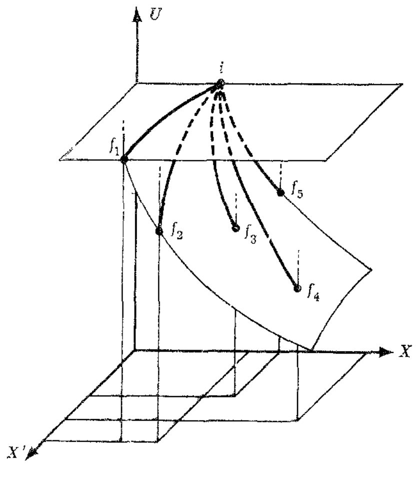

FIG. 2. All states that can be reached by reversible adiabatic processes starting at i lie on a surface.

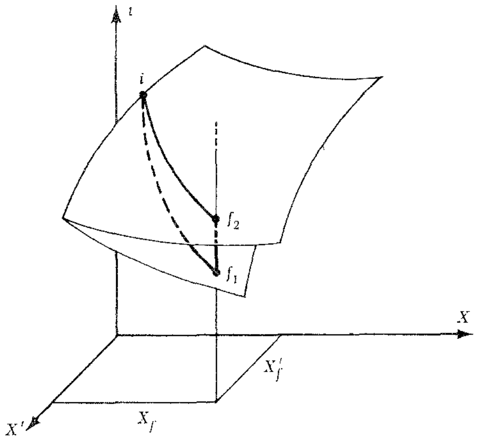

FIG. 3. If two reversible adiabatic surfaces could intersect, it would be possible to violate the second law by performing the cycle if_1f_2i.

II. THE INTEGRABILITY OF dQ

For a system whose coordinates are the empiric temperature t, two generalized forces Y and Y', and two corresponding generalized displacements, X and X', the heat transferred in an infinitesimal reversible process is given by the first law,

$$dQ=dU+YdX+Y'dX', \tag{2}$$

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, any point in this space may be determined by specifying the value of σ along with X and X', so that we may regard the internal energy function U, as well as Y and Y' as functions of σ, X, X'. Then

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

and

$$dQ=\frac{\partial U}{\partial\sigma}d\sigma+\left(Y+\frac{\partial U}{\partial X}\right)dX+\left(Y'+\frac{\partial U}{\partial X'}\right)dX'. \tag{3}$$

Since the coordinates σ, X, and X' are independent variables, this equation must be true for all values of $d\sigma$, dX, and dX'. Suppose two of the differentials, $d\sigma$ and dX are zero and dX' is not. The provision that $d\sigma=0$ (or $\sigma=\text{const}$) is the condition for an adiabatic process, where $dQ=0$, 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 σ, 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

$$dQ=(\partial U/\partial\sigma)_{\text{s.c.,s.c.}}\,d\sigma, \tag{4}$$

and if we *define* a function λ by the equation

$$\lambda=(\partial U/\partial\sigma)_{\text{s.c.,s.c.}'}, \tag{5}$$

we get the result that

$$dQ=\lambda d\sigma. \tag{6}$$

The function $1/\lambda$ is therefore seen to be an integrating factor, such that when dQ is multiplied by $1/\lambda$, there results an exact differential $d\sigma$. This result obviously holds for any number of independent variables. An infinitesimal of the type $Pdx+Qdy+Rdz+\cdots$, 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 dQ referring to a physical system of any number of independent coordinates possesses an integrating factor.*

Our final task is to impart physical significance to the integrating factor $1/\lambda$ and to the function σ.

III. THE PHYSICAL SIGNIFICANCE OF $\boldsymbol{\lambda}$

The quantity λ, as defined by Eq. (5), is a function of σ, X, and X' or, with equal validity, a function of σ, t and only one of the X's. Since λ involves t, let us go back to the fundamental concept of temperature as the property of a system determining thermal equilibrium between it and a reference system. Let us therefore consider two systems, each of three independent coordinates (for mathematical generality) in contact through a diathermic wall and at all times in thermal equilibrium with a common temperature t, and together constituting a composite system with five independent coordinates. Thus:

Main system. The three independent coordinates are t, X, and X', and the reversible adiabatic surfaces are specified by different values of the function σ. When heat dQ is transferred, σ changes by $d\sigma$ and $dQ=\lambda d\sigma$ where λ is a function of t, σ, and X.

Reference system. The three independent coordinates are t, $\hat{X}$, and $\hat{X}'$, and the reversible adiabatic surfaces are specified by different values of the function $\hat{\sigma}$. 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 $\hat{X}$.

