

MAIN IDEAS IN THE AXIOMATICS OF THERMODYNAMICS

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ABSTRACT

Recent advances in axiomatic treatments of thermodynamics are surveyed, by considering the new ideas rather than the mathematical technicalities. It is shown that the advance has been considerable, and can be summarized by the remark that the number of primitive concepts needed (for example to arrive at the notion of entropy) has been steadily decreased. The importance and significance of certain mathematical notions, notably those of various forms of order, is emphasized. It is explained in what connections broad continuity assumptions are convenient and indications are given of how these can be replaced by more rigorous procedures. Remarks about extensive properties and about the zeroth law are also included.

1. INTRODUCTION

Among scientists there exists a healthy ambivalence towards axiomatics. On the one hand there is the doubt whether one can arrive at any new science by axiomatizing; on the other, no one likes faulty arguments, and it is in the attempt to eliminate these that one is led in the direction of axiomatization.

Though no professional axiomatizer, I responded favourably to the request to deal with axiomatics here, because I believe that the progress which has recently been made in the understanding of the foundations of thermodynamics has in fact advanced scientific understanding. It is the purpose of this article to remove the thick shell of occasionally very pure mathematics, utilized in this work, in order to lay bare the essential ideas lying behind it. Our concern will be with systems which are free of adiabatic partitions and vacuous spaces, and in which the effects of long range forces, surface tension etc., are all neglected.

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2. AN EMPIRICAL ENTROPY VIA ORDER RELATIONS

In the axiomatic approach the thermodynamic phase space E of a system dwindles to a set of points $x, y, \dots \in E$, and each point becomes a state of the system only when our rules of interpretation are applied to the abstract mathematics. If an adiabatic transition is possible from state x to state y , we shall write xRy . Such relations R can pale into abstract objects of set

theory, and there be specified merely by their properties. Of these we note six :

- (i) Reflexivity: $(\forall x) (x \in E \Rightarrow xRx)$
- (ii) Transitivity: $(\forall x, y, z) (x, y, z \in E \text{ and } xRy \text{ and } yRz \Rightarrow xRz)$
- (iii) Symmetry: $(\forall x, y) (x, y \in E \text{ and } xRy \Rightarrow yRx)$
- (iv) Antisymmetry: $(\forall x, y) (x, y \in E \text{ and } xRy \text{ and } yRx \Rightarrow x = y)$
- (v) (Strong) connectedness or comparability:
 $(\forall x, y) (x, y \in E \Rightarrow \text{either } xRy \text{ or } yRx \text{ or both})$
- (vi) Conditional connectedness: $(\forall x, y, z)$
 $(x, y, z \in E \text{ and } xRy \text{ and } xRz \Rightarrow \text{either } yRz \text{ or } zRy \text{ or both}).$

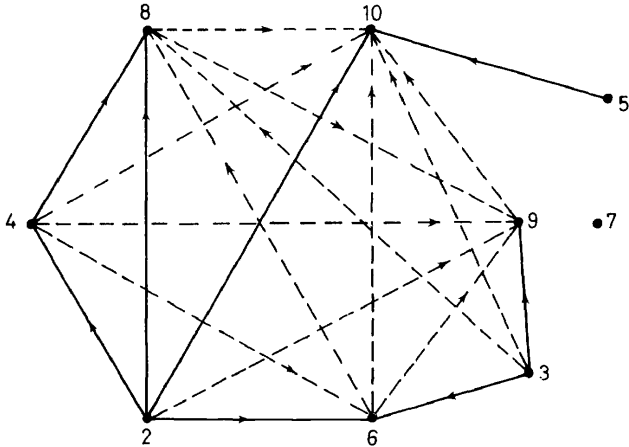


Figure 1. A set of points $E = \{2, 3, 4, 5, 6, 7, 8, 9, 10\}$ with partial preorder, and also exhibiting property (iv). Solid arrows mean that xRy . The set may be interpreted by the rule that xRy if and only if there exists an integer r such that $xr = y$.

The dashed arrows are needed if conditional connectedness is imposed in addition. For example, $2R4$ and $2R6$ then implies $4R6$ even though $4r = 6$ does not hold for any integer r .

