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Foundations of Thermodynamics

P. T. LANDSBERG

Marischal College, University of Aberdeen, Aberdeen, Scotland

CONTENTS

1. Introduction

Aim

THE purpose of this paper is to effect a geometrization of thermodynamics by a development of the axiomatic approach initiated by Carathéodory (1909)*, and developed by Born (1921). The elegance and power of this approach have been recognized only slowly, and, although it has been occasionally expounded by various authors (Born, 1949; Buchdahl, 1949, 1954, 1955; Chandrasekhar, 1939; Eisenschitz, 1955; Landé, 1926; Margenau and Murphy, 1943), the subject has not progressed to any extent since 1921. That it is being taken up at all is in large measure the result of the efforts made in this direction by Max Born.

In the writing of this paper discussions of those parts of the subject which are adequately covered elsewhere have been omitted. For instance, for the relation between the axiomatic and the conventional approach to

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* See references in Bibliography at end of article.

thermodynamics, for the discussion of the ideal gas case by the axiomatic method, and for the elementary properties of Pfaffian expressions, the reader is referred to the expositions cited. Thus most of the material presented appears here at least in a new form. It is as a result of this geometrization of thermodynamics that the third law appears in a novel form (Part III).

Only the elementary parts of thermodynamics (those required in the discussion of the properties of gases, the expansion of solids, etc.) are covered here. The extension of the basic concepts to gravitation, to the thermodynamics of the electromagnetic field, and to radiation, is not attempted. It can be achieved, once the basic concepts are established, with the aid of properly modified definitions (see Guggenheim, 1949).

For ease of reference the main results have been numbered as theorems. There are ten theorems in Part I, ten in Part II, and three in Part III. Six groups of assumptions, denoted by (A1) to (A6), are required. Assumption (A1) stipulates as known those parts of physics which lie outside thermodynamics; (A3) stipulates the existence of a certain partition; (A4) provides an assumption about the existence of certain physical processes from which the reversibility of a given process can be inferred. The remaining three assumptions each incorporate the elements of one of the laws of thermodynamics as conventionally stated. The definitions are denoted by (D1) to (D15).

Informal Characterization of Basic Concepts

Certain concepts which are essential to the geometrization of thermodynamics are formally introduced at appropriate points throughout the paper. It may help the reader to see the underlying unity of these developments if some of these concepts are briefly and informally discussed here. The paper deals throughout with sets of points in a suitably defined n-dimensional thermodynamic phase space E. Thus, for properly restricted ranges of the independent variables of a given system, there will exist a set of points β with the following properties: for any two points A, B of β, there exists an adiabatic linkage between the states which these points represent (the states, and the points which represent them, will be denoted by the same letter). The term "linkage" is meant to express that an adiabatic process which carries A into B is just as satisfactory as an adiabatic process which carries B into A. The requirement that processes of both types shall exist is much more restrictive and is not wanted. The first law of thermodynamics is concerned largely with the properties of such sets of points β. The possibility of drawing a continuous curve in E such that every point on the curve belongs to a given set β is not seriously discussed until the treatment of the first law has been completed (i.e., in Part II). For any given set of points β, one is now led to look for those subsets of β (if they exist) which fill an n-dimensional volume in E. The second law deals only with such subsets, which are denoted by γ, and it is essential that these subsets γ be open (i.e., they must exclude boundary points). When one has finished with the second law, certain questions are left unanswered. For instance, can a set β contain the boundary points of any of its subsets γ? Can a set β contain points which are neither in any of its subsets γ nor on the boundaries of such subsets? A third law of thermodynamics becomes therefore absolutely essential in the present approach if ambiguities are to be avoided. It settles the two questions which have just been raised, as discussed in Part III.

This paper aims not only at developing these new concepts, but also at removing certain deficiencies of the axiomatic approach as currently expounded. Some of these deficiencies will now be enumerated. A first group of criticisms can be directed against ambiguity in definitions. The terms "quasi-static" and "reversible," as applied to physical processes, are often regarded as synonymous, and the precise meaning of each left in doubt. Again, the term "diathermanous," as applied to a partition which allows thermal equilibrium to establish itself, is nowhere fully defined. The difficutly in devising a good definition is that one regards the notion of heat and of thermal equilibrium as still unknown when defining this term. It is often believed sufficient to regard a partition as diathermanous if it forces one new relation upon the parameters of the systems that it separates. The precaution, for instance, of excluding a partition which moves so as to equalize the pressures in the two compartments is usually omitted. The term "adiabatic," as applied to partitions, presents new difficulties. It is usual to introduce adiabatic enclosures in the axiomatic approach partly to give a definition of thermal energy in terms of purely mechanical quantities. This, however, leads to an unusual sense of the word "adiabatic," since this word is usually understood to mean that there is no exchange of thermal energy. An adiabatic enclosure, therefore, allows an exchange of electrical and electromagnetic energy; it also allows changes in long-range forces applied from the outside, as in adiabatic demagnetization. If, however, a definition is used at the outset which allows for all of these influences, then it cannot be claimed that thermal energy has been defined in purely mechanical terms. We shall deal here with this dilemma by introducing the term "adiabatic" in a restricted sense first and extending it later. A second group of minor criticisms can be directed against the usual statement of Carathéodory's principle and against the proof of the theorem on Pfaffian equations which is due to Carathéodory. These considerations do not refer to the domain of definition of the Pfaffian equations for quasi-static adiabatic processes, although this is, in fact, of considerable importance for changes in the state of aggregation of systems and for a discussion of states at the absolute zero of temperature. This limitation in the current expositions is the result of the assumption that the thermodynamic phase space is adequately represented by an *unbounded* space. This procedure is avoided here. A third criticism can be directed against the fact that the conventional treatments do not deal with any of the formulations of the third law.

While it is hoped that the above criticisms cannot be directed against the present work, the exposition given here has required such extensive reformulation of the conventional arguments of thermodynamics, and the introduction of mathematical tools which are new to this field of study, that the present paper is probably also not free from objections. Suggestions concerning the improvement of the presentation would therefore be particularly welcome.

PART I: THE FIRST LAW

2. The Nature of Thermodynamics

For the foundation of thermodynamics it is necessary to make the following assumption:

> **(A1)** Given any physical system which can be modified within certain defined limits, a finite set of finite macroscopic variables $x_1, x_2, \cdots$, known from other parts of science, can be listed and measured quantitatively, such that knowledge of a set of values of these variables defines one of a known sequence of equilibrium states of the system. Macroscopic nonthermodynamical information is assumed known.

The above variables, to be denoted by x, are called thermodynamic variables; these define the state of the system, its thermodynamic state. The circumstance that the variables are *macroscopic* and refer to *equilibrium* states is the main axiomatic criterion which distinguishes the thermodynamic variables from nonthermodynamic ones. The variables x, therefore, may include pressure, volume, molecular concentrations, etc., which can all be measured by known methods. There may also be electrical variables; for instance, when the thermodynamics of fields is discussed. If a variable x can have the value zero, the variable $y=1/x$ cannot be used instead of x, since the variables x must all be finite by (A1).

It follows from (A1) that the population of the separate quantum states of the particles constituting the system need not be deducible from thermodynamic information. Assumption (A1) implies, therefore, that a clear division can be made in any given case between thermodynamic and nonthermodynamic variables; and that the maximum number n of independent thermodynamic variables can be determined. Beyond a certain range of the variables $x_1, x_2, \cdots, x_n$, a phase change may occur (e.g., a liquid phase may disappear), and a new set of independent thermodynamic variables, $y_1, y_2, \cdots, y_m$, becomes appropriate. The physical interpretation of the set of x's will differ, in general, from that of the set of y's, and m need not equal n. Thus, for a given physical system, several entirely different sets of independent variables will, in general, be appropriate, depending on the *approximate* thermodynamic state of the system. For the satisfactory foundation of thermodynamics, the value of n and the interpretation of the x's, must, therefore, be left arbitrary.

The following definition is required:

> **(D1, a)** Given a physical system, and its approximate thermodynamic state, a thermodynamic variable is said to be *appropriate* to this system in this approximate state if, and only if, this variable enters into the specification of the approximate state.
>
> **(D1, b)** Given a physical system, and its approximate thermodynamic state S, the maximum number $n \geqslant 2$ of independent appropriate thermodynamic variables are made the coordinates of an n-dimensional phase space $E(S)$. This is called the *thermodynamic phase space of the system appropriate to the given state* S.
>
> **(D1, c)** Given a physical system, which can be modified within defined limits, the symbol E denotes any one of the thermodynamic phase spaces which may be appropriate to the system.

The phase space E must have the properties with which phase spaces in other parts of physics (e.g., classical mechanics) are usually endowed. However, this informal remark is insufficient for the present purpose, since the precise topological properties of E are required later on (e.g., in Sec. 9). In order to complete the definition (D1), some standard definitions from elementary topology must be given (Alexandroff and Hopf, 1935).

A *metric* is set up in a set X of points by associating with every pair of points $a,b \subset X$ ($\subset$ stands for "is contained in") a non-negative number $\rho(a,b)$ which has the following properties (a, b, $c \subset X$):

(i) $\rho(a,b)=0$ if, and only if, a and b are the same point (identity axiom);
(ii) $\rho(a,b)=\rho(b,a)$ (symmetry axiom);
(iii) $\rho(a,b)+\rho(b,c) \geqslant \rho(a,c)$ (triangle inequality).

Two metrics ρ, ρ' in X are said to be *equivalent* if, for any $x \subset X$ and for each fixed $a \subset X$, as $\rho(a,x)$ tends to zero, so does $\rho(a,x)$, and conversely. Let now X_r ($r=1, 2, \cdots, n$) consist of the set of all real numbers, and a metric $\rho_r(a,b)$ ($a,b \subset X_r$) which is equivalent to $|a-b|$. For instance, one may choose $\rho_r(a,b) = |\log(a/b)|$. Each of the sets of points X_r will serve as a coordinate axis in our thermodynamic phase space, and the choice of metric which has been allowed enables one to "plot" observed quantities logarithmically, or in other ways, provided only that the metric used is *equivalent* to the usual distance function $|a-b|$. It may be noted, though this remark is not required later, that the topologies induced by the metric ρ_r in the set X_r is identical with the usual topology of the real line.

With any two sets of points X_1, X_2, one may associate the set of all pairs (x_1,x_2), $x_1\subset X_1$, $x_2\subset X_2$. This new set is called $X_1\times X_2$. The formation of products† is an associative operation, so that there is no distinction between $(X_1\times X_2)\times X_3$ and $X_1\times(X_2\times X_3)$, which are both denoted by $X_1\times X_2\times X_3$. The phase space E consists of all n-tuples $(x_1,x_2,\cdots x_n)$, $x_j\subset X_j$. Hence

(D1, d) E is the set $X_1\times X_2\times\cdots\times X_n$.

One may define a metric in E which satisfies the three axioms above. For instance, one might define $\rho(a,b)=1$ when $a\neq b$ for all $a,b\subset E$. This is, however, an "unnatural" metric, i.e., it is not equivalent to the usual metric. There exist, however, an infinity of natural metrics for E. If $a\equiv(x_1,\cdots,x_n)$, $b\equiv(x_1',\cdots,x_n')$, and $p\geqslant 1$, these are

$$\rho(a,b)\equiv\left\{\sum_1^n[\rho_r(x_r,x_r')]^p\right\}^{1/p}.$$

No particular metric will be used in this paper, and all results are independent of this choice, provided that the metric chosen is equivalent to one of the above metrics.

The preceding discussion, using (A1) and (D1), leads to

Theorem 1. Given a physical system which can be modified within defined limits, then

(a) To every phase space E which may be appropriate to the system a natural metric may be assigned.

(b) Every equilibrium state of the system is represented by a point in an appropriate phase space E, but not conversely.

The converse is excluded, because there will in general be points of E which lie outside that range of the variables x, for which this phase space is appropriate.

3. Changes Which are Adiabatic in a Restricted Sense

The following definition is required:

(D2, i) Suppose a system is in equilibrium and contains two part systems which are physically separated from each other by an object O. If the equilibrium conditions of the total system can be so adjusted that, upon withdrawal of O, the two part systems attain a new equilibrium state, then O is called a *partition*. An *enclosure* is an object with similar properties, except that it separates a system inside the enclosure from a system outside it.

(ii) An *ideal* partition is an object O with the following properties: (a) it is infinitely thin; (b) when inserted into a system which is in equilibrium, it does not change this equilibrium state; (c) a situation exists such that a system which contains O and is in equilibrium, changes to another equilibrium state when O is removed.

An example is a wall separating two chemically reacting species. Another example is provided by the semipermeable membrane. In theoretical developments it is often convenient to hypothesize ideal partitions in order to avoid extraneous effects which the partition might have on the ideal experiments under consideration. Two partitions will be defined in this paper (in (D2, iii) and (D4)). To compare the properties of ideal partitions with those of real partitions, it suffices to imagine real partitions to be arranged in an ordered series, such that the properties of the members of the series approach more and more closely the properties of the particular ideal partition under discussion.

The definition of our first partition follows.

(D2, iii) An arbitrary physical system K shall be placed inside an enclosure F, and shall be allowed to attain an equilibrium state ϵ. The changes in long-range forces (electric, magnetic, gravitational) acting on F from the outside shall be kept negligible. Then F is said to be adiabatic in the restricted sense, if it has the following property. K remains in equilibrium (whatever physical processes take place outside F), unless there be mechanical changes produced in K by movement of parts of F (or by transmission through the walls of F). If, as a result of such change, a new equilibrium state ϵ' is established, the process linking ϵ and ϵ' is said to be adiabatic in the restricted sense.

It follows that the mechanical operation of stirrers and pistons from the outside is allowed in a restricted adiabatic process. Any other change which is brought about by a combination of mechanical and nonmechanical methods, or by nonmechanical methods alone, or which involves an exchange of mass, or a change in the long-range forces, is not adiabatic in the restricted sense.

One can build on (D2) in the following way.

(D3) A set of points in E, such that between any two points of this set a restricted adiabatic change is physically realizable, and no point that can be in the set is excluded, is denoted by the symbol α.

By Theorem (1), and (D2), a restricted adiabatic change is associated with two points, ϵ, ϵ' in the same (or in different) phase spaces. From those that are associated with a pair of points in the same phase space, the set α is constructed. The change has to be realizable in one direction, i.e., from ϵ to ϵ', or from ϵ' to ϵ. For some pairs of points it may be realizable in both di-

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† These products should strictly speaking be called *Cartesian* products, in order to distinguish them from the products introduced in Sec. 9.

rections. The states which the system assumes during the process need not have representative points in E or in α, since some or all of these states can be nonequilibrium states. Whether the definitions (D2), (D3) are useful cannot be stated on the basis of (A1), since all conceivable sets α may in fact contain no points at all (such sets are said to be "empty").

It has been seen that, given a system which can be modified within defined limits, several distinct phase spaces E_1, E_2, $\cdots$ may be required to represent the equilibrium states of the system. It is also possible that several distinct sets of points α exist in any one of these phase spaces. Let them be denoted by α_1, α_2, $\cdots$, numbering consecutively as one passes from E_1 to E_2, from E_2 to E_3, etc. If a set of points α is referred to, any one of the sets of points α_r is meant.

As an example, suppose that a phase space E contains only three points A, B, C, and that the given system is in one of these, A say. Suppose, further, that restricted adiabatic processes exist which take A into B and A into C, but that B and C cannot be linked in this manner (though it may be possible to link B and C by some other process). In virtue of (D3), E contains two sets α: α_1, which contains A and B, and α_2, which contains A and C. However, this type of situation will be excluded by Assumption (A2), which will now be discussed.

4. A Restricted Statement of the First Law

Experimental studies on the dissipation of mechanical work by friction led to a generalization which can be introduced into the theory in the form of the following assumption.

> **(A2, i)** Restricted adiabatic processes exist, and if two points can be linked to a third by such processes, they can be linked to each other by such processes.
>
> (ii) The mechanical work done in such processes is independent of the intermediate states.

Assumption (A2, i) can be used to rule out the type of situation envisaged at the end of Sec. 3, since it leads to an immediate proof of the following theorem.

> **Theorem** (2). Two nonempty sets of points α, α' in E are distinct if, and only if, no single restricted adiabatic process can be found which links a point of α with a point of α'.

Assumption (A2, i) also shows that the concept of a set of points α is useful, since there are such sets which are nonempty.

Consider (A2, ii) next. This is a restricted statement of the first law of thermodynamics, in which the notion of energy and temperature are still assumed unknown. But it follows from this statement, for instance, that the same amount of mechanical work, whether applied by a stirrer or by another mechanical method, has to be done in order to link two given equilibrium states of a given fluid.