Composite system. The five independent coordinates are t, X, X', $\hat{X}$, $\hat{X}'$, and the reversible adiabatic hypersurfaces are specified by different values of the function $\boldsymbol{\sigma}$ of these independent variables.

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

$$d\boldsymbol{\sigma}=\frac{\partial\boldsymbol{\sigma}}{\partial t}dt+\frac{\partial\boldsymbol{\sigma}}{\partial\sigma}d\sigma+\frac{\partial\boldsymbol{\sigma}}{\partial\hat{\sigma}}d\hat{\sigma}+\frac{\partial\boldsymbol{\sigma}}{\partial X}dX+\frac{\partial\boldsymbol{\sigma}}{\partial\hat{X}}d\hat{X}. \tag{7}$$

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

$d\mathbf{Q}=dQ+d\hat{Q}$, and $\boldsymbol{\lambda}d\boldsymbol{\sigma}=\lambda d\sigma+\hat{\lambda}d\hat{\sigma}$, or

$$d\boldsymbol{\sigma}=(\lambda/\boldsymbol{\lambda})d\sigma+(\hat{\lambda}/\boldsymbol{\lambda})d\hat{\sigma}. \tag{8}$$

Comparing the two expressions for $d\boldsymbol{\sigma}$ given by Eqs. (7) and (8), we get $(\partial\boldsymbol{\sigma}/\partial t)=0$, $(\partial\boldsymbol{\sigma}/\partial X)=0$, $(\partial\boldsymbol{\sigma}/\partial\hat{X})=0$, and therefore $\boldsymbol{\sigma}$ does not depend on t, X, or $\hat{X}$, but only on σ and $\hat{\sigma}$.

That is

$$\boldsymbol{\sigma}=\boldsymbol{\sigma}(\sigma,\hat{\sigma}). \qquad (9)$$

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

$$(\lambda/\boldsymbol{\lambda})=(\partial\boldsymbol{\sigma}/\partial\sigma),\quad (\hat{\lambda}/\boldsymbol{\lambda})=(\partial\boldsymbol{\sigma}/\partial\hat{\sigma}), \qquad (10)$$

and therefore the two ratios, $\lambda/\boldsymbol{\lambda}$ and $\hat{\lambda}/\boldsymbol{\lambda}$ are also independent of t, X, and $\hat{X}$. These two *ratios* depend only on the σ's.

Since the λ of the main system depends on t, σ, and X, while the $\boldsymbol{\lambda}$ of the composite system depends on t, σ, $\hat{\sigma}$, X, and $\hat{X}$, the question arises as to how the ratio $\lambda/\boldsymbol{\lambda}$ can depend only on σ and $\hat{\sigma}$. Clearly, λ cannot depend on X and $\boldsymbol{\lambda}$ cannot depend on X or $\hat{X}$, because if they did, the ratio $\lambda(t,\sigma,X)/\boldsymbol{\lambda}(t,\sigma,\hat{\sigma},X,\hat{X})$ could not reduce to a function of σ and $\hat{\sigma}$ only. Similarly, $\hat{\lambda}$ could not depend on $\hat{X}$. It follows that the three λ's *must* have the structure

$$\left.\begin{aligned}\lambda&=\varphi(t)f(\sigma),\\ \hat{\lambda}&=\varphi(t)\hat{f}(\hat{\sigma}),\\ \boldsymbol{\lambda}&=\varphi(t)g(\sigma,\hat{\sigma}),\end{aligned}\right\} \qquad (11)$$

so that, when ratios are formed, $\varphi(t)$ cancels out. Referring now only to our main system as representative of *any system of any number* of independent coordinates, we have from the first equation in the set indicated as Eq. (11)

$$dQ=\varphi(t)f(\sigma)d\sigma. \qquad (12)$$

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 reversible 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 reversible dQ that always admits an integrating factor regardless of the second law is of course interesting, 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.

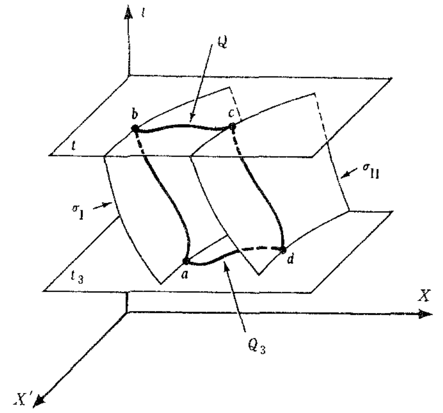

FIG. 4. Two reversible isothermal heat transfers, Q at t from b to c, and Q_3 at t_3 from a to d, between the same two reversible adiabatic surfaces σ_I and σ_{II}. The cycle *abcda* is a Carnot cycle.