The interpretation of R as adiabatic accessibility between states suggests that it is safe to impose conditions (i) and (ii) on R to obtain a *partial preorder* (or *quasiorder*). For states arbitrarily numbered from two to ten this type of order is illustrated in Figure 1 (solid lines). The relation is seen to lack properties (iii) and (vi) (and therefore also (v)). This is reasonable in the present interpretation. Thus :

Lack of (iii): (xRy) and (not yRx) can both be true for states of different entropy, when there is only a one-way adiabatic link.

Lack of (iv): (xRy) and (yRx) can both be true with $x \neq y$ for distinct states of the same entropy.

Lack of (v): (xRy) and (yRx) can both fail if x is an equilibrium state not connected with others by adiabatic processes.

This possibility of states like No. 7 (Figure 1) which are like isolated islands in a sea of adiabatically linked states shows that R is still too general for the simple systems in view here. The effect of conditional connectedness (ref. 1,

axiom 2.1.2 (i), pp 31, 126; axiom A.2.2, p. 193) is to add the dotted links in *Figure 1*. Arrows have been affixed to these according to the arbitrary convention xRy if $x > y$ (which rules out contradictions with transitivity).

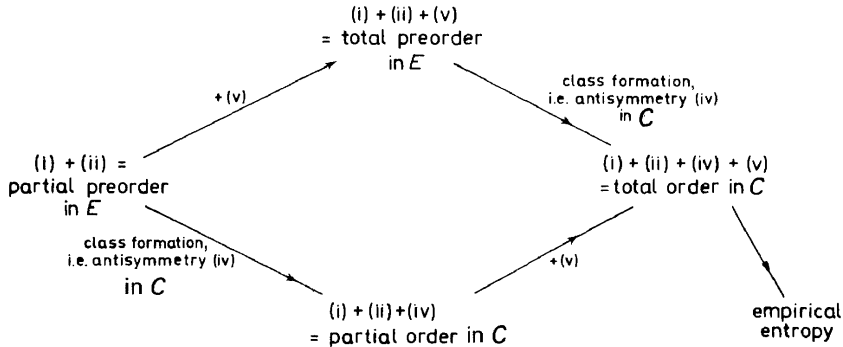


Figure 2. Types of order.

To remove islands like state 7 one needs the stronger *connectedness* and arrives at a *total preorder* (see *Figure 2*). This is exactly in accord with the now usual idea that any pair of states of normal systems are adiabatically linked. This idea originates from the remarks that there are no physical processes which involve such adiabatically isolated states (the processes of class P1 in ref. 2, and in ref. 3, pp 91, 93), and that thermodynamics makes statements about certain sets of points β in phase space^{2, 3}.

Mutual adiabatic accessibility has the additional property of symmetry (iii). This condition converts partial preorder to *equivalence*, and in the abstract scheme one defines it by

$$x \sim y \Leftrightarrow xRy \text{ and } yRx$$

Such a relation divides the set E into so-called equivalence classes. Each class contains all the states belonging to one and the same entropy. Let the class containing a certain state x be denoted by C_x . Then the properties of these classes are:

- (a) $y \in C_x \Rightarrow C_y = C_x$
- (b) $y \notin C_x \Rightarrow C_y \cap C_x = \emptyset$
- (c) $E = C_x \cup C_y \cup \dots$
- (d) If (xRy) , then $(x' \in C_x, y' \in C_y \Rightarrow x'Ry')$

Since all points of C_x and C_y are therefore ordered in the same sense, one can write

$$xRy \Leftrightarrow C_x \rho C_y,$$

where ρ is the ordering relation between the classes. Since R has property (v), so has ρ . But unlike R , ρ has the property (iv). This yields *total order* of the set C of equivalence classes (see *Figure 2*), which are said to form a *chain*.

A simple interpretation of the relation ρ is the relation \leq among real numbers, which clearly has the properties (i), (ii), (iv) and (v). This suggests

that (subject to additional assumptions) one can associate a real number $\sigma(C_x)$ with any equivalence class such that

$$(C_x \rho C_y) \text{ and } (C_x \neq C_y) \Rightarrow \sigma(C_x) < \sigma(C_y) \quad (2.1)$$

This function σ has the properties of an empirical entropy, and we have arrived at it without mention of work, temperature or phase space. Heat has also not been mentioned, though knowledge of it may (but need not) be assumed to define an adiabatic linkage of states. The realization that the introduction of these concepts can be delayed without errors in logic until after the empirical entropy has been introduced, is one of the results of recent work on the foundations of thermodynamics. Note that the important additive property of the entropy cannot necessarily be attributed to the empirical entropy, which is clearly a weaker concept.