For the mechanical work, the following conventions will be made. It will be reckoned positive if work is done on the system, and negative if work is done by the system in the sense that, if $W(a,b)$ is the mechanical work done on the system to bring it from a state a to a state b, then the mechanical work to be done for the reverse process, where possible, is $W(b,a)=-W(a,b)$. If the work done in a process is known to be independent of the intermediate states of the system, a typical increment will be denoted by δW. If, however, it must be assumed to depend on the intermediate states (until proved otherwise) then a typical increment will be denoted by $\delta' W$. If the set α contains curves and the increments are assumed to become infinitely small, δW is associated with an exact differential dW, and $\delta' W$ with a differential $d'W$, which is taken to be inexact, until and unless the contrary is established. A similar notation will be employed for other quantities. The notation emphasizes that the existence of differentials cannot be assumed when the set α is discussed.

Consider now two points α_1, α_2 of α, and let the mechanical work done in linking them by a restricted adiabatic process be δW_a, using (A2, ii) to justify the notation. Suppose it is also possible to link these points by a process which is not necessarily adiabatic in the restricted sense. Such processes are brought about by performing work which may be mechanical or nonmechanical, or a combination of the two. Since (A2) no longer applies to such processes, let $\delta' W_{na}$ denote the mechanical part of the work done during this process. This may now depend on the intermediate states.

Consider

$$\delta' Q \equiv \delta W_a - \delta' W_{na} \tag{1}$$

as a quantity which is associated with the second process, and which may be an inexact differential, if points lie infinitely close together in α. Hence,

> **Theorem** (3). $\delta' Q$ has the following properties.
>
> (i) If a process is adiabatic in the restricted sense, then $\delta' Q=0$ for every increment of it for which it is defined.
>
> (ii) If $\delta' Q\neq 0$ for some increment of the process, then the process is not adiabatic in the restricted sense.
>
> (iii) $\delta' Q$ is defined for *any* process linking two states represented by points in α, and for no others.
>
> (iv) For all processes specified under (iii), the sum (integral)
>
> $$\sum_1^2 (\delta' Q+\delta' W_{na})=W(1,2) \tag{2}$$
>
> is independent of intermediate states.
>
> (v) $\delta' Q$ is defined entirely in mechanical terms.

Any attempt to decide whether the converse of Theorem 3 (i) is true or not leads on to the following question:

> **(Q1)** Does a physical process exist which links two states of the set α, is not adiabatic in the restricted sense, and has $\delta'Q=0$ for every increment of it for which it is defined?

The assumptions made so far do not suffice to answer this question. If the process envisaged under (Q1) exists, then the converse of Theorem (3, i) and the converse of Theorem (3, ii) are both false. If it does not exist, these two converse results are true. In fact, a process of this type exists (see Sec. 6).

5. Heat Exchange and Thermal Equilibrium

Consider again the enclosure F of (D2), which is adiabatic in the restricted sense. During the experiment to be described, however, no mechanical work shall be transmitted through it, and the long-range forces acting on F must remain constant. Suppose the space inside F is divided into two parts by an ideal partition G whose full area is in intimate contact with an ideal partition H, which is adiabatic in the restricted sense. Let two physical systems K_1, K_2, whose sets of thermodynamic variables are denoted by x_1, x_2 respectively. be in equilibrium in the two spaces. Assume that neither system contains, or is enclosed by partitions (see (D2, i)), apart from a container whose sole purpose is to prevent an exchange of mass between the system and its surroundings. The systems are otherwise arbitrary. Denote the equilibrium (thermodynamic) states of K_1 and K_2 by ϵ_1 and ϵ_2, respectively. Upon withdrawing H, x_1 and x_2 may change until equilibrium is again established. Let the final states be denoted by ϵ_1' and ϵ_2'. Let the same procedure be repeated with system K_1 and a third system K_3, the initial states being such that the final states are ϵ_1', ϵ_3' for K_1 and K_3, respectively. The partition G is supposed to be of such a nature that if the procedure be repeated finally with systems K_2 and K_3, then it is possible to choose initial states such that the final states are ϵ_2', ϵ_3' for K_2 and K_3, respectively. The nature of G must now be specified further. It will be required to be a *diathermanous* partition, whose definition follows.

> **(D4)** A partition G is said to be diathermanous if it is rigid and fixed in position; it must not allow the exchange of mass, electricity, or electromagnetic radiation; given the initial thermodynamic states, the final thermodynamic states must, in all experiments of the type considered, be uniquely determined by single functional relationships of the form $f_{12}(x_1,x_2)=0$; if in the foregoing threefold repeated experiment these relations are
>
> $$f_{12}(x_1,x_2)=0,\quad f_{23}(x_2,x_3)=0,\quad f_{31}(x_3,x_1)=0, \quad \text{(3a, b, c)}$$
>
> then any two of these relations shall imply the third.

This last restriction is sometimes called the zeroth law of thermodynamics.

If a partition G satisfying (D4) exists,‡ the equilibrium which establishes itself across it may be supposed to be the result of a change of a physical quantity, z say, on either side of G. In anticipation of later results,§ one may speak of an "exchange" of z. The equilibrium may be called "z equilibrium." During the whole experiment, the systems on either side of G cannot exchange mechanical work, since G is rigid and fixed; nor can they exchange mass, electricity, and electromagnetic radiation. Hence z, if it exists, must refer to some other thermodynamic quantity. Indeed, there may be a choice of thermodynamic quantities to which it may refer: z, z', z'', $\cdots$.

It becomes desirable, therefore, to define

> **(D5)** Given the states ϵ_1, ϵ_2 of K_1 and K_2 respectively, suppose two partitions G, G' exist which satisfy (D4), and have the equilibrium conditions $f_{12}(x_1,x_2)=0$, $f_{12}'(x_1,x_2)=0$, which refer to z equilibrium and z' equilibrium, respectively. Then z and z' are said to be independent if a pair of systems K_1, K_2 in states ϵ_1, ϵ_2 exist such that the two conditions do not imply each other.

It is clear that there is no need to distinguish between z and z' if they are not independent. An example of such dependent quantities is obtained if one takes z' to be the name given to the quantity z^2. Let there be m independent quantities z: z_1, z_2, $\cdots$, $z_m (m>0)$. If a partition allows $r\geqslant 2$ independent quantities z to be exchanged simultaneously, it is conceivable that they may *under certain circumstances* react on each other in such a manner that only a single equilibrium condition can be found, instead of the r different equilibrium conditions, which one would expect if each of the r quantities behaved as if the other $r-1$ were absent. We shall refer to this effect as "interaction" between variables. Hence

> **Theorem** (4). If there is no interaction between the independent thermodynamic quantities $z_1, \cdots z_m$ when they are simultaneously exchanged, then each partition G, which satisfies (D4) allows the exchange of only one of them.

For if r of the m different z's are exchanged, r equilibrium conditions of the form (3a) have to be fulfilled by (D5), whereas a single condition is stipulated in (D4).

It may be observed that it would be meaningless to suppose that the exchange of another variable z *always* accompanies heat exchange, and always interacts with it so as to produce a single equilibrium condition. Since heat exchange is defined in terms of partitions such as

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‡ Owing to the ideal properties of this partition, the term "exists" is to be understood as implying merely existence *as the limit* of partitions which can actually be constructed (see (D2)).

§ See remarks following Theorem 6.

G, its resolution into component phenomena would require additional physical processes and definitions.

The theory has now m branches in which one z is allowed to the exclusion of the others; which one is studied depends on the additional properties of the quantities z_r, provided there are such quantities, which enable them to be separately distinguished and named.

In order to make progress, we require:

> **(A3, i)** A partition G satisfying (D4) can be found, such that the quantity z can be referred to as "heat exchanged." Elementary physiological statements "A is warmer than B, B can gain heat from A" are assumed familiar. (This assumption is completed at the end of Part I).

One can now develop the thermal branch of the theory in terms of ordinary language. Exchange of z (without a suffix) shall correspond to an exchange of heat, and z equilibrium to thermal equilibrium. By Theorem (4), and the remarks following it, the possibility that other z's, if they exist, are involved in this branch of the theory can be neglected.

Transfer of heat has been introduced by (D4) and (A3), and, therefore, is strictly defined for systems which are free of all partitions. By (A1) the existence of systems which contain real partitions (as contrasted with ideal partitions) can be assumed. By regarding such systems as a large number of homogeneous systems in contact, it follows that these can also partake in heat exchange. In the rest of this section, and also in the next section, the detailed nature of the experiment considered at the beginning of the section will not be involved, so that the restriction to systems that are free of partitions, which this experiment requires, must not be expected in this work. The only step needed to remove it from the present and the following section, is to infer, from the existence of heat exchange between systems which are free of partitions, the existence of heat exchange between arbitrary systems, in the manner indicated above. When the detailed form of Eq. (3) is required, as in Sec. 7, however, the restriction to systems which are free of partitions appears again; it is finally elucidated in Sec. 7.

It will be seen in Theorem (6) that heat can be measured quantitatively in terms of mechanical concepts. For the moment, assuming some measure of heat to exist, let us inquire what its properties must be.

Let a measure of the gain of heat be denoted by z, the same symbol used for the actual name of the thermodynamic variable involved. An increment of heat will be denoted by $\delta' z$, and by using the δ notation (see Sec. 4). It will be taken as positive if "heat is gained" by the system, and as negative if "heat is lost." The meaning of such statements is assumed known by (A3, i). Consider now any process (adiabatic in the restricted sense, or not) which links two states represented by points in α. The properties of z can be inferred through (A3) from the experimental procedure laid down at the beginning of this section. The properties derivable from this procedure are:

> **Theorem (5).** $\delta' z$ has the following properties.
>
> (i) If a process is adiabatic in the restricted sense, then $\delta' z = 0$ for every increment of it; no exchange of heat occurs.
>
> (ii) If $\delta' z \neq 0$ for some increment of a process, then the process is not adiabatic in the restricted sense; exchange of heat occurs.
>
> (iii) $\delta' z$, when nonzero, can be defined for those processes which involve exchange of heat; and in addition, they must involve electric and electromagnetic effects and changes in externally applied long-range forces to a negligible extent only.

Property (i) is due to the fact that there can be no exchange of heat in the processes defined in (D2) (iii). Any attempt to decide if the converse of Theorem (5, i) is true leads one to the following question, which can be answered only if additional assumptions are made:

> **(Q2)** Does a physical process exist which: links two states of the set α, is not adiabatic in the restricted sense, involves electric and electromagnetic effects and changes in externally applied long-range forces to a negligible extent, and has $\delta' z = 0$ for every increment of it?

If the process envisaged under (Q2) exists, then the converse of Theorem (5, i) and the converse of Theorem (5, ii) are both false. If it does not exist, these two converse results are true. In fact, depending on the nature of the system under consideration, a process of the type (Q2) may exist (see Sec. 6).

Consider now two states of a system, with the following properties:

> (T1) They are represented by points in α.
>
> (T2) They can be linked by a process P for which electric, electromagnetic effects and changes in long-range forces are negligible.

By (T1), Theorem (3) applies. For *any* process which links the two states, Eq. (1) can be used, therefore, to give a value to $\delta' Q$ for this process. By (T2), Theorem (5) applies. Therefore, in principle, a value can be given to $\delta' z$ (as well as $\delta' Q$) for any process P which links the two states, although how precisely the magnitude of $\delta' z$ is to be determined must still be specified. In view of the similarities between Theorems (3) and (5), the question arises if $\delta' Q$ can be taken as a measure of $\delta' z$ for any process P which links two states with properties (T1) and (T2).

To deal with this question, it is desirable to introduce the following assumption, which is based on experimental work connected with the mechanical equivalent of heat.

> **(A3, ii)** For a given process P which links two states with the properties (T1), (T2), $\delta'Q>0$ implies $\delta'z>0$ for this process, $\delta'Q<0$ implies $\delta'z<0$ for this process, and conversely.

Since the sign of $\delta'z$ has been defined above, but not its numerical magnitude, (A3, ii) gives the closest correlation between $\delta'Q$ and $\delta'z$ which at this stage can be introduced into the theory. It is permissible, therefore, to define the method of measuring $\delta'z$ as satisfying the following condition. If any two processes P, P_1 and P_2 say, which link the same or different pairs of states satisfying (T1) and (T2) are compared, then if $(\delta'Q)_1 > (\delta'Q)_2$ then also shall $(\delta'z)_1 > (\delta'z)_2$, and conversely. The same condition shall hold when the inequality sign is reversed. This stipulation implies that, whatever measure of $\delta'z$ is actually adopted, an instrument which measures $\delta'Q$ can, by recalibration, be converted into one which measures $\delta'z$. Hence,

> **Theorem** (6). For any process which links two states which are represented by points in α, $\delta'Q$ may be taken as a measure of the heat gained by the system ($\delta'z$), provided electric and electromagnetic effects, and changes in externally applied long-range forces, can be neglected.

An immediate consequence is the following. In the experiment used to define a diathermanous partition (see (D4)) the values of $\delta'z$ have by (A3, i) opposite signs for the two systems K_1, K_2. In fact, by Theorem 8, below, the values are equal and opposite. In this sense, one can speak of an exchange of heat. Suppose next that a system is brought from a state a to a state b by a process P, so that the system gains an amount of heat $\delta'z(a,b)=\delta'Q(a,b)$. For any inverse process p', which starts with b and ends with a, the amount of heat gained by the system is

$$\delta'z(b,a)=\delta'Q(b,a)=-\delta'Q(a,b)=-\delta'z(a,b).$$

This follows immediately from the change in sign of every term in Eq. (1), Sec. 4, when the terminal states are interchanged.

Another consequence of Theorem (6) is that the amount of "heat gained," as so far defined, can be expressed entirely in mechanical terms. The reason is that δ_2' has been defined up to now only for processes linking two points which can also be linked by a process that is adiabatic in a restricted sense.

Some comments are now required on the restrictions imposed on G. (a) Since G does not allow the exchange of mechanical work, it is not a partition which can be used for processes which are adiabatic in the restricted sense. But the requirement that G must not be a partition which can be used in this way is clearly not a sufficient specification (as has sometimes been stated). Any partition which allows the exchange of mechanical work and of electricity only would satisfy this requirement, but could clearly not be used, instead of G, in the discussion of thermal equilibrium. (b) Again, if one of the systems K_1, K_2 had a restricted adiabatic enclosure as part of it, the initial states of these systems would always coincide with their final states, and the conditions (3) would not imply any restriction for the variables concerned. (c) If the systems K_1, K_2 were allowed to contain restricted adiabatic partitions, then, by suitably matching the partitions on both sides of the diathermanous partition G, one may conceivably find pairs of physical systems K_1, K_2 such that the equilibrium condition is always expressed by more than a single condition (3a). Partitions of this type are not allowed, therefore, in K_1 and K_2. (d) If the partition H, rather than G, were fixed in position, then the partition G might move, when H has been withdrawn, so as to equalize the pressures in the two enclosures. In this case, G would be connected with the idea of mechanical equilibrium, but not with thermal equilibrium.

Another comment concerns the introduction of the zeroth law of thermodynamics into the *definition* of diathermanous wall. This is essential, since this law could not be inferred from the remainder of the Definition (D4). It enables one to define a function which will be called an "empirical temperature" in the thermal branch of the theory (see Sec. 7).

6. Energy. Generalizations

By Theorems (3, iv) and (6) it is seen that heat gained and mechanical work done add up to a constant for processes which link two given states, and are otherwise arbitrary within wide limits. It is convenient, therefore, to regard mechanical work done and heat gained as manifestations of a more fundamental quantity, to be called energy. Thus, the convention that heat gained shall be measured by the quantity $\delta'Q$, defined in (1), leads to

> **Theorem** (7). Given two states represented by points in α, the sum of mechanical and thermal energy expended in any process which links them is fixed, provided electric and electromagnetic effects, and changes in externally applied long range forces, are negligible.

Once this idea of energy is introduced, the knowledge that there are other forms of energy is extra-thermodynamical in origin, and may be assumed by (A1).

Table I. Allowed changes of energy by closed partitions (all changes in long range forces assumed negligible).

	Diathermanous	Restricted adiabatic	Adiabatic
Mechanical	No	Yes	Yes
Thermal	Yes	No	No
Other	No	No	Yes

Consider now the first column of Table I. The first entry is "No" by (D4). The second entry is "Yes" by (A3). The last entry is "No" by (D4) and by Theorem (4). It follows, in fact, that a diathermanous partition is one which allows the exchange of only thermal energy, and no other. By (D2) the entries in the second column are as shown. By (D2) and (D4) neither partition allows the exchange of mass.

The generalization of the results of the preceding sections requires

> **(D6, i)** A closed system is one which can exchange energy, but not mass, with its surroundings.
>
> **(ii)** A physical system undergoes an adiabatic change if, and only if, it does not exchange thermal energy.
>
> **(iii)** An ideal adiabatic enclosure is an infinitely thin enclosure which does not allow the exchange of thermal energy or of mass.

This definition enables one to complete Table I. If no energy other than mechanical and thermal energy existed, an adiabatic enclosure and a restricted adiabatic enclosure would be identical. To show that they are different, one must use the fact that other forms of energy exist. One must also note, for example, that an electric current for the supply of a heating coil can be taken through the walls of an adiabatic enclosure, but not through the walls of an enclosure that is adiabatic in the restricted sense. Note that (D6, ii) does not require the terminal states to be equilibrium states, nor does it imply that the system involved be closed.