It has been stated that the function λ of *any system of any number of independent coordinates* may be expressed in the form

$$\lambda=\varphi(t)f(\sigma)d\sigma,$$

as shown by the first equation of the set numbered (11). The second equation in this set shows this to be true for the reference system whose independent coordinates may be taken to be t, $\hat{\sigma}$, and $\hat{X}$. The third equation for the composite system, however, is not in the proper form unless it can be shown that

$$g(\sigma,\hat{\sigma})=\mathbf{f}(\boldsymbol{\sigma}).$$

This may be done as follows: Substituting Eqs. (11) into Eqs. (10), we get

$$f=g(\partial\boldsymbol{\sigma}/\partial\sigma),\quad \text{and}\quad \hat{f}=g(\partial\boldsymbol{\sigma}/\partial\hat{\sigma}).$$

Differentiating f with respect to $\hat{\sigma}$, and also $\hat{f}$ with respect to σ, setting the two derivatives equal to zero, and subtracting the two equations, we get a vanishing Jacobian, which indicates functional dependence between g and $\boldsymbol{\sigma}$.

IV. THE KELVIN TEMPERATURE SCALE

Consider a system of three independent variables t, X, and X', with two isothermal surfaces and two reversible adiabatic surfaces drawn in Fig. 4. 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 σ_I to another state c lying on another reversible adiabatic surface specified by σ_{II}. Then, since Eq. (12) tells us that $dQ=\varphi(t)f(\sigma)d\sigma$, we have

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

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

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

Taking the ratio of Q to Q_3 we get

$$\frac{Q}{Q_3}=\frac{\varphi(t)}{\varphi(t_3)}=\frac{\text{A function of the temperature at which } Q \text{ is transferred}}{\text{The same function of temperature at which } Q_3 \text{ is transferred}}$$

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

$$\frac{Q(\text{between } \sigma_I \text{ and } \sigma_{II} \text{ at } T)}{Q_3(\text{between } \sigma_I \text{ and } \sigma_{II} \text{ at } T_3)}=\frac{T}{T_3}. \tag{13}$$

Thus, *two temperatures on the Kelvin scale are to each other as the heats transferred reversibly between the same two reversible adiabatic surfaces at these two temperatures.*

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°K, then the Kelvin temperature is defined to be

$$T=273.16°\text{K}(Q/Q_3). \quad \left\{\begin{matrix}\text{Between the same two reversible}\\ \text{adiabatic surfaces.}\end{matrix}\right\} \tag{14}$$

V. THE CONCEPT OF ENTROPY

In a system of any number of independent variables, all states accessible from a given initial state by reversible adiabatic processes lie on a surface (or hypersurface) $\sigma(t, X, X', \cdots)=\text{const}$. The entire $t, X, X', \cdots$ space may be conceived to be crossed by many nonintersecting surfaces of this kind each corresponding to a different value of σ. In an infinitesimal *reversible nonadiabatic* process involving a transfer of heat dQ, a system in a state represented by a point lying on a surface σ, changes until its state point lies on another surface $\sigma+d\sigma$. We have seen that $dQ=\varphi(t)f(\sigma)d\sigma$. Since the Kelvin temperature T is defined so that $T/T'=dQ/dQ'$, $d\sigma$ being the same for both heat transfers, it follows that $T=k\varphi(t)$, where k is an arbitrary constant. Therefore, $dQ/T=1/kf(\sigma)d\sigma$. Since σ is an actual function of $t, X, X', \cdots$, the right-hand member is an exact differential, which we may designate by dS, whence

$$dS=dQ/T. \tag{15}$$

The quantity S is called the *entropy* of the system, and dS is an infinitesimal *entropy change* of the system. In a finite change of state from i to f, the entropy change is S_f-S_i where

$$S_f-S_i=\int_i^f \frac{dQ}{T}. \tag{16}$$

A third relation may be obtained by integrating Eq. (16) around a *reversible* cycle, so that the initial and final entropies are the same. The result is the Clausius theorem

$$\oint \frac{dQ}{T}=0. \tag{17}$$

The author would like to emphasize that the preceding methods of arriving at the Kelvin temperature scale and the concept of entropy are not more general or more rigorous than the old engineering methods involving the use of the Carnot engine. They are merely more revealing, more open; they enable one to see better what is going on.

ACKNOWLEDGMENTS

The author is very much indebted to Louis A. Turner for the opportunity to discuss these matters with him and for his helpful advice. All teachers of thermodynamics should be indebted to him for his pioneer work in (to use his words) "by-passing some of the more difficult mathematical nonessentials of Caratheodory."