3. PROBLEMS OF CONTINUITY

Current mathematical work on the foundations of thermodynamics tends to exhibit either an emphasis on algebraic and group theoretical properties (Approach A) or on topological and analytical concepts (Approach B). A good combination of them may emerge in due course. A and B will be illustrated by recent attempts to find quick and intuitive (though unrigorous) ways of deriving equations of the form $d'Q = \lambda d\sigma$ for an increment of heat.

(A) *From order.* One wants to argue⁵

(A1) Given that for distinct C_x, C_y, C_z , if $C_x \rho C_y, C_y \rho C_z, \dots$ then $\sigma(C_x) < \sigma(C_y) < \sigma(C_z) \dots$ (monotonic empirical entropy)

(A2) There exists a function λ in E such that $d'Q = \lambda d\sigma$ (integrating factor)

The difficulty is that the inferences (2.1) and (A1) are necessarily valid without additional hypotheses only if the set is denumerable, while (A2) requires a non-denumerable set.

(B) *From Carathéodory's theorem*⁶. In §9 of his paper, Carathéodory used accessibility considerations from a given point in phase space to show that entropy changes in a standard direction in adiabatic processes. This argument

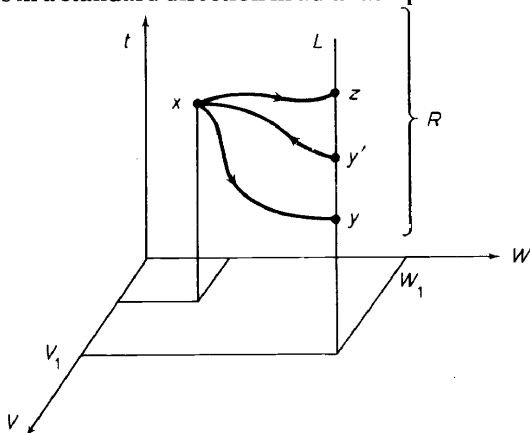


Figure 3. Diagram for the argument showing that L contains one point which is in a special relation to x .

can be extended. Denote deformation coordinates (volume, magnetic field, etc.) by V and W and the thermodynamic coordinate (empirical temperature or internal energy) by t . We seek to get adiabatically from a state x to the line L defined by $V = V_1, W = W_1$ (Figure 3). Among the range R of accessible states on L will be a state which can be reached by *quasistatic* adiabatic processes. If it is in the position y' , one can get from y' to all neighbouring points on L by adiabatic processes $y' \rightarrow x \rightarrow y, y' \rightarrow x \rightarrow z$. By then changing V and W slightly a whole neighbourhood of y' is seen to be adiabatically accessible from y' , contrary to Carathéodory's principle. So the state which is accessible from x by quasistatic adiabatic processes must lie at an endpoint of R , say at y . On changing V and W , y may be expected to generate a surface⁷ on which x itself will also lie. Starting with a different state x , other surfaces are found. From these surfaces one can argue to the existence of an empirical entropy σ labelling these surfaces, and eventually to an equation $d'Q = \lambda d\sigma$.

Alternatively, from Kelvin's principle, a quasistatic adiabatic linkage between the state x and the line L is possible only for one point y on L . For if there were two such points y, y' then, choosing t to represent the internal energy, one can construct a cycle $xyy'x$ which violates Kelvin's principle. On the path yy' the energy is changed by a supply of heat Q and in the rest of the cycle it is changed by the performance of mechanical work W , whence $W = Q$. One again arrives at surfaces generated by the single states y as V and W are changed. If two (quasistatic adiabatic) surfaces intersect one would again violate Kelvin's principle, and one would also have a -points [defined in equation (4.1), below] if the surfaces are smooth enough.

Each of the procedures A and B requires continuity assumption, as pointed out in ref. 8 [see also refs. 9, 10].¹ To axiomatize these, one has to borrow results from pure mathematics.