It is now desirable to generalize Secs. 3 and 4 by replacing "restricted adiabatic changes of physical systems," by "adiabatic changes of closed systems" throughout. The idea that the system is closed is already implied by the qualification that a change be adiabatic in a restricted sense. In Sec. 3 the result of this generalization is to replace the sets of points α by a correspondingly defined set β.

> **(D7)** Given a closed physical system, a set of points in E, such that between any two points of this set an adiabatic change is physically realizable, and no point that can be in the set is excluded, is denoted by the symbol β. Whether boundary points of β belong to β is not laid down (this is decided in Part III).

There may again be a number of distinct sets of points $\beta, \beta', \beta'', \cdots$.

In Sec. 4 one can now introduce the stronger, experimentally verified, assumption (A2, i) with the term "restricted" omitted, and

> **(A2′, ii)** The energy supplied to a closed system in an adiabatic process, linking two states of β, is independent of the intermediate states.

The analog of Theorem (2), holds in consequence. In Eq. (1) $\delta'Q$ is now explicitly taken to denote an increment of thermal energy, but δW_a and $\delta' W_{na}$ can now denote increments of any form of nonthermal energy (excepting energy derivable from rest mass) given to the system. This interpretation makes Theorem (3, v) inapplicable, but the rest of this theorem holds exactly, provided α is replaced by β in (iii). The interpretation of (iv) yields now, instead of Theorem (7),

> **Theorem (8).** In order that two states of the set β of thermodynamic states of a closed system may be linked by a physical process, the same amount of energy must be supplied, whatever the nature of the process used.

The advantages over Theorem (7) are manifest. It is the most general form of the first law of thermodynamics for closed systems, and a special case of the law of conservation of energy. The latter is, strictly speaking, not part of equilibrium thermodynamics, since it can also deal with nonequilibrium systems, such as colliding particles. The first law for open systems is still under discussion (see, for instance, Tolhoek and de Groot, 1952), and in any case it is outside the scope of the present paper.

One can now deal with Question (Q1) of Sec. 4 (using the interpretation of the symbols as given there). The process envisaged in (Q1) is not adiabatic in the restricted sense, and therefore involves the exchange of at least one increment‖ $\delta' N \neq 0$ of nonmechanical energy by (D2). For every increment of the process $\delta' Q = 0$, so that the mechanical work M expended is the same as the mechanical work expended in the corresponding restricted adiabatic process. Thus two states can be linked: (a) by a restricted adiabatic process, using energy M, and (b) by the process envisaged in (Q1), using energy $(\Sigma\delta' N)+M$. Hence, if the process exists, then, by Theorem (8), $\Sigma\delta' N = 0$. Such processes exist since this situation may be realized, for instance, by flashing a pencil of light along a nonabsorbing path through the system while the original process (a) is carried out.

The process envisaged in (Q2) exists if two points of α can be linked, without change in the externally applied long range forces, by supplying nonthermal, nonelectric, nonelectromagnetic energy to the system. In order to ensure that the process is not adiabatic in the restricted sense, some of the energy supplied must either involve exchange of mass or exchange of nonmechanical energy. Thus, if the allowed modifications of the system include a change of mass, such processes exist.

For adiabatic processes the corresponding question is: given a closed system, does a nonadiabatic process exist, which links two points of β, and has $\delta' Q = 0$ (no

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‖ With regard to the δ notation, it should be noted that the increments $\delta' Q$ have points of α as end points, since $\delta' Q$ is not otherwise defined. On the other hand, the end points of $\delta' N$ need not lie in α.

exchange of thermal energy) for every increment? By (D6) there are no such processes. Hence

Theorem (9). Consider a process linking two points of β. It is (i) adiabatic if, and only if, $\delta' Q=0$ for every increment of it; (ii) nonadiabatic if, and only if, $\delta' Q\neq 0$ for one increment of it.

Since only differences in thermal energy and total energy have been used, the quantities involved are defined except for an arbitrary additive constant. If a standard state of the system, denoted by the suffix "*o*" is selected, the internal energy of a system in a state 1 may be defined by

$$U_1=U_0+\Sigma_0^1\delta W_a=U_0+W(0,1), \tag{4}$$

where (2) has been used. The internal energy is defined here in terms of any form of nonthermal energy (excepting energy derivable from rest mass). But if one confines attention to restricted adiabatic processes, then U is determined in terms of mechanical quantities only.

Each distinct set of points β in the phase space E has its own function U, since by (D7) no adiabatic process can be realized which links points belonging to different sets.

7. The Empirical Temperature

Consider again the threefold repeated experiment of (D4). Let w_j be one of the variables included in the set denoted by x_j ($j=1, 2, 3$), and let y_j denote the remaining set of variables. Hence one can use (3a) and (3b) to determine functions ϕ_1 and ϕ_2, such that

$$w_2=\phi_1(x_1,y_2)=\phi_2(y_2,x_3). \tag{5}$$

Even though it may not be possible to solve (3a) and (3b) algebraically to yield the functions ϕ_1, ϕ_2 it will be possible to determine them as two families of curves. Equations (3a) and (3b) are then fully equivalent to Eq. (5). All consequences of these equations must therefore be of the form

$$\Phi(w_2)=\Phi[\phi_1(x_1,y_2)]=\Phi[\phi_2(y_2,x_3)], \tag{6}$$

where Φ is an arbitrary function. By the zeroth law of thermodynamics, one of the consequences (6) must be (3*c*), which does not involve y_2. Hence a function ψ must exist, such that for $\Phi=\psi$, y_2 drops out of (6), and (6) implies (3*c*). Hence functions t_1, t_3, ψ_1, ψ_2 must exist such that

$$\psi[\phi_1(x_1,y_2)]\equiv t_1(x_1)\psi_1(y_2)+\psi_2(y_2), \tag{7a}$$

$$\psi[\phi_2(y_2,x_3)]\equiv t_3(x_3)\psi_1(y_2)+\psi_2(y_2). \tag{7b}$$

Here $\psi_1(y_2)$ is a nonzero function for, if it vanishes for some case of thermal equilibrium, (3a) and (3b) become equivalent to $w_2=\psi_2(y_2)$, from which it is not possible to infer (3c). Hence, one can define

$$t_2(x_2)\equiv\frac{\psi(w_2)-\psi_2(y_2)}{\psi_1(y_2)}. \tag{8}$$

The functions t are called "empirical temperatures."

Suppose that for two different sets of values $x_1'\neq x_1''$ of x_1 the empirical temperatures, on a certain scale, turn out to be the same: $t_1(x_1')=t_1(x_1'')$. Then, by (7a), $\phi_1(x_1',y_2)=\phi_1(x_1'',y_2)$, and, therefore, if $f_{12}(x_1',x_2)=0$, then also $f_{12}(x_1'',x_2)=0$. In such a case, the final thermodynamic states of the two systems that have come into equilibrium with each other as specified in (D4) are not always *uniquely* determined by $f_{12}(x_1,x_2)=0$, and this is in contradiction with (D4). It follows that $x_1'\neq x_1''$ implies $t_1(x_1')\neq t_1(x_1'')$ if the variables y_2 are kept constant. Similarly, if, for a given set of values x_1, there are two empirical temperatures $t_1(x_1)\neq t_1'(x_1)$, then the final thermodynamic states of the two systems are again not uniquely determined by $f_{12}(x_1,x_2)=0$. It follows that the function $t_j(x_j)$ has no turning points or finite lengths of zero slope, when regarded as a function of one of the variables of the set x, the others being kept constant. Functions of this type are called strictly increasing ($x>y$ implies $f(x)>f(y)$ for all x, y within the range of definition), or strictly decreasing ($x>y$ implies $f(x)<f(y)$).

The temperature function $t(x)$ is not uniquely determined by these considerations. For if $t'(x)$ be any strictly increasing or strictly decreasing function of its argument, $t'[t_1(x_1)]$, $t'[t_2(x_2)]$ can be used instead of $t_1(x_1)$ and $t_2(x_2)$, respectively. The curves $t(x)=\text{constant}$ are called the isotherms of a system in the thermodynamic phase space E.

These considerations lead to

Theorem (10, i) For any two systems j, k that are free of partitions, and can be in thermal equilibrium, functions $t_j(x_j)$, $t_k(x_k)$ exist, such that if $t_j=t_k$, then they are in thermal equilibrium, and conversely;

(ii) the functions $t(x)$ are not uniquely defined, but each function $t(x)$ is a strictly increasing or a strictly decreasing function of each of its arguments when the others are kept fixed.

Theorem (10, i) was already stated in essentials by Carathéodory (1909), but the publication of an analytical proof was neglected for many years (Miller, 1952).

The restriction to systems which are free of partitions in Theorem (10) has its origin in the restrictions imposed on the experimental arrangement discussed in Sec. 5. One can now ask to what extent this restriction can be relaxed without affecting the essentials of the experiment. From the point of view of this section, the crucial requirement of the experiment is that the final equilibrium state of the two bodies be uniquely determined by a single functional relationship, which has now been interpreted as an equality between the empirical temperatures. It follows that nothing in the argument which has taken us to the present point is altered if the bodies contain partitions, provided only that each system has a *single* empirical temperature. In other words, the only type of homogeneity on which one must insist is that the bodies be free of adiabatic partitions and vacuous spaces. Theorem (10) will be interpreted in this sense (see, for instance, (A4), below).

For each of the other $m-1$ branches of the theory, if they exist, concepts analogous to internal energy, thermal energy, and temperature can be similarly defined. However, if several of the variables z_1, z_2, $\cdots$, z_m are simultaneously present, considerable difficulties can then arise concerning the interpretation of $\delta' Q$, as defined in Eq. (1). It is not worth pursuing these speculations, and in all that follows attention is confined to situations in which the effect of the remaining $m-1$ z's, if they exist, can be neglected. This ambiguity may also be removed by restricting attention at the outset to systems whose n thermodynamic variables include $n-1$ arbitrarily variable external parameters, plus one other coordinate which may later be identified as the internal energy, the entropy, or some other purely thermal variable. This was the procedure adopted by Carathéodory (1909) by concentrating on his *einfache Systeme*.

It is now easy to show that the empirical temperature must vary with at least one of the n thermodynamic variables. For if the temperature t is a constant for the specified range of variation of all variables, then the equation $t=t(x)=\text{constant}$ expresses a relation between the variables, and they are therefore not all independent. This contradicts our hypothesis. Suppose next that the temperature depends only on the internal energy U of Eq. (4). In this case let the system be adiabatically enclosed. This does not restrict the other thermodynamic variables (which determine $\delta' W$). Then in the equation $\delta' Q=\delta U+\delta' W$, $\delta' Q$ must be zero for all changes in the variables which determine $\delta' W$. But, by hypothesis, none of these changes affect the empirical temperature t, and therefore, by hypothesis, they do not affect U. It follows that $\delta' W=0$ for all such changes. This means, by the conservation of energy, that there is a relation among the $n-1$ supposedly independent variables which determine $\delta' W$. This persists when the adiabatic enclosure is removed, and contradicts our assumption that all n variables are independent. Hence from (ii)

> **Theorem (10, iii).** If the n independent variables of a system be x_1 (internal energy), x_2, $\cdots$, x_n, then the empirical temperature depends on at least one of the variables x_2, $\cdots$, x_n.

There is a final question which has to be considered. Given a physical system and its approximate thermodynamic state, does the sum of all the sets of points β, corresponding to the thermodynamic phase space E, exhaust all the points of E which represent equilibrium states? In other words:

> **(Q3)** Is there a physical system which can take up an equilibrium state that cannot be realized by adiabatic methods?

Such a state, if it exists, is not linked to any of the states represented in β by (D7), and processes leading to this state, or from this state, must involve the exchange of thermal energy with a heat reservoir. There is nothing in the assumptions made so far which would enable one to dispose of the possibility envisaged in (Q3). It is necessary, therefore, when speaking about the states represented in β, to describe them as *adiabatically attainable* equilibrium states (see, for example, Theorems (14, iii). Question (Q3) is discussed again in Sec. 12.

Consider now a device which, in attaining equilibrium with a physical system S, disturbs S only to a negligible extent, and which measures nonthermal quantities (e.g., a mechanical or electrical variable) when equilibrium has been attained. Suppose also that the reading obtained from this device increases or decreases as S gains (or loses) heat, provided only that the device remains always in a state which lies within its range of calibration. Such an arrangement is called a thermometer. If it is regarded as system "K_1," and separated from an arbitrary (homogeneous) system "K_2" (in the sense of Sec. 5, above) by a diathermanous partition, the condition for equilibrium $f_{12}(x_1,x_2)=0$ is equivalent to $t_1(x_1)=t_2(x_2)$. The device, if it exists, can be used, therefore, to set up an empirical temperature scale.

Completing (A3), the obvious assumption is made that

> **(A3, iii)** thermometers exist!

Therefore, (A3) introduces the basic results of calorimetry into the theory.

Any scale of empirical temperatures may be set up in two alternative ways, typified by the following example. One may take as the empirical temperature indicated by a mercury-in-glass thermometer either the length of the mercury thread or the length of the column which is unoccupied by mercury. Thus, while the empirical temperature is a strictly increasing or strictly decreasing function of the thermodynamic variables (Theorem (10, ii)), the direction in which it increases is left unspecified. This introduces a first important element of choice into the present developments:

> **(C1)** The empirical temperature scale may be chosen so that heat tends to flow, either from places of high empirical temperatures to places of low empirical temperatures, or else so that it flows in the reverse direction.

The present section might have been introduced immediately after assumption (A3, i), but it has been held over for convenience of exposition. That empirical temperatures can be discussed *after* the first law may seem strange, and requires comment. The reason is that the thermodynamic state of a system can in fact be defined satisfactorily in terms of: the external parameters, the arbitrarily assumed value U_0 for the internal energy of a suitably chosen standard, state, and the energy $W(0,1)$ required to bring the system adiabatically from the standard state into the state of interest (see Eq. (4)). It may be necessary to evaluate $W(0,1)$ by finding the energy required to bring the system adiabatically from the state of interest into the standard state. This result is due to Assumption (A2′), and does not depend on the existence of a temperature function. The existence of this function is an additional property of thermal phenomena, introduced by Assumption (A3, i), and is not required for the formulation of the first law.

PART II. THE SECOND LAW

8. Quasi-Static Processes

The set β may, or may not, contain parts of curves. In this section some implications of this *possibility*¶ are considered.

In many cases the forces which act on the system of interest so as to produce a change of state can be characteristic, at least in part, of the device which induces the change. Therefore, they cannot be used, in general, to characterize the system of interest. This applies also to the work done, $\int d'W$, as the thermodynamic variables are changed. For, in this case too, the forces exerted by the device which induces the change, and the resistive forces exerted by the system of interest, need not be equal. It is desirable, therefore, to consider $\int d'W$ in the limit in which the time derivatives of the thermodynamic variables tend to zero (Carathéodory, 1909). We define, therefore,

> **(D8, i)** A process is said to be quasi-static if, and only if, it consists exclusively of a sequence of static equilibrium states. A process is nonstatic if it is not quasi-static.
>
> **(ii)** A curve AB in a phase space is said to "represent" a physical process, if every one of the sequence of states which constitutes the process is represented by a point on AB, and conversely.

Since nonstatic processes involve nonequilibrium situations, they cannot be represented in E or β in the sense of (D8). Their representation requires a phase space E', which has more than n dimensions and has E as a subspace. This may not always be possible in practice. Thus, in the case of turbulent flow the number of effectively independent variables can become intractably large. A curve C which "represents" a nonstatic process linking equilibrium states, has the following properties: (i) The terminal points of C are in E; (ii) all points of C are in E'; (iii) a point of C is not in E. To every point of C there now corresponds a fully defined physical situation. This includes velocities and accelerations, temperature and concentration gradients, in the components of the system. One can therefore define the "state" of a system undergoing a nonstatic process (for use in (D8 ii) and elsewhere) by

> **(D8, iii)** The states of a system undergoing a nonstatic process are in one-one correspondence with the points in a suitably defined phase space (such as E').

Also,

> **(D8, iv)** A physical system is said to undergo a reversible process, if another process exists which can force the identical system to pass through an identical sequence of states in reverse time order.

This shows that the forward and backward part of a nonstatic reversible process, if one exists, are represented by the same curve in E'.

It is to be noted that (i) involves the notion of equilibrium states, but not of time, whereas (iv) involves the notion of time, but not of equilibrium states. The basic assumption about these processes is

> **(A4, i)** The increment of nonthermal energy supplied to a system of interest (assumed free of adiabatic partitions and vacuous spaces) in a quasi-static change has the form
>
> $$d'W=\sum_{t=2}^{n} p_t da_t, \tag{9}$$
>
> where the a's are "external parameters," and arbitrarily variable within their specified limits of variation. The independent thermodynamic variables can be taken to be the internal energy U, and the $n-1$ a's.
>
> **(ii)** Consider two states of static equilibrium, ϵ, ϵ' (of the same physical system), which differ infinitesimally in the sense that they are represented by position vectors $\mathbf{r}$, $\mathbf{r}+d\mathbf{r}$ in an appropriate phase space. Then a physical process exists, represented by $+d\mathbf{r}$ in this phase space, which enables one to pass from ϵ to ϵ', and another process exists which enables one to pass from ϵ' to ϵ.

A quasi-static method of supplying heat to (or abstracting heat from) a system is to place it into contact with a sequence of heat reservoirs whose temperatures differ from each other infinitesimally. This method may be limited by the nonavailability of temperatures, and corresponding heat reservoirs, outside a certain range

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¶ When *curves of* β are mentioned in this or the following section, one ought to add each time the phrase: *if they exist.* The same remark applies to *points of the interior of* β, which are discussed in Sec. 9. However, it is more convenient to omit this phrase, and, instead, to point out here that this qualification is understood in this section and the next.

of temperatures (see Sec. 16). Such temperatures, however, cannot be represented in β, because they are not (adiabatically) attainable.

The concepts introduced by (D8) and (A4) can be applied both to purely mechanical systems and to purely thermodynamic systems, since these statements contain no reference to the set of points β. Therefore, they can also be applied to mechanical systems in which generation of heat occurs. General results to be deduced about these processes are valid, therefore, for both mechanical and thermodynamic systems.

By (1), (4), and (9), the adiabatic condition $\delta' Q=0$ takes the form

$$d'Q \equiv dU - \sum_{t=2}^{n} p_t da_t \equiv \sum_{j=1}^{n} X_j dx_j = 0$$

$$(x_1 = U;\, x_j = a_j \quad \text{for} \quad j=2,\cdots,n) \qquad (10)$$

for quasi-static adiabatic processes. Here $x_1, x_2, \cdots, x_n$ are the independent variables for the thermodynamic phase space of interest, and the X's, are appropriate functions of the x's. It is convenient to define the n-dimensional vectors

$$\left.\begin{aligned} \mathbf{v}(\mathbf{r}) &\equiv [X_1(\mathbf{r}),X_2(\mathbf{r}),\cdots,X_n(\mathbf{r})], \\ d\mathbf{r} &\equiv (dx_1,dx_2,\cdots,dx_n). \end{aligned}\right\} \qquad (11)$$

Here $\mathbf{r}$ denotes the position of the vector $\mathbf{v}$ in β relative to a convenient origin. The equation for every increment of a quasi-static adiabatic process then takes the form

$$d'Q \equiv \mathbf{v}(\mathbf{r}) \cdot d\mathbf{r} = 0, \qquad (12)$$

where the "·" denotes the scalar product. A vector $\mathbf{v}(\mathbf{r})$ is defined at all points of those curves in β which represent quasi-static adiabatic processes.

The following results can be deduced.

Theorem (11) Consider a system which is free of adiabatic partitions and vacuous spaces.

Curves representing quasi-static processes:

(i) Every quasi-static process is represented by a curve in E, but not conversely.

(ii) Every curve in β represents a quasi-static process.

(iii) For every increment of a quasi-static process which is represented in β, an equation of the form (9) is valid.

Reversibility:

(iv) Every quasi-static process is reversible, and conversely.

(v) If a process is irreversible, then the system which undergoes this process passes through a nonequilibrium state, and conversely,

Quasi-static adiabatic changes:

(vi) If a process is quasi-static adiabatic, then it is represented by a curve in β, but not conversely.

(vii) If a process is quasi-static adiabatic, then, for every increment along its representative curve in β, $d'Q$ satisfies an equation of the form (12), and conversely.

Proof

(i) By (D1) and (D8) every quasi-static process is represented by a curve in E. The converse fails, since a curve in E may lie outside the range of the variables for which physical processes are possible (see Theorem (1*b*)). (ii) A curve in β represents a sequence of equilibrium states. A physical process corresponds to such a sequence by (A4). The converse may fail. For some equilibrium states which are represented in E may not be included in the corresponding set β, as discussed in connection with (Q3), Sec. 7. Therefore, there may be quasi-static processes represented in E, but not in β. (iii) holds as already discussed. Its converse is not stated, but it follows from (ii) in the form: if an equation of the form (9) applies to a curve in β, then a quasi-static process exists which corresponds to it. The results (iv) and (v) follow from (D8) and (A4). The two converse results hold for the following reason. A nonstatic process involves nonequilibrium states, and, therefore, nonvanishing velocities also, gradients (of temperature, concentration, etc.), or the like. On reversing the process, at least one of these quantities must be reversed, so that the reverse process cannot involve the same "states." It follows from (D8) that a nonstatic process is irreversible. Hence a reversible process is quasi-static, and the converse results hold. (vi) supplements (ii) in an obvious manner. It follows directly from (D7). The converse must be excluded for the following reason. Consider a curve in β; then a quasi-static process corresponds to it. Also any two points on this curve can be linked by an adiabatic process in virtue of (D7), and such a process can involve nonequilibrium states. No assumption has been made which would enable one to assert that a process corresponding to this curve exists which is *at the same time* quasi-static and adiabatic. For such processes one must turn to the result (vii). This follows from what has been said here, and by Theorem (9).

As a simple example of these concepts for a purely mechanical system, consider a rigid body which is projected forward and backward between two perfect springs. The process is nonstatic by (D8) and, therefore, irreversible by Theorem (11, v). If the springs are imperfect, so that heat is dissipated, these conclusions remain valid. The system is then no longer a purely mechanical system.

The converse results of Theorems (11, iv) and (v) amount to a proof that nonstatic processes are irreversible. It must be emphasized that this result depends on the meaning given here (D8, iii) to the "states" constituting a nonstatic process. By including velocities and gradients in the specification of a "state," and by requiring the same "states" to be passed through in reverse time order for reversibility, it follows immediately that nonstatic processes are irreversible. However, these definitions are not the only possible ones. A system of definitions can be given, which is equally reasonable, and allows for the existence of nonstatic reversible processes.** But this would lead to a use of technical terms which diverges considerably from current usage in *thermodynamics*, and this possibility will therefore not be pursued here.

9. Definitions Required to Elucidate the "Interior" of β

It is now desirable to add to (D1, c), some further topological concepts. They will be introduced by definitions which are sufficiently general for our purpose; utmost generality has not been regarded as desirable.

(D9, i) Given any set of points E, a subset X of E, a metric ρ in E, and a real number $\delta>0$, $U_X(y,\delta)$ is the set of all points z, where y, $z\subset X$, such that $\rho(y,z)<\delta$. Thus $U_X(y,\delta)=U_E(y,\delta)\cap X$.†† $U_X(y,\delta)$ is called an X-neighborhood of the point y of X.

(ii) If with every point of a set of points X it is possible to associate at least one X-neighborhood, X is called a neighborhood space.

The particular set of points E defined in (D1, c), is a product of metric spaces. It may be made into a neighborhood space by the following device. Given any X_1 neighborhood of a point $x_1\subset X_1$, any X_2 neighborhood of a point $x_2\subset X_2$, etc. up to X_n, regard the product of these n neighborhoods as an E neighborhood of the point $(x_1,x_2,\cdots,x_n)$ of E. This convention will be made for every set of n neighborhoods, each neighborhood being defined on one of the coordinate axes. In this way one can use freely the idea of neighborhood in E, without introducing a metric in E.

The following definitions are also required.

(D10, i) The closure, X^*, of a subset X of E is the set of all points y of E such that any neighborhood of y meets X. If $X=X^*$, X is called a closed set.

(ii) The compliment $C(X)$ of a subset X of E is the set of all points of E which are not in X.

(iii) The frontier, $F(X)$, of a subset X of E is the set of all points which belong both to the closure of X and to the closure of the compliment of X, i.e., $F(X)=X^*\cap C(X)^*$.

(iv) $J(X)$ is the set of points x of X which have an E neighborhood which is also an X neighborhood. These are the "internal" points of X. If every point of X is an internal point, X is called an open set.

In order to illustrate these definitions, consider a finite number of finite arc A in E, which may or may not intersect. The term "arc" shall include the end points of the arcs. Then A^* coincides with A. $C(A)$ is the whole of E, except for the points on the arcs. $C(A)^*$ is therefore E. Now $F(A)=A^*\cap C(A)^*=A\cap E=A$. If we now form the difference between the set of points A and the set of points which constitutes its frontier and belong to A, $A-A\cap F(A)$, the resulting set of points is empty (i.e., it contains no points). This need not be so. Let B_0 be the set of all points within a circle of finite and nonzero radius, let B_1 be any set of points of $F(B_0)$, let B_2 be an isolated point elsewhere in E, and let $B=B_0+B_1+B_2$. $F(B_0)$ is clearly the set of points which constitutes the circumference of the circle. One finds

$$B^*=B_0+F(B_0)+B_2,\quad C(B)=E-B_0-B_1-B_2,$$
$$C(B)^*=E-B_0+F(B_0)+B_2,$$

so that $F(B)=F(B_0)+B_2$. Note that the frontier of B and the frontier of B_0 need not coincide. Hence if one subtracts from B the points of B which lie on the frontier of B one finds

$$B-[B_0+B_1+B_2]\cap[F(B_0)+B_2]=B_0+B_1+B_2-B_1-B_2=B_0.$$

These are just the "internal" points of B. The result $J(B)=B-B\cap F(B)$ is true for all sets of points B.

A set γ will be defined in (D11) as $J(\beta)$. Therefore γ is an open set, and $\gamma^*=\gamma+F(\gamma)$.

It is easy to see that every point of the set β has, for a given δ, a β neighborhood which can differ considerably from the corresponding E neighborhood. In other words, when one moves an infinitesimally small distance away from a point of β, one may leave β. For many thermodynamic purposes, such points have rather special properties, and, therefore, have to be considered separately. Suppose, for instance, that β consists of all points lying within, and on the boundary of, two circles which have no points in common, and that it contains also the points on a line joining the two circles without passing through them. Then a set γ, defined as $J(\beta)$, contains the points lying within the two circles. Therefore, γ consists of two separate regions, each region being connected,‡‡ but every point of γ has a γ neighborhood which coincides with the corresponding E neighborhood. In other words, one can pass an infinitesimally small distance away from *any* point of γ, and still be in γ. When the set γ is referred to in the sequel, it is understood that any one of these open, connected subsets of E is meant. The following definition is of a predominantly thermodynamic nature.

(D11, i) With any subset β of E, a subset γ of β is associated, and defined by $\gamma\equiv J(\beta)$.

** The process in the above example may then become reversible in the new sense. This would be in agreement with current usage in *mechanics*, provided the springs are perfect; but it would be in disagreement with current usage in *thermodynamics*. It seems desirable, however, to have a nomenclature, such as the one adopted here, which is applicable to both mechanical and thermal phenomena.

†† If A and B be two sets of points, $A\cap B$ is the set of all points common to both A and B. It is called the product of A and B, and must not be confused with the *Cartesian* product of (D1, d), Sec. 2.

‡‡ A set X is connected if it is impossible to find two closed nonnull subsets X_1, X_2 of X such that $X=X_1+X_2$, $X_1\cap X_2=0$.

(ii) A point y of γ is called an i point if, and only if, every γ neighborhood of it contains a point which is adiabatically inaccessible from y.

(iii) A point y of γ is called an a point if it is not an i point.

The following elementary properties follow.

Theorem (**12, i**) Every point of γ has, for a given δ, a γ neighborhood which coincides with the corresponding E neighborhood.

(ii) A point of y of γ is an a point if, and only if, it has a γ neighborhood, such that all points of this neighborhood are adiabatically accessible from y;

(iii) Every point of γ is either an a point or an i point;

(iv) An a point becomes an a or an i point, and an i point remains an i point, if nonstatic processes are disallowed.

The result (iv) is due to the fact that a state may be adiabatically accessible from a given state either by a quasi-static process or by a nonstatic process. Only the former process can with certainty be described by a Pfaffian form (9), Sec. 8. Thus the theory of these forms does not suffice to identify i points. For, although every γ neighborhood of a point y of γ may contain a point which is adiabatically inaccessible from y by quasi-static processes, this point may become adiabatically accessible if nonstatic processes are used. This completes the enumeration of the elementary properties of a points and i points.

The definition of the set of points β is based on the adiabatic linkage of equilibrium states, for which the direction in which the process is possible is of no interest. The introduction of a points and i points into the theory makes it possible to discuss the direction in which adiabatic processes can take place, since (D11) deals with adiabatic accessibility of neighboring points *from* a given point.

The following properties are less elementary.

Theorem (**13**) Consider a set of points γ for a physical system (assumed free of adiabatic partitions and vacuous spaces), and suppose that for all quasi-static adiabatic processes $\Sigma X_j dx_j = 0$, the X's are finite, continuous, and differentiable functions of the x's.

(i) If all points of γ are i points, then $d'Q$ has an integrating factor (Carathéodory's theorem). The converse holds only for systems in which nonstatic processes are disallowed.

(ii) If $d'Q$ has no integrating factor, then γ contains an a point. The converse holds only for systems in which nonstatic processes are disallowed.

(iii) If each i point of γ, (if there is one), has a γ neighborhood, every point of which is again an i point, if the X's are analytic functions of their arguments, and if nonstatic processes are disallowed for the system, then the points of γ are either all a points or all i points.

(i) Carathéodory's proof of his theorem requires only trivial changes. The construction of cylinders, on which it depends, may have to be applied to several regions, since E may contain curves $ABCD$ such that AB and CD lie in γ, while BC lies outside γ. The existence of level surfaces, and hence of an integrating factor, can then be inferred for both parts of γ. Conversely, the existence of an integrating factor, so that $d'Q = \lambda d\phi$ say, implies the existence of level surfaces $\phi = \text{constant}$; now a quasi-static adiabatic process connects only those points which lie on the same level surface, since $d'Q = 0$ for every increment of such a process. Thus, provided nonstatic processes are disallowed, all points of γ are i points. The need for this restriction is also clear from Theorem (12, iv). (ii) follows from (i). It is stated separately to avoid the misconception that the absence of an integrating factor implies necessarily that *all* points of γ are a points (this error has appeared in the literature, see T. Ehrenfest-Afanassjewa, 1925). (iii) Under the assumptions stated, the existence of an i point y implies, by (i), the existence of an integrating factor for the region of i points surrounding y. In this region the $\frac{1}{6}n(n-1)(n-2)$ equations

$$X_p\left(\frac{\partial X_q}{\partial x_r} - \frac{\partial X_r}{\partial x_q}\right) + X_q\left(\frac{\partial X_r}{\partial x_p} - \frac{\partial X_p}{\partial x_r}\right) + X_r\left(\frac{\partial X_p}{\partial x_q} - \frac{\partial X_q}{\partial x_p}\right) = 0 \quad (p,q,r = 1,2,\cdots n) \quad (13)$$

must be satisfied, by the usual theory of differential equations. Since the X's are analytic in their arguments, it follows by analytic continuation that these conditions must be satisfied throughout γ. But Eq. (13) is sufficient as well as necessary for the existence of an integrating factor. Hence, using the converse of (i), all points of γ are i points. (iii) follows.

It follows from Theorem (13, iii) that, for a large class of differential forms $d'Q = \Sigma X_j dx_j$, *all* points of γ are either a points or i points when nonstatic processes are disallowed. Though this result is not required in the sequel, it may be of interest to link it with the general theory of Pfaffian forms (Theorem (13, iv), to follow). This result, which is also not used again in this paper, will now be derived.

If the $X_j(x_1,\cdots,x_n)$ are analytic, the vector $\mathbf{v}(\mathbf{r}) = (X_1,\cdots,X_n)$ of Eq. (12) can at the point $(x_1,\cdots,x_n)$ be brought into one of the forms $(k \leq n)$

$$v = \begin{cases} (1,0,x_2,0,x_4,0,\cdots,x_{k-1},0,0,\cdots,0) & (k \text{ odd}) \quad (14) \\ (0,x_1,0,x_3,0,\cdots,x_{k-1},0,0,\cdots,0) & (k \text{ even}) \quad (15) \end{cases}$$

by choosing suitable curvilinear coordinates. Equations (14) and (15) are called the canonical forms for $\mathbf{v}$ (see, for instance, Goursat, 1922; Schouten and van der Kulk, 1949). k is called the class of the Pfaffian form. Consider arbitrary but fixed points $P=(p_1,\cdots,p_n)$, $Q=(q_1,\cdots,q_n)$ of γ, which it is desired to link, if possible, by quasi-static adiabatic processes. For such processes

$$d'Q=\begin{cases} dx_1+x_2dx_3+x_4dx_5+\cdots+x_{k-1}dx_k & (k \text{ odd}) \quad (16) \\ x_1dx_2+x_3dx_4+\cdots+x_{k-1}dx_k & (k \text{ even}). \quad (17) \end{cases}$$

In case (14), define intermediate points A, B by

$$A=(p_1,r_2,p_3,r_4,p_5,\cdots,r_{k-1},p_k,q_{k+1},\cdots,q_n),$$
$$B=(q_1,r_2,q_3,r_4,q_5,\cdots,r_{k-1},q_k,q_{k+1},\cdots,q_n).$$

The straight line PA lies in the hyperplane $x_1=p_1$, $x_3=p_3$, $\cdots$, $x_k=p_k$, so that the process represented by PA is quasi-static adiabatic in virtue of Eq. (16). The same argument applies to the straight line BQ. Along AB

$$\int d'Q=q_1-p_1+r_2(q_3-p_3)+r_4(q_5-p_5) +\cdots+r_{k-1}(q_k-p_k),$$

and this can be made zero by appropriate choice of one of the r's, provided only $k\geqslant 3$. It follows that along AB

$$dx_1+r_2dx_3+r_4dx_5+\cdots+r_{k-1}dx_k=0, \qquad (18)$$

so that this line too represents a quasi-static adiabatic process.