Method A

Chronologically the first result to be invoked^{3,8,9} was the theorem that a chain C is isomorphic to a subchain of the reals, provided¹¹ C contains a denumerable subset order-dense in C . This enables one to associate with any point $C_x \in C$ a real number $\sigma(x)$ such that for $C_x \neq C_y$

$$C_x \rho C_y \text{ implies } \sigma(C_x) < \sigma(C_y)$$

The natural order of the real numbers thus mirrors the order of the equivalence classes. However, gaps can exist in this representation in the sense that for all C_z such that $C_x \rho C_z$ one might have

$$\sigma(C_z) \geq a + b > a \geq \sigma(C_x)$$

where $(a, a + b)$ is a non-zero interval.

One can remove these gaps (and ensure continuity) by imposing on C additional conditions which can readily be granted for normal thermodynamic systems (C to be continuous, with a denumerable subset dense in C , and without first or last element). C then becomes similar to the real numbers in their natural order¹². Thus one can construct an empirical entropy which is continuous in the following sense: If $\sigma(C_a) - \epsilon < \sigma(C_a) < \sigma(C_a) + \epsilon$ there exist elements y and z such that $C_y \rho C_a \rho C_z$ and such that for any x

satisfying $C_y \rho C_x \rho C_z$ we have

$$\sigma(C_a) - \epsilon < \sigma(C_x) < \sigma(C_a) + \epsilon$$

This second procedure does not appear to have been used explicitly, though it is very direct, and yields a continuous empirical entropy without using Carathéodory's axiom.

Method B.

Let N_x denote a *neighbourhood* of any element x of E . Then a third way of ensuring continuity derives from this axiom:

$$[(\forall N_x)(\exists x')(x' \in N_x \text{ and not } xRx')], \text{ i.e. } [x \text{ is an 'i-point'}] \quad (3.1)$$

The notion of neighbourhood in the original set E implies the existence of a topology in E (E becomes a *topological space*), and continuity means that closeness in E according to this topology must be linked to the preorder relation R already defined in E . Thus one requires that any x and y satisfying xRy and not yRx have neighbourhoods N_x, N_y such that

$$x' \in N_x \text{ and } y' \in N_y \Rightarrow x'Ry' \text{ and not } y'Rx'$$

In addition to this continuity condition for R , first used⁹ in 1962, a separable topological space E is needed^{13, 14}. The separability of E guarantees the existence of a denumerable subset dense in C . To exclude gaps in C , i.e. to make C dense in itself (and in that sense 'continuous') one must assume that E is connected in the topological sense^{9, 14}.

For different equivalence classes to be represented by a surface and for σ to be also differentiable, E has to be a locally Euclidean space (a 'differentiable manifold') and it is sufficient that quasistatic adiabatic transitions be characterized by a condition $\sum X_j(x_1, x_2, \dots) dx_j = 0$ where the X_j are differentiable functions. Falk and Jung consistently avoided the mathematical problem of ensuring continuity (ref. 4, pp 120, 125, 131, 142).

4. THE 'OLD' CARATHÉODORY APPROACH

The qualification 'old' in the title of this section is intended to avoid confusion between Carathéodory's own work and its recent developments¹⁴.

The 'old' Carathéodory approach shared with the conventional Clausius treatment a number of demerits^{4, 15}: (α) Though strict axiomatics was not intended by these authors, it was always prevented by the occurrence of unstated assumptions which supported stated 'laws' or 'axioms'. (β) The introduction *together* of absolute temperature and entropy was a cause of confusion. Approaches A and B have removed these defects. Only partial removal of the following additional defects appears to have taken place: (γ) The combination of the inaccessibility *axiom* and the *restriction* to simple system led Carathéodory to peculiar results. One of these is that an empirical entropy can be found for an ideal gas without any appeal being made at all to his *axiom* (3.1). (δ) The stipulation that all but one coordinate of the thermodynamic phase space be 'non-thermodynamic' meant that a clear distinction between mechanisms and thermodynamics was not yet part of the formal

structure. (ε) Insufficient attention is paid to the fact that thermodynamic functions are defined strictly only for interior points of a phase space.

At the present time, then, these shortcomings of the old Carathéodory approach are becoming clearer, and the few specialists who *are* working on the foundations are leaving this approach in order to develop instead approaches A and B. It is an interesting thought that this is just the time when the nature of the old Carathéodory argument, and how it relates to the Kelvin and Clausius treatments, is becoming clearer¹⁶ so as to endow the old Carathéodory approach with some popularity among a wider group of scientists.