In the case of Eq. (15), define intermediate points C, D by

$$C=(r_1,p_2,r_3,p_4,r_5,\cdots,r_{k-1},p_k,q_{k+1},\cdots,q_n),$$
$$D=(r_1,q_2,r_3,q_4,r_5,\cdots,r_{k-1},q_k,q_{k+1},\cdots,q_n).$$

The previous argument is easily amended to apply to the straight lines PC, CD, DQ. The r's must this time be chosen to satisfy

$$r_1(q_2-p_2)+r_3(q_4-p_4)+\cdots+r_{k-1}(q_k-p_k)=0,$$

and this is always possible provided $k>3$. Then along CD

$$r_1dx_2+r_3dx_4+\cdots+r_{k-1}dx_k=0, \qquad (19)$$

so that this line represents also a quasi-static adiabatic process.

Thus, provided all intermediate points required lie in γ, all points of γ are *a* points for Pfaffian forms whose class exceeds 2. If $k=2$, only two variables occur in Eq. (15), and an integrating factor exists, so that all points are *i* points. Thus,

Theorem (13, iv) If all the coefficients of a Pfaffian form $d'Q=\Sigma X_jdx_j$ associated with quasi-static changes are analytic, and the required intermediate points lie in γ, and if nonstatic processes are disallowed, then (a) the points of γ are either all *a* points or all *i* points. (b) If a point of γ is an *i* point, then $d'Q$ has an integrating factor, and conversely. In this case, all points of γ are *i* points and the class of the Pfaffian form is $k=1$ or 2 $(\leq n)$. (c) If a point of γ is an *a* point, then $d'Q$ has no integrating factor, and conversely. In this case, all points of γ are *a* points, and the class k of the Pfaffian form satisfies $3\leq k\leq n$.

Part (b) of this result is stronger than Carathéodory's Theorem (13, i), and part (c) also goes beyond Carathéodory's theorem. Part (a) is based on slightly different assumptions than Theorem (13, iii), although it is very similar to it.

10. The Existence of Entropy and of Absolute Temperature

The preceding two sections have prepared the ground for the possibility of curves being contained in the set β. These considerations may be anchored to physical facts by introducing into the theory the following assumption, which represents a generalization from experimental findings.

(A5) Consider any physical system which is free of adiabatic partitions and vacuous spaces, and for which the functions $X_j(x_1,\cdots,x_n)$ $(j=1,\cdots,n)$ are finite, continuous, and differentiable throughout γ. Then (i) γ contains a curve satisfying $d'Q=0$;

(ii) All points of γ are *i* points.

This is a modified form of the principle of Carathéodory. It makes the considerations of Secs. 8 and 9 applicable to thermodynamics, since the set γ is now nonempty for the important class of systems which are free of adiabatic partitions and vacuous spaces.

The following results can now be deduced.

Theorem (14) Consider a physical system which satisfies (A1) to (A5).

(i) Every point of γ lies on a curve representing a quasi-static adiabatic process.

(ii) $d'Q$ has an integrating factor and, in whatever form it is chosen and whatever the empirical temperature scale (t), it may be written in the form $d'Q=TdS$, where T depends only on t, and S is independent of t.

(iii) T, S, and dT/dt are either all nonpositive or all non-negative for adiabatically attainable equilibrium states which do not lie on the boundary of the set γ. They are thermodynamically undefined for other states.

(i) Since every point of γ has the property of Theorem (12, i), it follows that the existence of a curve C in γ implies the existence of an infinity of curves in γ. Since vector $\mathbf{v}(\mathbf{r})$ of Eq. (12) is defined at every point of C, it is defined, therefore, at all points of some γ neighborhood of every point of C, i.e., in an n-dimensional region of γ. In virtue of A5 (ii) and Theorem (13, i), Sec. 9, the equation $d'Q=\Sigma X_jdx_j$ has therefore an integration factor λ, which is finite and nonzero:

$$d'Q=\lambda d\phi. \tag{20}$$

From the ordinary theory of differential equations the whole of γ is filled, therefore, with hypersurfaces, for each of which ϕ is a constant. Every curve on such a surface satisfies $d'Q=0$. Since $d'Q=\Sigma X_j dx_j$ is the general expression for an increment of thermal energy quasi-statically supplied to the system, each such curve represents a quasi-static adiabatic process by Theorem (11, vii). (ii) Since $\mathbf{v}(\mathbf{r})$ is defined throughout γ, so is $d'Q=\lambda d\phi$. By (10), Sec. 8,

$$X_1=1, \quad X_j=\frac{\partial U}{\partial x_j}-p_j \quad (j=2,3,\cdots,n).$$

Hence

$$\lambda\frac{\partial\phi}{\partial U}=1, \quad \lambda\frac{\partial\phi}{\partial x_j}=\frac{\partial U}{\partial x_j}-p_j \quad (j=2,3,\cdots,n).$$

The first of these equations shows that $\partial\phi/\partial U$ is not zero and therefore that the equation $\phi=\phi(U,a_2,\cdots,a_n)$ can be solved for U. Hence ϕ can be used instead of U as one of the independent thermodynamic variables of the system. Similarly, by Theorem (10, iii), the empirical temperature can be used instead of one of the other variables, a_2 say. With these explanations, one can now show in the usual way (Born, 1921) that

$$d'Q=\lambda(t,\phi,a_3,\cdots,a_n)d\phi=\lambda(t_0,\phi,a_3,\cdots,a_n)\times\exp\left[\int_{t_0}^{t}g(t)dt\right]d\phi. \tag{21}$$

Here t_0 is regarded as a standard empirical temperature, and

$$g(t)\equiv(\partial\log\lambda/\partial t)_{\phi,a_3,\cdots}. \tag{22}$$

This result is obtained by considering any two systems which satisfy the requirements of (A5), and supposing them to be in thermal equilibrium with each other, but otherwise isolated. If C is an arbitrary constant, let

$$T(t)\equiv C\exp\left[\int_{t_0}^{t}g(t)dt\right],$$
$$S\equiv\frac{1}{C}\int\lambda(t_0,\phi,a_3,\cdots,a_n)d\phi \tag{23}$$

be the definitions of absolute temperature and of entropy, respectively. Then

$$d'Q=TdS, \tag{24}$$

where T depends only on the empirical temperature and S is independent of it. Since λ is finite and nonzero, so is T. These results can be shown to be formally independent of the choice of either integrating factor (λ) or empirical temperature scale (t) (Carathéodory, 1925). (iii) λ will be chosen positive, which is always possible, so that $g(t)$ is real; it follows from (23) that T and S both have the sign of C, and so has

$$\frac{dT(t)}{dt}=C\exp[g(t)].$$

This proves (iii). In fact dT/dt is never zero, since $g(t)$ is a finite function for points in γ. Note that T is defined only for states represented in γ, i.e., for adiabatically attainable equilibrium states which do not lie on the frontier of β. A temperature and an entropy can, however, be associated with points on the frontier of γ in the following way. If f be a point of $F(\gamma)$, then $f=\lim_{n\to\infty}(g_n)$, g_n in γ; one can now *define* $T(f)\equiv\lim_{n\to\infty}T(g_n)$, $S(f)\equiv\lim_{n\to\infty}S(g_n)$, provided these limits exist. This procedure can be followed with respect to every point on $F(\gamma)$, whether the point is in β or not. Hence there may be points *outside* β with which an absolute temperature can nonetheless be associated. It will be seen that states at the absolute zero of temperature are of this type.

The law for the addition of entropies can now be deduced in the usual way (Born, 1921).

It is clear from Eq. (23) that there is a second element of choice in the present development of thermodynamics:

> **(C2)** Entropies and absolute temperatures may be both non-negative or both nonpositive (i.e., the quantity C in Eq. (23) may be positive or negative).

In addition the choice (C1), exists. In virtue of Theorem (14, iii) this can now be reformulated:

> **(C1′)** Given the sign of C in Eq. (23), the choice of the empirical temperature scale may be such that heat tends to flow either from places of high absolute temperature to places of low absolute temperature, or else so that it flows in the reverse direction.

In order to deduce further properties of entropy and absolute temperature, the following definitions are convenient:

> **(D12, i)** A physical system is said to be in a definite configuration if it can be characterized by a fixed set of values for the $n-1$ external parameters.
>
> (ii) If an increment of thermal energy $\delta'Q$, when added to a system, produces a change δT in absolute temperature when the external parameters are kept fixed (or are changed in a certain specified manner), then the heat capacity of the system under these conditions is defined as $\delta'Q/\delta T$ in the limit when $\delta'Q\to 0$ (i.e., it is $T(\partial S/\partial T)$, if the process is quasi-static).
>
> (iii) A variable x has a lower bound if a number x_0 exists such that x cannot have a value $x<x_0$, and for any positive y x can have a value $x<x_0+y$. x_0 is called the lower bound of x. The upper bound is defined similarly.

TABLE II. Comparison of various temperature scales. C is the quantity introduced in Eq. (23).

	Heat tends to flow from high to low empirical temperatures.		Heat tends to flow from low to high empirical temperatures.	
	$C>0$	$C<0$	$C>0$	$C<0$
Tendency of heat flow in terms of absolute temperatures.	high→low	low→high	low→high	high→low
If supply of heat produces a quasi-static change, the absolute temperature of the system (assumed in fixed configuration and free of adiabatic partitions and vacuous spaces):—	increases	decreases	decreases	increases
Set of corresponding absolute temperatures for specific temperature scales.	T	$T_1=-T$	$T_2=\frac{1}{T}$	$T_3=-\frac{1}{T}$
	0	0	∞	$-\infty$
	1	-1	1	-1
	10	-10	0.1	-0.1
	∞	$-\infty$	0	0
Type	I	II	III	IV

The main possibilities which arise from choices (C1), (C2) are detailed in Theorem (15), and Table II.§§

Theorem (15) Consider the set of points γ of a system which satisfies (A1) to (A5). Result (i) is independent of (C1) or (C1′) and (C2).

(i) The absolute temperature is a strictly increasing or strictly decreasing function of the empirical temperature, and therefore also of each of the n thermodynamic variables when the remaining $n-1$ are kept fixed.

Results (ii) to (iv) depend on (C2), but not on (C1) or (C1′), and the amendments in round brackets apply if absolute temperature is nonpositive.

(ii) The temperatures and entropies of the adiabatically attainable equilibrium states of the system have lower (upper) bounds T_0, $S_0 \geqslant 0 (T_0, S_0 \leqslant 0)$.

(iii) The system can exhibit negative (positive) temperatures only if it is in a nonequilibrium state [or if it is in an equilibrium state which is not adiabatically attainable] for which "temperature" is defined nonthermodynamically.

(iv) For a fixed configuration the internal energy increases (increases), when heat is supplied to the system; if the heat is supplied quasi-statically, the entropy increases (decreases).

Results (v) to (vii) depend on (C1′), but not on (C2), and the amendments in brackets apply if heat flows from low to high absolute temperatures.

(v) When heat is supplied to the system in a fixed configuration so as to produce a quasi-static change, the absolute temperature increases (decreases);

(vi) The quasi-static heat capacity $T(\partial S/\partial T)$ of the system in a fixed configuration is positive (negative);

(vii) If two parts of the system, when it is adiabatically isolated, attain thermal equilibrium quasi-statically, then the change in entropy is non-negative (nonpositive).

Result (viii) depends on both (C1) and (C2).

(viii) $\partial S/\partial T$ is positive for a configuration of the system if heat tends to flow from higher to lower absolute temperatures and absolute temperatures are non-negative; $\partial S/\partial T$ is negative if one of these two conditions is not fulfilled; it is positive if neither of these two conditions is fulfilled.

(i) follows from Theorem (10, ii) and the fact that dT/dt is positive or negative. (ii) follows from Theorem (14, iii), and (iii) follows from (ii). The clause in square brackets must be added since the question (Q3) has not been answered. An example of (ii) is provided by a spin system which is partially aligned by a magnetic field $+|H|$, when the field is changed to a negative value in a time which is short compared with the time of relaxation of the system (Purcell and Pound, 1951). In such cases the entropy can be estimated by statistical mechanics, and hence the "temperature" defined as $\delta' Q/\delta S$. (iv) For a fixed configuration $d'W=0$, so that by Eq. (10) $d'Q=dU$. Therefore, the internal energy increases if heat is supplied. If the process is quasi-static, $d'Q=TdS$ and (iv) follows. (v) If thermal equilibrium is established quasi-statically, a difference of absolute temperature is removed by passage through equilibrium states only, so that if heat flows to regions of lower absolute temperature, the temperature of that region increases (external parameters being assumed fixed); if heat flows to regions of higher absolute temperature, the temperature of that region decreases. To complete the proof of (v), it must still be shown that a fixed configuration cannot lose or absorb a finite amount of heat, and remain at constant temperature. This would mean that the absolute temperature, and, therefore, the empirical temperature, is not a strictly increasing or decreasing function of its arguments, in contradiction with Theorem (10, ii). This theorem applies because of the assumption made in (A5) that the system is free of adiabatic partitions and vacuous spaces. (vi) and (viii) are immediate consequences of (v). (vii) If a small increment of heat is transferred quasi-statically (as explained in Sec. 8) from a part of the system which is at a higher absolute temperature T_2, to a part at a lower temperature T_1, in the process of reaching equilibrium, then the change of entropy is $\delta S=\delta' Q(1/T_1-1/T_2)>0$. If heat tends to flow to the higher temperature, however, $\delta S=\delta' Q(1/T_2-1/T_1)<0$. (vii) follows. The possibility $\delta S=0$ must be allowed; it applies when the two parts of the system are in equilibrium in the first place.

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§§ A special system which can exhibit either positive or negative "temperatures" has recently been considered by Ramsey (1956). It may be seen by inspection of his Fig. 2 that this system exhibits properties in agreement with those which are stated in theorem 15. The choices (C1) and (C2) preferred in that paper correspond to a system of Type IV according to the classification proposed in Table II.

It is not claimed in Theorem (15, vii) that once the choices (C1), (C2) have been made, the changes of entropy in an adiabatically isolated system are *always* non-negative (or nonpositive). This statement is, in fact, true, but it depends on the properties of nonstatic adiabatic processes about which nothing is said in (vii). These processes therefore must be investigated next. It will be seen in the following section (Theorem (16, iv)) that the restriction to quasi-static process in parts (iv) and (vii) of the above theorem can, in fact, be removed. The restriction to quasi-static processes in (v) and (vi) remains, and is briefly discussed at the end of the following section.

11. Nonstatic Processes

One can now deduce the following result.

Theorem (16) Consider a system which satisfies (A1) to (A5). The following results are independent of the choices (C1) and (C2).

(i) Every curve in γ, for every increment of which $dS=0$ and T is finite, represents a quasi-static adiabatic process, but not conversely.

(ii) Two hypersurfaces of constant entropy, which belong to different values of the entropy, do not intersect in γ. Any curve in γ which represents a quasi-static adiabatic process lies in such a hypersurface.

(iii) Any two points of γ which are on hypersurfaces of different constant entropies can be linked by an adiabatic process; and such a process is nonstatic.

(iv) In nonstatic adiabatic processes, linking states of unequal entropy, the entropy of the system *always* either increases or decreases (this merely presumes a choice (C1) and (C2) to have been made once and for all).

(i) is a consequence of Theorem (9, i) and Eq. (24). The converse must be excluded, since there may be quasi-static adiabatic processes which are represented by curves on the frontier of β. (ii) is self-evident, since all complications which may arise from boundary properties of β are excluded when attention is restricted to γ. (iii) Any two points of γ can be linked adiabatically by the definition of β and γ. If the two points lie on hypersurfaces which belong to different entropy values, the process cannot be quasi-static adiabatic, since $d'Q=dS=0$ for every increment of such processes. Given that it is adiabatic, it follows that it is therefore nonstatic. (iv) Consider the entropy values S attainable by arbitrary adiabatic processes, which commence at a fixed state whose entropy is S_0. Since any two points of β (or γ) can be adiabatically linked by definition, the values of S comprise a continuous range of entropy values. The value S_0 is contained in it, since the quasi-static adiabatic processes are contained among the arbitrary adiabatic processes. If S_0 is an internal point of this interval, all neighboring values of the entropy can be attained from the initial state. Since the external parameters are also arbitrarily variable within γ by (A4, i), it follows that (A5, ii) would be violated. Hence S_0 is an end point of this range. Therefore the entropy can either not decrease or not increase in arbitrary adiabatic changes (provided, of course, definite choices (C1) and (C2) have been made). By varying the initial state in an arbitrary manner, it is seen that, for the entropy to be a continuous function, the sense in which it changes in nonstatic adiabatic processes is the same for the whole of γ. (iv) follows.

Theorem (16, iv) leads immediately to the following result.

Theorem (17) Consider a system which satisfies (A1) to (A5), for which definite choices (C1) and (C2) have been made, and which is adiabatically enclosed. Then, either

(a) its entropy cannot decrease, and the adiabatically inaccessible points in every γ neighborhood of a given point in γ are the points of lower entropy (the "real" world); or

(b) its entropy cannot increase, and the adiabatically inaccessible points in every γ neighborhood of a given point in γ are the points of greater entropy (the "reversed" world).

It is clear from this result that the present development of thermodynamics allows for a third choice between alternatives:

(C3) Thermodynamic statements can be made about the "real" or the "reversed" world (in the sense of Theorem (17)).

The three choices which have been enumerated will not be eliminated by special assumptions, since the foundations of thermodynamics may easily be developed for any of the eight possibilities generated by the choices (C1) to (C3). But in Part III attention will be confined to statements about "regular" systems (see Sec. 16) for which certain definite choices (C1) to (C3) have been made.

Consider now the reversible adiabatic processes.

Theorem (18) For a system which satisfies (A1) to (A5):

(i) any reversible adiabatic process links states of equal entropy of the system.

(ii) the converse of (i) fails.

(i) Reversible adiabatic processes are quasi-static (by Theorem (11, iv) and are represented, therefore, by curves in β (Theorem (11, i)). Since they are reversible, it follows from Theorem (17) that the entropy of the whole system must remain constant during such processes. (ii) The converse of (i) may be disproved with the aid of the following example. Consider the usual ideal piston and cylinder arrangement for effecting adiabatic changes in an ideal gas. Suppose that the motion is transmitted via a toothed wheel, and that the moveable arm of a fixed ratchet slides smoothly on the teeth, which are rigid. The gas, cylinder, toothed wheel, and ratchet form the system which is being studied, and which is adiabatically enclosed. The piston is supposed to move in a quasi-static manner. The ratchet arm falls under gravity from one tooth to the next, thus dissipating mechanical energy which is turned into heating the gear wheel. The machine undergoes therefore a nonstatic (and irreversible) process. Since the system is free of adiabatic partitions, the heat generated will be conducted to the gas, so that it no longer undergoes a strictly adiabatic process. However, all the complications arising from the ratchet can be avoided by noting that the time required for the ratchet arm to fall from one tooth to the next is independent of the mass of the arm. If this is made infinitesimally small, the ratchet can still operate, but the energy dissipation becomes also very small. In the limit it actually vanishes, but the process remains irreversible, because of the purely mechanical constraint, imposed by the ratchet, which prevents the wheel being turned backwards. One can think of other limiting situations of this type. This establishes (ii).

It may be supposed that the arrangement considered under (ii) is inadmissible because it represents a limiting situation which cannot be realized. However, this attitude would be inconsistent with that taken up in the rest of this paper: ideal partitions have been defined, and their existence has been postulated. But they can be regarded as "existing" only in the sense that actual partitions can be arranged in a series in such a way that a particular property of an ideal partition may be obtained by extrapolation to a limiting situation. The arrangement considered under (ii) is of a similar type, and is therefore admissible (see also footnote in Sec. 5).

It is now convenient to return to the definition of heat capacity in general, (D12, ii), and its relation to the *quasi-static* heat capacity which enters into Theorem (15, vi). For simplicity consider a system of type I (see Table II). Suppose also that the only external parameter is the volume V, and that this is kept constant while an increment of heat $d'Q(>0)$ is added to the system. For this simple situation it follows from (D12) and $d'Q \leqslant TdS$ (Theorem (17a)) that the heat capacity at constant volume satisfies

$$\begin{array}{lll} \text{either} & \text{(A)} & 0<C_v\leq T(\partial S/\partial T)_v, \\ \text{or} & \text{(B)} & T(\partial S/\partial T)_v\leq C_v<0. \end{array}$$

(A) holds if addition of an increment of heat raises the temperature, and (B) if it lowers it. (A) holds with the equality sign if the system undergoes a quasi-static process. But, by Theorem (15, vi), (B) does not hold for quasi-static processes. If situation (B) can arise for systems of type I at all, therefore, it can arise only if the system undergoes a nonstatic process.

The possibility of situation (B) for a system of type I will be established by example. Consider a box which contains a real gas in one part of it, separated from a vacuous part by a partition. At all temperatures $T+\sigma(\sigma>0)$ the partition is unstable and collapses. Now add an increment $d'Q$ of thermal energy to the system when it is in equilibrium, with gas at temperature T, and the total volume fixed at V. The partition collapses, the gas expands, and, when equilibrium reestablishes itself, the temperature has fallen, so that this is indeed a situation of type (B). The collapse of the partition and the expansion of the gas makes the process nonstatic.

The example just considered, and similar examples of this type, show that rather unusual effects are, in fact, avoided by restricting attention to systems which are free of adiabatic partitions and vacuous spaces. It will be recalled that these two restrictions are all that is left of the original restriction to systems which are free of partitions of all kinds, introduced in Sec. 5 (and relaxed in Sec. 7) in connection with diathermanous partitions. Since these two restrictions are often satisfied for systems considered in thermodynamics, they have been introduced into our general theory in assumptions (A4) and (A5). This does not remove case (B) from the physical situations to be considered in this paper. As an example of case (B) which is not ruled out by forbidding the use of adiabatic partitions, one need only think of a partition with a sharp melting point whose only purpose is to prevent an endothermic reaction from occurring.

12. Survey of Physical Processes Used

Figure 1 shows some of the relationships established in Theorems (11), (16), and (18). Additional relations can be deduced from these theorems by the logical rule that if A implies B, then "not B" implies "not A." Some of these additional relations are also shown in the figure.

It has been found impossible to prove certain converse results. In particular, it has been seen that the development of thermodynamics allows for the existence of the following classes of processes:

(P1) Nonadiabatic processes which include equilibrium states that cannot be achieved with adiabatic processes (see (Q3));
(P2) Irreversible adiabatic processes linking states of equal entropy (see Theorem (18)).

It may be conjectured that the class ($P1$) is empty. An argument which makes this conclusion plausible is as follows. An equilibrium state represented by a point A in E, which cannot be reached by adiabatic methods, can be reached only by methods involving the exchange of heat with a heat reservoir. If the reservoir has to

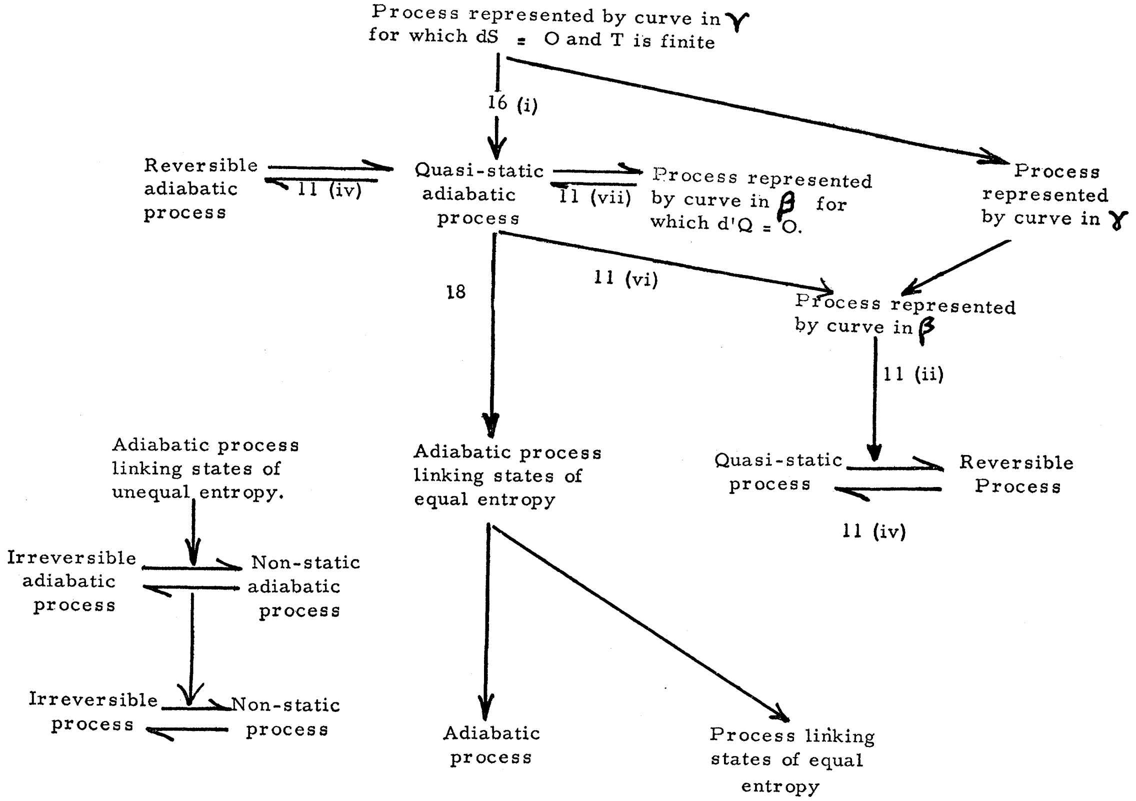

FIG. 1. Classification of processes for a system which satisfies (A1) to (A5). $A\rightarrow B$ means that a process of type A is always a process of type B, but that the converse is not necessarily true. $A\rightleftharpoons B$ means that a process of type A is always a process of type B, and conversely. The numbers refer to the theorems used.

give up heat, an entirely equivalent effect could be produced by dissipating an equal amount of mechanical energy, by friction with the surface which would otherwise be put into contact with the reservoir. This assumes that the system has a solid surface there. If it is fluid, stirring should be an equivalent adiabatic procedure. Hence, if the reservoir has to give up heat, an equivalent adiabatic procedure should be possible. There is now no need to consider the case when the reservoir has to subtract heat from the system. In order to show that A is in β, it suffices to show that an adiabatic process exists which links A to a point in β. Thus, assuming the usual choices in (C1) to (C3), if A is a "low entropy" state, one can act adiabatically on the system, until a state is reached which is represented in β. If A is a "high entropy" state one can act adiabatically on a state which is represented in β until A is reached. Adiabatic linkage is established in either case. This argument is probably physically sound, but it cannot lay claim to mathematical rigor.

For most purposes it will be satisfactory to regard as equivalent: (i) reversible adiabatic processes and adiabatic processes which link states of equal entropy; and to regard also as equivalent: (ii) irreversible adiabatic processes and adiabatic processes which link states of unequal entropy. However, this identification is permissible only if a proof has been given, or a convention been made, which ensures that the set (P2) of physical processes is empty.

There are three other classes of physical processes which are of interest in connection with Part III, and it is convenient to define them here.

(P3) Nonadiabatic processes which include nonequilibrium states that cannot be achieved with adiabatic processes (see Sec. 15, below).

This corresponds to (P1), except that nonequilibrium states are now considered instead of equilibrium states.

For reasons which will become obvious at the end of this section, it is convenient to use a different symbol, P(x), for the next class of processes.

P(x) Processes used to vary the temperature of a given physical system, which has x as an external parameter, in the following manner. For systems of types I and IV (see Table II), heat reservoirs at and above the initial temperature, T_1 say, of the system, are assumed available. By using these reservoirs quasi-statically, and effecting a quasi-static adiabatic change in x, the system can be brought into a state having a different (lower) temperature, T_2

say. A heat reservoir at this temperature may now be constructed, and the temperature of the system may be changed again by a repetition of this type of procedure. Throughout these processes the other external parameters must have fixed values (see (D12, i)). For systems of types II and III, heat reservoirs at, and below T_1 are assumed available, and changes of x are used to raise the temperature of the system.

The last class of processes may be defined as follows:

> **(P4)** Processes which can be used to achieve temperatures that cannot be obtained by processes of the type P(x) (see Sec. 16, below).

It is usual to assume that each of the classes (P1) to (P4) of physical processes is empty, but this does not follow from the assumptions which have been made here.

13. CARNOT'S PRINCIPLE[‖‖]

The results of Theorem (17) can be applied immediately to a thermodynamic (Carnot) engine, which in each cycle passes through the same sequence of physically accessible states, withdraws an amount Q_1 from an infinitely large heat reservoir of constant temperature T_1, delivers an amount Q_2 to a similar reservoir at temperature $T_2(<T_1)$, and exchanges no other heat with its surroundings. The condition that the change in entropy per cycle be non-negative is

$$\mp\frac{Q_1}{T_1}\pm\frac{Q_2}{T_2}\geqslant 0. \tag{25}$$

The bottom signs apply to the reversed cycle, and have a meaning only if the engine can be reversed. The work done per cycle is $W=Q_2-Q_1$, and the efficiency is $y\equiv W/Q_1$, so that Eq. (25) yields

$$y\leqslant\frac{T_1-T_2}{T_1}\text{(forward)},\quad y\geqslant\frac{T_1-T_2}{T_1}\text{(reverse)}, \tag{26}$$

Here we have assumed Theorem (17, a). If (17, b) holds, one finds instead of (20)

$$y\geqslant\frac{T_1-T_2}{T_1}\text{(forward)},\quad y\leqslant\frac{T_1-T_2}{T_1}\text{(reverse)}. \tag{27}$$

From Eqs. (26) and (27) one may conclude:

> **Theorem (19, a)** If Theorem (17, a) holds, then a Carnot engine has an efficiency $(T_1-T_2)/T_1$ if it is reversible, and cannot be more efficient if it is irreversible (real world).
>
> **(b)** If Theorem (17, b) holds, then a Carnot engine has an efficiency $(T_1-T_2)/T_1$ if it is reversible, and cannot be less efficient if it is irreversible ("reversed" world).

This shows that for reversible Carnot engines $y=(T_1-T_2)/T_1$ both in the "real" and the "reversed" world (Ruark, 1925). It also shows that the assumption, which is often made, to the effect that an irreversible engine must differ in efficiency from a reversible one, is incorrect, if the limiting cases of Theorem (18) are allowed (see also Bridgman, 1943, p. 123). As an example of the effect of an irreversible process, consider the working of a Carnot engine when there is a leakage between the heat reservoirs (Ehrenfest-Afanassjewa, 1925). In the real world heat will leak from the hot to the cold reservoir and decrease the efficiency of the engine. In the reversed world, i.e., if Theorem (17, b) holds, heat will leak from the cold to the hot reservoir, and increase the efficiency of the engine.

The other formulations of the second law (due to Lord Kelvin and to Clausius) can now be deduced and discussed. The following definition is required.

> **(D13)** Consider a situation in which bodies are heated or cooled and in which mechanical work is done. We define as *thermodynamically equivalent* a situation in which the system of interest goes through the same sequence of absolute temperatures and the same changes of energy and entropy, but in which the following differences are introduced. (a) Heating and cooling is done by establishing contact with infinitely large heat reservoirs. (b) The source or sink of mechanical work is arranged to be an appropriate Carnot engine.

The argument may be formalized as follows:

> $H-W$ denotes the withdrawal of heat from a heat reservoir, and its conversion into mechanical work.
>
> $W-H$ denotes the utilization of mechanical work to heat a reservoir.
>
> $h-c$ denotes the transfer of heat from a body to one cooler than itself.
>
> $c-h$ denotes the converse process.
>
> $A\rightarrow B$ indicates that B is a necessary accompaniment of A when a working fluid is taken through a cyclic process confined to physically accessible states.

The required principles are

> **Theorem (20, i)** If heat is converted into work by taking a working fluid through a cyclic process then, for the thermodynamically equivalent situation, $H-W\rightarrow h-c$ (Kelvin's principle, real world). Similarly, for the reversed world, $W-H\rightarrow c-h$. Both results hold for both worlds if all processes involved are reversible.

[‖‖] In this section it is assumed for simplicity that all systems considered are of type I (see Table II).

(ii) If heat is transferred, by taking a working fluid through a cyclic process, from a body to one warmer than itself, then, for the thermodynamically equivalent situation, $c-h\rightarrow W-H$ (Clausius's principle, real world). Similarly, for the reversed world, $h-c\rightarrow H-W$. Both results hold for both worlds if all processes involved are reversible.