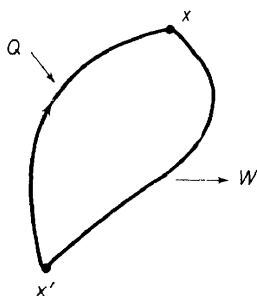


Figure 4. A circuit to relate the principles of Kelvin and Carathéodory.

The key idea here is the straight deduction of Carathéodory's axiom from Kelvin's principle! If Carathéodory's axiom is not satisfied, there exists for at least one state x a neighbourhood N_x of x such that

$$(\forall x')(x' \in N_x \Rightarrow xRx'), \text{ i.e. } x \text{ is an a-point.} \quad (4.1)$$

Keeping the deformation coordinates such as volume and magnetic field fixed, choose a state $x' \in N_x$ such that the transition from x' to x can be performed by adding an amount of heat ($Q > 0$, say) to the system. One can then return the system from x to x' adiabatically so that work W is performed by the system. This means that for the cycle $(x'xx')$ $Q = W$, and heat energy can be completely converted into work. This violates Kelvin's principle. The initial assumptions must therefore have been in error. Carathéodory's axiom (3.1) follows from this contradiction.

Suppose now the violation of Carathéodory's principle, i.e. the existence of the a-point x is granted, while one maintains Kelvin's principle. This feat can be achieved only if the system is such that there are no states $x' \in N_x$ with the required property that the transition from x' to x can occur with $Q > 0$ and fixed deformation coordinates. One must ask: What kind of systems are these? The answer is simple, the existence of a-points signifies that these are purely *mechanical* systems.

These above considerations suggest that Carathéodory's paper should no longer be regarded as an attempt at axiomatics. Instead its contribution is to distinguish between the simpler forms of mechanical and thermal systems in terms of the topology of the phase space:

Simple mechanical systems: All points are a-points.

Simple thermal systems: All points are i-points.

5. METRIC VARIABLES: EXTENSIVITY OR ADDITIVITY

Basic to the notion of length, weight, etc., is the existence of a 'joining' operation. The theory of measurement postulates it so that two equal standard rods joined in a line end to end can be equated (in the sense of equal lengths) to another rod which is then two units long. It is this operation which makes measurement possible. From this notion there then emerges the idea of a metric (i.e. measurable) variable. The quantities measured in this way are additive in this sense: if q_1 is measured as a join of n_1 units of weight, q_2 as a join of n_2 units, then there exists a join (q_1, q_2) of the weights which will be measured as a join of $n_1 + n_2$ units. Weight is said to be additive; alternatively it is said to be extensive.

These notions are deeper than the foundations of thermodynamics, for they lie at the basis of the theory of measurement itself. One must, therefore, expect any axiomatic treatment of thermodynamics to lay bare the need for an operation of joining. While the empirical entropies do not necessarily add on joining two systems, the absolute entropies do, and one must discover what axioms make such extensive quantities possible.

To find an extensive energy one may start with a system in 'energetic isolation'. Possible transitions are then restricted to occur between equilibrium states x, y of equal energy. The corresponding relation will still be denoted by R . In this case $xRy \Rightarrow yRx$, and this, together with transitivity, yields an equivalence relation. It enables the states x to be divided into classes as described in section 2 for adiabatic isolation. However, there is no obvious way of ordering these classes of constant energy in a way which corresponds to the ordering of the entropy classes C_x . The new idea here is to consider two equilibrium systems which are joined, energetically isolated from the surroundings, and allowed to interact. Possible transitions in which the first part of the system loses energy (say) are

$$(x_1, x_2) \rightarrow (x'_1, x'_2), (x_1x_2) \rightarrow (x'_1, x'_2), (x_1, x''_2) \rightarrow (x'_1, x''_2), \dots$$

The transition $x_1 \rightarrow x'_1$ of the first part is here used rather like a measuring rod, and this induces an ordering of the equivalence classes of the second part. A metric energy $U(x)$ results if one associates real numbers $U(x)$ with states x such that

$$U(x'_2) - U(x_2) = U(x''_2) - U(x'_2) = \dots\dots\dots$$

It is found that the derivation of a metric and additive variable is possible by this method whenever the variable is subject to a conservation law⁴. It follows that, by confining attention to quasistatic adiabatic processes, when the entropy is conserved, a metric entropy can also be found.