(i) Regard the working fluid as the system of interest, and confine attention to the thermodynamically equivalent situation. Heat is withdrawn from a reservoir whose entropy decreases by s say ($s>0$). We are interested only in the change of entropy after a complete cycle, so that the change in entropy of the working fluid may be neglected (it gains as much as it loses in a cycle). All bodies taking part in the process are regarded as adiabatically enclosed, and at the end of the cycle the total change of entropy is non-negative. It follows that there has been a gain S of entropy in a part of the system, such that $S-s\geqslant 0$. Hence $S\geqslant s>0$. The processes represented by the change S of entropy are thermodynamically equivalent to processes of type $h-c$. Hence, for the thermodynamically equivalent situation, $H-W\rightarrow h-c$. If all processes are carried out reversibly, it follows immediately that $W-H\rightarrow c-h$. For a reversed world entropy has a tendency to decrease, and one must start with a process $W-H$ in which entropy increases. One can then infer the need for a process $c-h$ (in which entropy decreases). Clausius's principle may be deduced by a similar argument, or it may be deduced from Kelvin's principle as follows: $c-h$ is true by hypothesis, hence $h-c$ is false, and "not $h-c$" is true. By (i) $H-W\rightarrow h-c$, so that "not $h-c$"$\rightarrow$ "not $H-W$." This implies either $W-H$ or else that there is no interchange of mechanical and thermal energy. This last possibility is easily ruled out, and Clausius's principle follows. Similarly, Kelvin's principle can be deduced from Clausius's principle.

PART III. THE THIRD LAW

14. Deducible Properties of the Hypersurface $T=0$

In passing from the properties of γ to those of β this question arises: are physical systems such that the boundary points of γ can be adiabatically linked with the internal points of γ. If so, such points are in β. In addition other points may be in β, which are neither in γ nor on $F(\gamma)$. It is desirable, therefore, to trace, in the first place, those consequences of the assumptions already made, which throw light on the properties of the boundary points of β.

Special interest attaches in this connection to those points of E for which $T=0$, and a special symbol is desirable for this set:

(D14) The set of all those points of an appropriate phase space E of a system which correspond to states at the absolute zero of temperature will be denoted by δ.

The set of points $\beta\cap\delta$ represents those states of the system which, though at the absolute zero of temperature, can nevertheless be adiabatically linked with the rest of β. The study of this set is conveniently divided into two parts by using the result $\beta-J(\beta)=\beta\cap F(\beta)$; this is the set of those points on the frontier of β which belong to β. Thus one may write $\beta=\gamma+\beta\cap F(\beta)$, so that $\beta\cap\delta=\gamma\cap\delta+\beta\cap F(\beta)\cap\delta$. It is shown in Theorem (21) that $\gamma\cap\delta=0$.

Theorem (21) Consider a system which satisfied (A1) to (A5). Then

(i) $\gamma\cap\delta=0$;

(ii) Every curve which lies in the set $\beta\cap\delta$ represents a quasi-static adiabatic process;

(iii) If a point L of $\beta\cap\delta$ has an E-neighborhood N, such that all points of N for which $T>0$ (or $T<0$, depending on the choice (C2)) lie in β, then all δ neighborhoods of L contain points which are not in β.

(iv) For every point in the set $\beta\cap\delta$ one can find a point of δ which is infinitely close to it and does not belong to β.

(i) If the temperature T_0, introduced in connection with Theorem (15, ii), satisfied $T_0>0$, (or $T_0<0$, depending on the choice (C2)), then the temperature $T=0$ has not been reached by adiabatic processes. It follows that no part of the hypersurface $T=0$ lies in β. If $T_0=0$, take the absolute temperature as one of the thermodynamic coordinates in E. Since T is a strictly increasing or a strictly decreasing function of all the thermodynamic variables concerned, by Theorem (10, ii) all points of the surface $T=0$ lie on the frontier of β, and are, therefore, not a part of γ. Hence (i) holds again. (ii) Every curve in β represents a quasi-static process by Theorem (11, ii). It represents an adiabatic process if $d'Q=TdS=0$ for every increment of it [Theorem (9, i)]. (iii) Consider an n-dimensional E-neighborhood, N say, of a point L for which $T=0$. N is to be such that for every state represented in N, $T\geqslant 0$. We shall show that if *all* points of N are in β, then one has a contradiction with (A5). It will be assumed that entropy is among the independent thermodynamic variables. If all points of N are in β, then N contains parts of hyperplanes of constant entropy and some of these meet the hypersurface $T=0$ in β. Now pass from any point in N which is also in γ (i.e., not on the frontier of β) along the hyperplane of constant entropy, on which it lies by Theorem (14, i) until the hypersurface $T=0$ is reached. Pass, on this hypersurface, to any of the neighboring hyperplanes of constant entropy, and along them back to the neighborhood of L. By (ii) the processes represented by the curves traced in this manner are quasi-static adiabatic, so that L is an *a* point. Since this contradicts (A5), all δ neighborhoods of L contain points which are not in β. This proves (iii). (iv) is a restatement of this result in different terms. For consider a system, which can be modified within certain limits at the lowest attainable temperature compatible with this specification. If the set $\beta\cap\delta$ is empty, there is nothing to be proved. If the set $\beta\cap\delta$ is not empty, consider any point P of the set. Then, by the preceding argument, in *every* δ neighborhood of P there are points which do not belong to β, even if all points of this neighborhood belong to $F(\beta)$.

One can conclude that for *every* physical system that satisfies (A1) to (A5) *every* δ neighborhood contains a nonenumerable infinity of points representing states which are not in β (i.e., they are not adiabatically linked with states having $T>0$). However, the possibility of a *limited* adiabatic attainability of the absolute zero, at critical points or in critical regions of the sets δ, still exists. An example is furnished by any set of points G which lie in $\beta\cap\delta$ such that all points of G belong to the same value of the entropy. This is still compatible with the requirement that all points of β are i points and adiabatically linked with each other. The principle of the unattainability of the absolute zero goes beyond the present conclusions, in requiring that the set $\beta\cap\delta$ be empty for all systems.

Consider a system which is free of adiabatic partitions and vacuous spaces, and can exist within certain ranges at temperatures $T>0$ (or $T<0$, depending on the choice (C2)). Our deductions so far may then be expressed (somewhat loosely) as follows: The range of absolute temperatures that can be mutually and adiabatically linked with each other have a lower bound $T_0\geqslant 0$ (or upper bound $T_0\leqslant 0$, depending on the choice (C2)). If $T_0=0$, T_0 is *usually* not adiabatically linked with temperatures for which $T\neq 0$, but *it may be so linked in special cases.* If $T_0>0$ (or $T_0<0$, depending on the choice (C2)), no statement can be made about the adiabatic linkage of T_0, though in this case the absolute zero is *certainly* not adiabatically linked with temperatures $T\neq 0$. These conclusions are independent of the direction in which heat tends to flow or entropy tends to change.

The discussion in this section has largely been confined to those points (if any) on the frontier of γ which lie on the hypersurface $T=0$. The reason is that curves in this surface represent quasi-static adiabatic processes, so that our assumptions can be applied to such curves. However, as has been seen, one can even in this case argue only in a hypothetical manner of the form: if a certain point is in $\beta\cap\delta$ then certain other properties must follow. It is therefore seen that an additional assumption is required, since there is no clear-cut specification of which points of $F(\beta)$ belong to β and which do not belong to β.

A boundary point of γ is a point which is the limit of an infinite sequence of points of γ. But, since the number of experiments which can be performed is finite, the introduction of this concept needs some justification. The explanation is that γ is in fact usually of a very simple nature geometrically and it is assumed by (A5) that the variables can be continuously changed within the given ranges of variation in γ (though not, as has been seen, in β). It is for this reason that curves can occur in γ, and that the question of boundary points arises.

15. The Boundary of β: A Generalized Unattainability Principle

A possible way of stating the conventional unattainability principle is to assert "$\beta\cap\delta=0$ for all systems," so that the points for which $T=0$ do not belong to the points which are adiabatically linked with temperatures $T\neq 0$. Viewed in a more general way, the unattainability principle becomes an assumption which regulates the status of the boundary points of β. Now the sets β have other boundary points—those, for instance, at which changes in a state of aggregation occur. On one side of such a boundary, and for an appropriate range of variables, a set of points β_j, must be used, while on another side of the boundary, and for an appropriate range of variables, a set of points $\beta_k(k\neq j)$ may have to be used. Since the points on this type of boundary are adiabatically attainable, and should therefore belong to the set β_j, or β_k, or both, it is no use stipulating that *all* boundary points of sets β shall not belong to these sets: $\beta\cap F(\beta)=0$. We must formulate our requirement in a different manner.

For this purpose denote by y_0 the value of any thermodynamic variable y which has the following properties: (a) no equilibrium system exists which can exhibit values $y>y_0$ (or, alternatively, no equilibrium system exists which can exhibit the values $y<y_0$); (b) an equilibrium system exists which exhibits a nonzero range of variation of y. (a) ensures that a point for which $y=y_0$ cannot lie in the interior of β (i.e., in γ), but only on the frontier of β or else outside the closure of β. This would enable one to take heat flow as an example of y, when y_0 would have the value $y=0$. Condition (b) rules out this type of variable. However, entropy and absolute temperature are two examples of physical variables which fulfil both condition (a) and (b), since they both have an upper or a lower bound (see Theorem (14, iii)). Let η be the set of all points on the hypersurface $y=y_0$ of any variable y, in any phase space E. Our assumption is

(A6, i) $\eta\cap F(\gamma)=0$ for all variables y introduced above, and all sets of points γ. All boundary points of γ not excluded by this condition belong to β.

(ii) $F(\beta)=F(\gamma)$.

The effect of (i) is to make the points on $F(\gamma)$, at which phase changes occur, part of the appropriate sets β. These points are linked, therefore, by adiabatic processes to the remaining points of β (for all sets γ). On the other hand, the surfaces for which $y=y_0$ lie outside the sets β. Hence the value $y=y_0$ is (for all y) not adiabatically linked with the rest of β (for all β). The values y_0, therefore, are not attainable by adiabatic processes from any point of β. This is a general unattainability principle.

In order to complete (A6), it is convenient to examine various unattainability principles for y_0:

(U1) (a) $\beta\cap\eta=0$ for all systems.

(b) The value $y=y_0$ does not occur in the specifications of equilibrium states which are adiabatically linked with other values of y.

(U2) The value $y=y_0$ does not occur in the specifications of attainable equilibrium states of systems.

(U3) The value $y=y_0$ does not occur in the specifications of states which are adiabatically linked with other values of y.

(U4) The value $y=y_0$ does not occur in the specifications of attainable states of systems.

It is clear that (U1, a) and (U1, b) are equivalent, that (U2) implies (U1), and that (U4) implies (U3). Conversely (U1) implies (U2) for all conceivable y_0 only if it can be established that an equilibrium state which cannot be attained adiabatically from some point in some set β can also not be attained by any nonadiabatic method. Thus (U1) implies (U2), and (U1) and (U2) are therefore equivalent, if the class (P1) of physical processes (see Sec. 12) is empty. If it is not empty one cannot state without further assumptions if (U1) implies (U2) or not. Similarly, one can be sure that (U3) and (U4) are equivalent only if the classes of processes (P1) and (P3) are both empty. There is, however, a real difference between the first two propositions (U1) to (U4), and the last two. For the last two exclude the possibility of y_0 being attained even in a transient nonequilibrium state, whereas the first two deal only with the unattainability of y_0 in equilibrium situations.

The assumption (A6, i) implies unattainability principles of the type (U1), and, if the class of processes (P1) is empty, it also implies unattainability principles of type (U2). (U3) and (U4) are of a more general nature, and cannot be inferred from (A6, i).

An obvious application of the generalized unattainability principle (A6, i) is provided by the absolute temperature T, and is independent of the choices (C1) to (C3). Let T_0 be again the lower bound (or upper bound, depending on the choice (C2)), of the adiabatically linked absolute temperatures. By Theorem (15, ii), (A6, i), and Theorem (21, i), a critical temperature T_c exists subject to $0\leq T_c\leq T_0$, such that T_c is not an equilibrium temperature which is adiabatically linked with the rest of β. The sets of points β, therefore, do not contain points which represent states whose temperatures satisfy $0\leq T\leq T_c$. The absolute zero of temperature is therefore unattainable in the sense (U1). This unattainability is thus seen to be implied by (A6, i). Similarly the lower (or upper) bound of the entropy is also (U1)-unattainable. This represents a second application of the generalized unattainability principle.

(A6, i) settles which boundary points of γ belong to β, but it does not settle completely which boundary points of β belong to β. Thus, any completely isolated point or arc of β is in $F(\beta)$ but is not in $F(\gamma)$, so that whether or not it is to be counted as part of β is not decided by (i). This question is settled by (A6, ii) which asserts that there are no such points because $F(\beta)$ and $F(\gamma)$ are in fact identical.

It has been seen that (U1)-unattainability of a value y_0 of a variable y does not enable one to infer any of the stronger unattainability principles. To achieve this an additional assumption is required, and will now be stated.

(A6, iii) For the values y_0 of (A6, i) (U1)-unattainability shall imply (U4)-unattainability.

This makes the lower (upper) bound of the absolute temperature and of the entropy unattainable by all processes.

16. Entropy Properties Engendered by the Unattainability Principle

In the preceding pages, it has been seen how only minor verbal changes are necessitated by the various choices (C1) to (C3), while the basic structure of thermodynamics is independent of them. This section concludes¶¶ the exposition of the new approach, and it will be used to illustrate incidentally how, if one is not interested in these various choices, simple and correct statements can be made which do not refer to these choices at all. For this purpose one merely requires the following definition:

(D15, i) A physical system is said to be regular if it satisfies (A1) to (A6) and is of type I (see Table II).

It follows that a regular system is free of adiabatic partitions and vacuous spaces, exhibits in equilibrium a single positive absolute temperature; in nonequilibrium heat tends to flow to relatively low absolute temperatures, and, when isolated, its entropy cannot decrease. Hence, from Theorem (15, viii). $\partial S/\delta T$ is positive for any state, represented by a point in γ, of any configuration of a regular system. This implies that the entropy near $T=0$ must be assumed finite for any configuration of a regular system.

¶¶ The last two sections of this paper are devoted to certain comparisons with previous work.

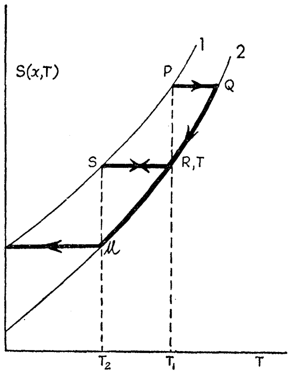

FIG. 2

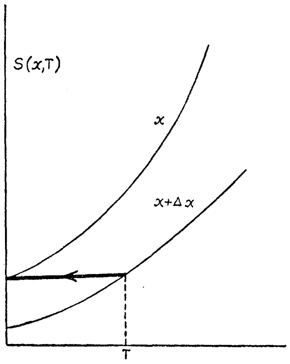

FIG. 3

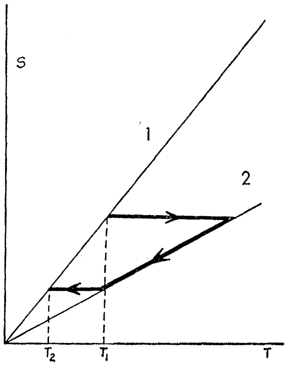

FIG. 4

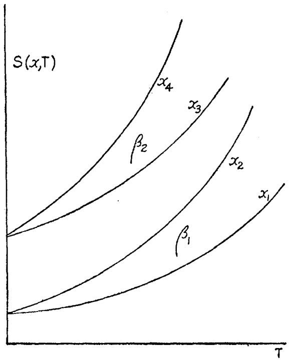

FIG. 5

FIGS. 2 and 3. Attainability of the absolute zero by processes of type $P(x)$.
FIG. 4. Unattainability of the absolute zero by processes of type $P(x)$.
FIG. 5. Possible entropy-temperature characteristics of a regular system near the absolute zero for configurations generated by a variable external parameter x ($x_1<x_2<x_3<x_4$).

The following definition is also helpful:

(D15, ii) Let $S(x,T)$ denote the entropy of a configuration of a regular system as a function of absolute temperature and an external parameter x, the remaining external parameters being fixed. If

$$\lim_{T\to 0}[S(x_1,T)-S(x_2,T)]=0$$

for all functions $S(x,T)$ of all systems, then *Nernst's heat theorem* will be said to be valid.

Consider now (Figs. 2 to 4) possible entropy-temperature curves for two configurations of a regular system near $T=0$. It is assumed that all curves drawn, and the space between them, lie in γ, except for the points for which $T=0$. It is also assumed that all changes in external parameters can be carried out in a quasi-static adiabatic manner.

We now wish to consider what properties of the entropy are required by the (U2)-unattainability of the absolute zero. For this purpose, *let the unattainability principle (A6) be forgotten*, and let configuration 2 in Fig. 2 represent the state of a system with a magnetic field (H) applied, configuration 1 without magnetic field, all other external parameters being the same in the two cases. If a heat reservoir at temperature T_1 is available, one can start at P, magnetize to reach Q, cool by contact with the reservoir to reach R, and demagnetize to reach S. This provides a lower temperature T_2 for a new heat reservoir. Now repeat the cycle to reach $T=0$, via points T and U. Since contact with heat reservoirs has taken place, this process is compatible with (U1)-unattainability, but violates (U2)-unattainability, of the absolute zero (and, therefore, it violates also (U4)-unattainability). This has been achieved by using processes of the type P (H), defined in Sec. 12.

What general conditions must be imposed on the entropy in order to prevent the construction of processes which could, in principle, be used to attain the absolute zero? A partial answer may be formulated as follows:

> **Theorem** (22) Consider the entropy-temperature characteristics $S(x,T)$ of a regular system near $T=0$, x being one of the external parameters. Assume (i) the only boundary points which need to be considered are those for which $T=0$; (ii) only processes of type P(x) are allowed. Then the necessary and sufficient condition that the absolute zero be unattainable by this system is that $S(x,0)$ be independent of x (Nernst's heat theorem for the configurations of the system generated by the variable x). Unattainability may be understood here in either of the senses (U2) and (U4).

By Theorem (15, viii), and by hypothesis (i) of the theorem $(\partial S/\partial T)_x>0$ for $T>0$. For a small increment Δx, and for a temperature T close to absolute zero we can write

$$\Delta S\equiv S(x+\Delta x,T)-S(x,0)=(\partial S/\partial x)_T\Delta x+(\partial S/\partial T)_x T.$$

If $(\partial S/\partial x)_T$ does not converge to zero as $T\to 0$, one can find a pair of values $(\Delta x,T)$ which reduce ΔS to zero. By assumption (i), therefore, there exists a quasi-static adiabatic process from the state $(x+\Delta x,T)$ to the state $(x,0)$; the end point of this process is at the absolute zero (Fig. 3). This situation must be ruled out for unattainability of the absolute zero. It is in fact excluded if, and only if, $(\partial S/\partial x)_T\to 0$ as $T\to 0$. Since

$$S(x+\Delta x,T)-S(x,T)=(\partial S/\partial x)_T\Delta x,$$

this implies, if Δx is fixed and T tends to zero,

$$\lim_{T\to 0}[S(x+\Delta x,T)-S(x,T)]=0$$

for all values of x. Hence the system satisfies Nernst's heat theorem for the configurations generated by allowing the external parameter x to be variable. Analogous theorems hold if other choices are made in (C1) to (C3).

By Theorem (15, i) a set of independent thermodynamic variables is furnished by the absolute temperature and the $n-1$ external parameters, so that one can write

$$dS=\frac{\partial S}{\partial T}dT+\sum_{k=2}^{n}\frac{\partial S}{\partial x_k}dx_k, \tag{28}$$

and this vanishes for quasi-static adiabatic processes. Hence, provided $\partial S/\partial T\neq 0$, which holds by Theorem (15, viii), Sec. 10, a change Δx in x produces a change in the absolute temperature given by

$$-\Delta T=\frac{(\partial S/\partial x)_T}{(\partial S/\partial T)_x}\Delta x \tag{29}$$

for the configurations generated by varying one only of the external parameters. Theorem (22) may be interpreted, therefore, as implying that Δx must increase beyond all bounds to produce a further lowering of the temperature as the absolute zero is approached, because $(\partial S/\partial x)_T\rightarrow 0$ as $T\rightarrow 0$.

The following simple calculation illustrates the unattainability of the absolute zero, by varying an external parameter only, for configurations which satisfy Nernst's heat theorem. Suppose

$$S(x_1,T)=aT,\quad S(x_2,T)=bT,\quad a>b>0,$$

where $S(x,0)$ has been taken as the zero of entropy. If a reservoir at temperature T_1 is available, change the external parameter to reach configuration 2 (Fig. 4), cool by contact with the reservoir, and then change the external parameter to reach configuration 1 by a quasi-static adiabatic process. This makes a lower temperature $T_2=(b/a)T_1$ available to act as another reservoir. After n cycles of this type a temperature

$$T_{n+1}=(b/a)^nT_1$$

is obtained. It is clear that the absolute zero cannot be reached in a finite number of steps. Note also that the flatter the entropy curve of the second configuration, the more efficient the process.

The additional assumptions (i) and (ii) in Theorem (22) must now be considered. (i) is very useful in ruling out a large variety of complicated entropy-temperature characteristics. A simple example of a situation which is ruled out by (i) is given in Fig. 5. The solid lines, apart from the coordinate axis, belong to $F(\beta)$. The system of interest can exist only for two non-overlapping continuous ranges of the external parameter x, and quasi-static adiabatic processes which link them cannot be carried out. It follows that if (i) is omitted in Theorem (22), *but (ii) is retained*, then the condition stated in the theorem is no longer necessary, though it remains sufficient to insure the unattainability of the absolute zero. Thus, in spite of (U2)-unattainability $S(x_1,0)\neq S(x_3,0)$.

It may be supposed that the separation between the branches of β near the $T=0$ axis can be interpreted as due to disordered parts of the system which have been frozen in, and therefore, cannot be linked by reversible adiabatic processes, unless a certain minimum temperature is exceeded during the process. Such systems are, of course, of considerable importance (Simon, 1927), but this interpretation is inadmissible, unless new conventions are made, since the preceding discussion is confined to equilibrium states.

Assumption (ii) is required for definiteness: it specifies the processes which may be used to reach the absolute zero, and one then looks for conditions which are necessary and sufficient to ensure that the absolute zero cannot be attained with the aid of such processes. Suppose now that assumption (ii) is dropped, so that *any* process may be used to cool down the system, *but assumption (i) is retained*. Then the condition stated in the theorem is still necessary to ensure unattainability; but it is not possible to show that it is also sufficient, unless an additional assumption is made. A suitable assumption would be to presume the class (P4) of physical processes (see Sec. 12) to be empty.

In the present axiomatic approach, therefore, one arrives at the following result (which deviates from the result conventionally stated):

> **Theorem (23, i)** The principle of the (U4)-unattainability of the absolute zero does not imply Nernst's heat theorem.
>
> (ii) Nernst's heat theorem does not imply the (U4)-unattainability of the absolute zero.

(i) is proved by using the system of Fig. 5 as example: even though one may suppose that the absolute zero cannot be attained by the system it violates Nernst's heat theorem (in our formulation (D15, ii)). (ii) is proved by observing that Nernst's heat theorem, *by itself*, does not exclude the possibility of a process of type (P4) being available to attain the absolute zero.

It may be thought desirable to investigate the consequences which can be deduced if certain thermodynamic relations are supposed to hold at the absolute zero. An interesting attempt to do this is due to Bennewitz (1926) but, as is shown here (Secs. 17, 18) and elsewhere (Landsberg, 1954), it is unfortunately difficult to carry out such an investigation in a rigorous manner. It may suffice, therefore, to summarize the relations of implication which have been obtained in this paper. These are shown in Fig. 6.

The remaining two sections deal briefly with some previous work.

17. Comments on the Relation between the Unattainability Principle and the Second Law

It is well known that Nernst (1912) attempted to deduce the unattainability principle from the second law. Defining a perpetuum mobile of the second kind

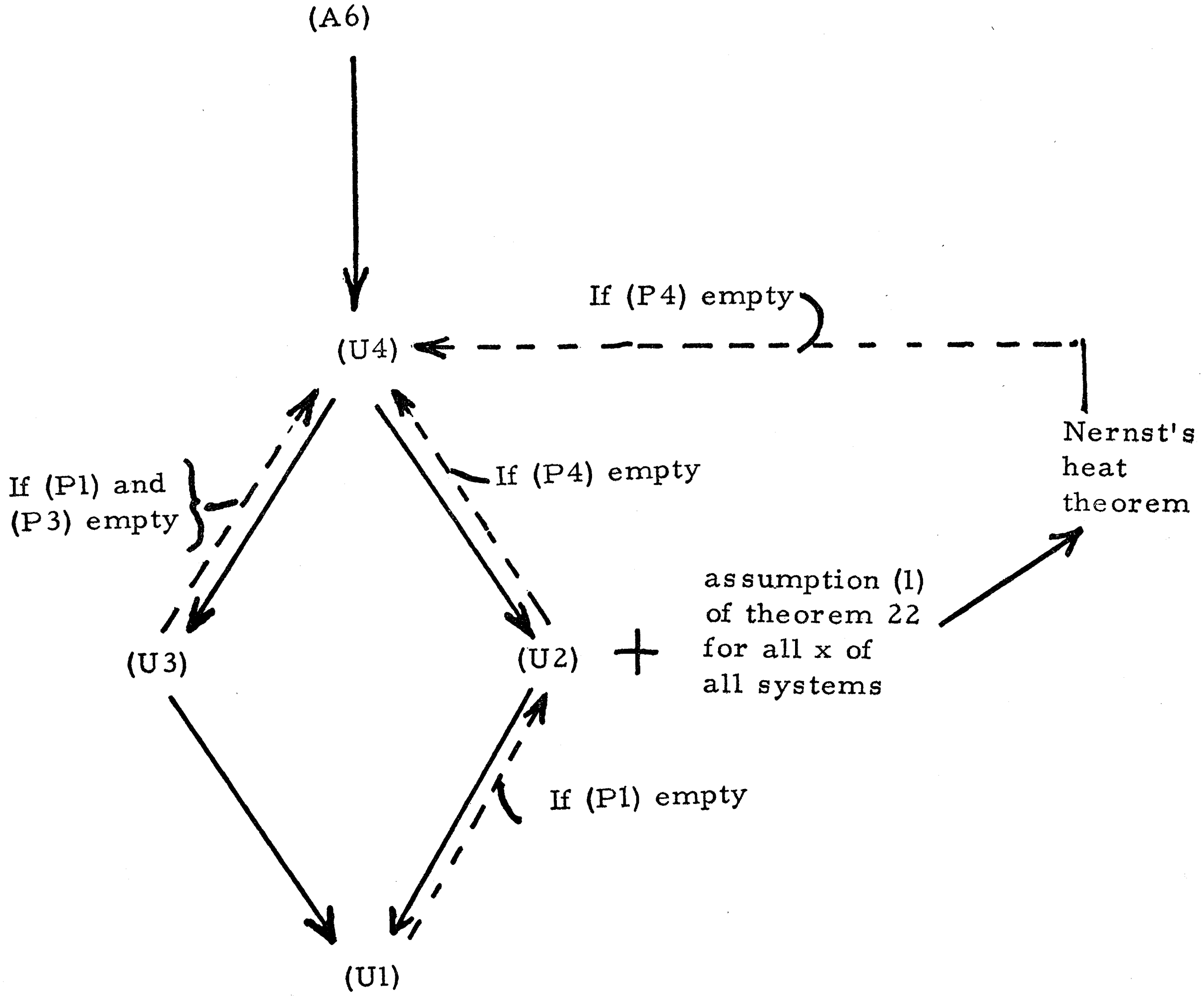

FIG. 6. Relations among unattainability principles assuming the variable y in (A6), and in (U1) to (U4), to be the absolute temperature T, and y_0 to be $T=0$.

as an engine which can convert all the heat energy in a reservoir (above the zero point energy) into mechanical work, he took the second law in this form:

(N) It is impossible to construct a perpetuum mobile of the second kind.

He then considered a Carnot engine whose lower isothermal is at $T=0$, and which therefore converts all the heat energy of the high temperature reservoir into mechanical work. Invoking (N), he then inferred the unattainability principle. Einstein (1912) objected to this argument on the grounds that the slightest irreversibility would detach the low temperature isothermal from $T=0$; and he pointed out that this was an instance where the effect of irreversibility was of qualitative importance. He argued that the process can therefore not be carried out in practice. Bennewitz (1926, p. 172), on the other hand, remarked that no part of Nernst's cycle contradicts the second law, and that therefore the unattainability cannot be inferred.

It will be shown now that Bennewitz's comment is unsound. It is well known (Theorem (19a)) that the efficiency of a Carnot engine (in the real world) satisfies

$$\text{(B)}\quad \eta \leqslant \frac{T_1 - T_2}{T_1}.$$

Bennewitz, in his comments, took this result as the formulation of the second law. But (B) is not a satisfactory formulation of the second law, since it allows the possibility of a perpetuum mobile of the second kind (by chosing $T_2=0$). On the other hand, (N) leads immediately to $\eta<1$ for any Carnot engine. Thus a discussion of Nernst's view which takes Carnot engines as basic, should start with a statement of the second law which is not of the form (B), but of the form

$$\text{(B}'\text{)}\quad \eta \leqslant \frac{T_1 - T_2}{T_1} < 1$$

instead. Bennewitz's comment then becomes invalid. This criticism is in broad agreement with remarks by Simon (1951). In this paper other discussions of this problem are also reviewed (see also Simon, 1930, 1937; Epstein, 1936; Cross and Eckstone, 1942; Schottky, 1943).

In our terminology, the whole controversy is one as to the status of certain boundary points of an open set of points γ, any two of which can be linked by adiabatic processes. In mathematics the status of such points is often the subject of a separate assumption. Nernst assumed that, in the absence of information to the contrary, the points could be regarded as belonging to the set. Einstein suggested that they should not belong to the set. From the axiomatic point of view, however, both views represent an additional postulate. Once this is appreciated, it would seem just as satisfactory to increase the number of postulates by introducing an unattainability principle immediately, instead of following either of the two suggestions just discussed. This view of Einstein's remarks as introducing a new postulate may be regarded as a development of Simon's (1951) comment that Einstein's argument does not seem to be *directly* connected with Nernst's train of thought.

However, even if this view (that an additional assumption enters as soon as boundary points are considered) is adopted, one can still extract a useful piece of information from the Nernst cycle. In the simplest case this cycle can be represented in a two-dimensional T-S diagram. One can now argue as follows. Suppose a *continuous portion* of the axis $T=0$ lies in β, and that the points $T>0$ also lie in β (subject to restrictions on the ranges of the variables). One can then use the Nernst cycle to show that this contradicts (N), and is therefore impossible. One arrives at precisely the conclusion stated in Sec. 14. Generalizing these considerations to an n-dimensional phase space, one obtains Theorem (20, iii). But it is to be emphasized that (U4)-unattainability of the absolute zero is not implied by this result.***

Bennewitz (1926) considered the somewhat different problem as to what thermodynamic relation must be assumed to be valid at $T=0$, so that an unattainability principle may be implied. He concluded that the condition

$$(\partial U/\partial T)_v=(\partial F/\partial T)_v \quad \text{at } T=0$$

is sufficient, where U is the internal energy, F the free energy of the system. This condition is equivalent to

$$-S=T(\partial S/\partial T)_v \quad \text{at } T=0. \tag{30}$$

If, however, the processes P(x), Sec. 12, are used, condition (30) is found to be insufficient. This is easily seen by considering Figs. 2 and 3 for the case $S(0)=0$. Equation (30) is then satisfied, but the absolute zero can nevertheless be reached. Equation (30) is therefore not sufficient to ensure (U2)-unattainability of the absolute zero.

18. Comments on the Relation between the Unattainability Principle and Nernst's Theorem

To what extent does Nernst's theorem go beyond the unattainability principle? This question has been discussed by two different methods, which led to two different answers.

Bennewitz (1926) used equations such as (28) and (29), and concluded that unattainability was ensured by requiring

$$-\Delta T\rightarrow 0 \quad \text{as} \quad T\rightarrow 0 \quad (\text{for all finite } \Delta x). \tag{31}$$

This is not sufficient to ensure that two different configurations must reach the same value of the entropy as $T\rightarrow 0$. It was concluded that Nernst's theorem goes beyond the unattainability principle.

However, it can be shown by example that (31) is not an adequate expression of the unattainability principle. Consider a regular system whose only external parameter is the volume V, and whose free energy is given by (a, b, c positive constants)

$$F=(a-bT-cT^{\frac{3}{2}})V, \quad S=(b+\tfrac{3}{2}cT^{\frac{1}{2}})V. \tag{32 a, b}$$

By Eqs. (29) and (32)

$$-\Delta T=\frac{4}{3}\frac{b}{C}T^{\frac{1}{2}}\frac{\Delta V}{V}, \tag{33}$$

so that (31) is fulfilled. By Eq. (32b), the curves of constant entropy are as shown in Fig. 2, where configuration 1 corresponds to $V=V_1$, configuration 2 to $V=V_2<V_1$. Thus, ordinary finite quasi-static adiabatic changes of volume would suffice to reach the absolute zero, although (31) is fulfilled.

This shows that caution must be exercised when arguing simply from (29). A fuller discussion must lead to Theorem (22), or a similar result.

Another approach (Simon, 1937; Fowler and Guggenheim, 1939) considers processes P(x) as discussed in Sec. 16. The assumptions made in this argument are that entropy is a strictly increasing finite function of the temperature for each configuration, and that any two configurations of the system can at any temperature be linked by quasi-static adiabatic processes. These assumptions furnish for the present purpose, the same logical foundation as that supplied by assumptions (A1) to (A5) of the present paper, together with the special assumptions of Theorem (22). In fact this theorem reproduces, in a modified form, the arguments of these authors. Nonetheless, their conclusion that the unattainability principle implies Nernst's theorem differs from the conclusion arrived at in this paper, (Theorem (23)). The reason is that, in accordance with the axiomatic nature of the present approach, the two

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***Isolated points of the $T=0$ axis may still lie in β.

special assumptions of Theorem (22) cannot be invoked as general laws; indeed, regarded as general laws, they are certainly wrong.

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