The additivity of the entropy in Giles's method is more troublesome, no doubt due to the fact that he tries to describe the theory and the rules of interpretation in directly experimental terms. The main ideas are:

- (i) One uses states x of systems (not necessarily equilibrium states) which evolve in isolation into other states y : xRy . Adiabatic isolation and equilibrium come much later, so that the partial preorder R has a generalized interpretation.

- (ii) The joining operation acts on *states* rather than systems. Being commutative and associative, it is denoted by $+$. It makes the theory of partially preordered semigroups relevant.
- (iii) The connection between additivity and conservation laws occurs here through components of content (e.g. energy) $Q(x)$ which are defined by

$$Q(x + y) = Q(x) + Q(y)$$

$$xRy \Rightarrow Q(x) = Q(y)$$

- (iv) The connection between additivity and absolute entropy $S(x)$ is defined through the properties

$$S(x + y) = S(x) + S(y)$$

$$xRy \Rightarrow S(x) \leq S(y)$$

- (v) The axioms are sufficient¹⁷ to establish the existence of an absolute entropy and a family $F(Q)$ of components of content such that

$$xRy \Leftrightarrow S(x) \leq S(y) \text{ and } Q(x) = Q(y) \text{ for all } Q \in F(Q).$$

Within this interesting and elegant framework, it has so far proved difficult to add simple axioms¹⁷ which ensure that the set $F(Q)$ is finite and that its members are well behaved. Also the existence of metric variables is established by somewhat complicated procedures^{1, 17} involving components of content. Lastly, there are a few difficulties of interpretation and this can be illustrated by the definition of non-equilibrium state (ref. 1, p 83). Using R to denote a 'natural process' x is a *non-equilibrium* state if a state y exists such that

$$xRy, \text{ and not } (yRx) \tag{5.1}$$

But for any *equilibrium* state x , as normally understood, one can construct a state y , e.g. by withdrawing a partition, so as to satisfy (5.1).

An alternative procedure^{4, 13, 18} for additivity is to put for the absolute entropy $S(x_0) = 0$, $S(x_1) = 1$ for arbitrary states x_0 and x_1 . If one has adequate assumptions concerning joins of systems A_1, A_2, \dots, A_n , i.e. about states (x_1, x_2, \dots, x_n) of such systems, one can require $S(x_1) + S(x_2) = S(x'_1) + S(x'_2)$ if (x_1, x_2) goes over into (x'_1, x'_2) by a quasistatic adiabatic process. Such an equation can be used to identify one unknown entropy value. For example, if (x, x) goes over into (x_1, x_1) in this way, then $S(x) = \frac{1}{2}$. By continuing in this way additivity of the entropy can be established.

6. THEORY OF ELEMENTARY INEQUALITIES

Following quasistatic (or reversible) processes and the attendant additivity of thermodynamic functions (§5), we now return to the general (non-static or irreversible) processes of §§2-4. The important relations to be considered are inequalities. We shall denote functions of specified variables by small letters (x), and variables, when they are not considered as functions, by corresponding capital letters (X). Sets of variables X_1, X_2, \dots will be denoted by vector symbols (\mathbf{X}). The following properties are noteworthy:

(α) Monotonic increase of f with X_1 :

$$[f(X_1', X_2, \dots)] \rho [f(X_1, X_2, \dots)] \Leftrightarrow X_1' \rho X_1 \quad (6.1)$$

where ρ can stand for 'greater than'; it can alternatively stand for 'equal'.

(β) Homogeneity (of degree unity): For all real $a \neq 0$

$$f(a\mathbf{X}) = af(\mathbf{X})$$

(γ_1) Superadditivity and (γ_2) subadditivity :

$$\{f(\mathbf{X} + \mathbf{Y})\} R\{f(\mathbf{X}) + f(\mathbf{Y})\}$$

(δ_1) Concavity and (δ_2) convexity :

$$\{f[\frac{1}{2}(\mathbf{X} + \mathbf{Y})]\} R\{\frac{1}{2}[f(\mathbf{X}) + f(\mathbf{Y})]\}$$

Here R is \geq for (γ_1) and (δ_1) and \leq for (γ_2) and (δ_2).

Assuming (α), it is possible to invert $F = f(X_1, X_2, \dots)$ to yield

$$X_1 = x_1(F, X_2, \dots)$$

so that for all X_2, \dots the function x_1 satisfies

$$F = f[x_1(F, X_2, \dots), X_2, \dots].$$

It can now be shown (see Appendix), on putting the function to which a condition applies in brackets behind it, that

$$\text{given } \left\{ \begin{array}{l} \beta(f) \Leftrightarrow \beta(x_1) \end{array} \right. \quad (6.2)$$

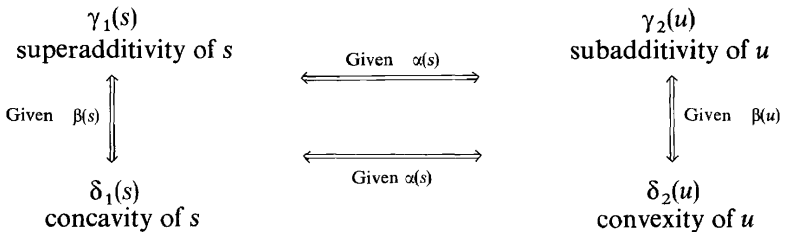
$$\text{(\alpha) as stated } \left\{ \begin{array}{l} \gamma_1(f) \Leftrightarrow \gamma_2(x_1), \gamma_2(f) \Leftrightarrow \gamma_1(x_1) \end{array} \right. \quad (6.3)$$

$$\text{in (6.1) } \left\{ \begin{array}{l} \delta_1(f) \Leftrightarrow \delta_2(x_1), \delta_2(f) \Leftrightarrow \delta_1(x_1) \end{array} \right. \quad (6.4)$$

$$\text{given } \left\{ \begin{array}{l} \gamma_1(f) \Leftrightarrow \delta_1(f) \end{array} \right. \quad (6.5)$$

$$\beta(f) \left\{ \begin{array}{l} \gamma_2(f) \Leftrightarrow \delta_2(f) \end{array} \right. \quad (6.6)$$

Write $S = s(U, V, N)$ for the entropy, so that X_1 becomes the internal energy. The equivalence of certain thermodynamic statements then emerges as follows:



One can with the aid of this scheme again arrive at the continuity of the entropy. Assume from a 'fourth law' (ref. 3, p 142) the homogeneity of the entropy, from a form of the second law the superadditivity of the entropy¹⁹, and from some form of the third law that the entropy is bounded in the interval considered. It then follows:

(i) from the above scheme that the entropy s is concave or $-s$ is convex.

(ii) from the theory of convex functions²⁰ if V and N are fixed then s is continuous in the interval of U , and has right-hand and left-hand derivatives which are decreasing functions of U .

This set of ideas is of importance in presentations of thermodynamics, to be called approach C , in which the existence of an entropy is assumed. An important part of Gibbsian thermodynamics comes under this heading. The inequalities introduced here are also useful in discussing limiting properties of statistical mechanical ensembles²¹.

7. THE ZEROth LAW

If u_K be the thermodynamic variable for a system K , let $F_{12}(u_1, u_2) = 0$ be a relation specifying thermal equilibrium between systems 1 and 2. Then the zeroth law states that any two of the relations

$$F_{12}(u_1, u_2) = 0, F_{23}(u_2, u_3) = 0, F_{31}(u_3, u_1) = 0$$

imply the third (transitivity). It is then inferred that functions $t_j(u_j)$ ($j = 1, 2, 3$) exist such that thermal equilibrium between systems 1 and 2 may be equivalently expressed by

$$t_1(u_1) = t_2(u_2)$$

Such a result assumes certain uniqueness properties of thermal equilibrium (ref. 3, p 11 and ref. 22). Sometimes this caution has not been made explicit, and perhaps scientists can be excused for not always stating that the existence of a thermometer is an assumption (ref. 2, p 373; ref. 3, p 117) in an axiomatic treatment! In fact the following assumption is needed: Suppose that the values of all but one of the variables u_1 are specified. Then for each state of system 2 (for example) there must be a unique value of this remaining variable for which the systems 1 and 2 are in equilibrium.

As an illustration of alternative mathematical situations, let a_{ij} , b_{ij} , be positive numbers, and let

$$F_{ij}(u_i, u_j) \equiv a_{ij}(\theta_i - \theta_j)^2 + b_{ij}(\phi_i - \phi_j)^2$$

It is then true that any two of the equilibrium conditions imply the third but there are now two 'temperatures' since the equilibrium condition for systems 1 and 2 is equivalent to

$$\theta_1 = \theta_2 \text{ and } \phi_1 = \phi_2$$

This example has been suggested by the specification of a line j by the position a_j of a point on it, together with two angles θ_j , ϕ_j in a cartesian coordinate system. The equilibrium condition $F_{ij} = 0$ is then the condition for parallelism of the lines i and j , and transitivity is valid. But a single 'temperature' function is clearly not adequate: there are two such functions θ and ϕ . A system with a built-in adiabatic partition can also have two temperatures.

8. CONCLUSION

Axiomatics does not make new science; this is seen very clearly by the references which were made by Carathéodory⁶ and Giles¹ to relativistic thermodynamics (already in the conventional Planck-Einstein form by 1907).

Table 1. Concepts needed to arrive at an empirical entropy
(√: concept is needed, x: concept is not needed)

Approach	Concepts	Heat $d'Q$	Absolute temperature T	Adiabatic processes and equilibrium states
e.g. Clausius (ca. 1850)		√	√	√
Carathéodory (1909)		x	√	√
Falk and Jung (1959)		x	x	√
Giles (1964)		x	x	x

The criticism of this formulation was to come in the middle sixties from the scientists rather than from the axiomatizers. In spite of the limitations of axiomatics, I tried to show that recent foundations research in thermodynamics is nonetheless of importance to scientists, and of intrinsic interest.

Perhaps it will be illuminating to sum up one aspect of this work by saying that there has been an attempt to decrease the number of basic concepts needed. This is illustrated in Table 1. The axiomatic schemes indicated there, though not yet fully satisfactory, represent considerable advances. That these advances are surprising shows that entropy retains 'an untarnished lustre of novelty and an aura of unplumbed depth'²³. Perhaps its study may lead to more surprises in the future.

It is regretted that space did not permit adequate discussion of otherwise relevant work in which the existence of entropy is assumed²⁴.

APPENDIX

(See also ref. 19.)

In condition (α) substitute as follows:

$$F, X_2, \dots \rightarrow \begin{cases} aF, aX_2, \dots, & \text{if } f \text{ satisfies } (\beta) \\ F' + F'', X'_2 + X''_2, \dots, & \text{if } f \text{ satisfies } (\gamma_1) \\ \frac{1}{2}(F' + F''), \frac{1}{2}(X'_2 + X''_2), \dots, & \text{if } f \text{ satisfies } (\delta_1) \end{cases}$$

In the first case one has from (α) and (β)

$$f[x_1(aF, aX_2, \dots), aX_2, \dots] = aF = af[x_1(F, X_2, \dots), X_2, \dots] \\ = f[ax_1(F, X_2, \dots), aX_2, \dots]$$

whence $x_1(aF, aX_2, \dots) = ax_1(F, X_2, \dots)$

Since one can also argue backwards from the last equation, this yields (6.2). In the second case one has from (α) and (γ_1):

$$f[x_1(F' + F'', X'_2 + X''_2, \dots), X'_2 + X''_2, \dots] \\ = f[x_1(F', X'_2, \dots), X'_2, \dots] + f[x_1(F'', X''_2, \dots), X''_2, \dots] \\ \leq f[x_1(F', X'_2, \dots) + x_1(F'', X''_2, \dots), X'_2 + X''_2, \dots]$$

whence

$$x_1(F' + F'', X'_2 + X''_2, \dots) \leq x_1(F', X'_2, \dots) + x_1(F'', X''_2, \dots).$$

This is part of (6.3). The other relations (6.3), (6.4) are obtained similarly.

Assume next that f satisfies (β) and (γ_1) . Then choosing $a = 2$,

$$f\left[\frac{1}{2}(\mathbf{X} + \mathbf{Y})\right] \geq f\left[\frac{1}{2}(\mathbf{X})\right] + f\left[\frac{1}{2}(\mathbf{Y})\right] = \frac{1}{2}[f(\mathbf{X}) + f(\mathbf{Y})]$$

which is part of (6.5), and the remaining relations are established similarly.

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