Mathematical Foundations of Thermodynamics

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BY

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PREFACE

THIS monograph is an attempt to give an account of the foundations of thermodynamics which is more than usually rigorous, not only in its logical structure but also in the "rules of interpretation" in which physical meaning is assigned to the theoretical terms. It has not been my aim to discuss the applications of thermodynamics; only the fundamentals of the subject are treated, such examples as are discussed being introduced purely for illustrative purposes. Another important aspect of thermodynamics which is not treated in this book is its relation to statistical mechanics. Statistical mechanics provides a mechanical explanation of thermodynamic concepts and it might be supposed that the most logically satisfactory treatment of thermodynamics would be one based on statistical mechanics. However this book offers a formulation of pure thermodynamics, in which no such explanation is contemplated. Several reasons may be advanced in favour of this choice. The first and most cogent reason is the absence of a sufficiently rigorous formulation of statistical mechanics: the concepts of statistical mechanics are much more complex than those of thermodynamics and an axiomatic treatment of the mathematical theory together with an adequate set of rules of interpretation has not yet been developed. In any case, just because it is independent of these more sophisticated concepts, an independent formulation of pure thermodynamics is much better able to exhibit the essential nature of the subject. Moreover it provides a structure which can be at once superimposed on a suitable formulation of statistical mechanics when the latter becomes available.

My concern with thermodynamics originated with a teaching assignment in 1955, and a paper comprising in a condensed form the contents of Chapters 1–4 of this book was sent to Professor E. A. Guggenheim in December 1957. His comments induced me to rewrite the paper and in particular to introduce the concept of a mechanical state (Chapter 5). While doing this I realised that it should be possible to

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make the mathematics involved fully rigorous. This programme, together with the inclusion of a treatment of relativistic thermo-dynamics, resulted eventually in the present book.

The book may appeal to several categories of reader: to physicists who are not entirely satisfied with the logical basis of their subject, to mathematicians who may be interested to discover a novel appli-cation of pure mathematics, and to philosophers who will find here not only a statement of a well-defined philosophical approach to physical theory but the explicit formulation of a theory in accordance with this approach.

I have endeavoured to cater for this mixed readership in two ways. First I have tried to assume in writing each chapter only the minimal knowledge which is essential to the work in hand. Thus, although for a full understanding of the book an honours degree in mathe-matics or physics, preferably including an elementary course in thermodynamics, is desirable, much of the book should be accessible to those without these qualifications. On the other hand there are some sections, notably in the appendixes, which assume a greater maturity.

Secondly, the book is arranged so that it may be read at several levels. A first introduction to the new approach, addressed to the average physicist, will be found in the introduction followed by a summary of the whole book, and a more detailed summary of the work may be obtained by reading the individual chapter summaries at the beginnings of the chapters. For a preliminary but complete account of the whole theory the reader should peruse Chapters 1–6 and Chapter 9; in particular Chapter 1 contains an account of the philosophical approach. A completely rigorous treatment is given olyn in Appendixes A and B, but the motivation and physical signi-ficance of the work presented there is described informally in Chapter 7. Chapters 11–13 are devoted to illustrative examples, and Chapters 14–16 with Appendix C to a development of relativistic thermodynamics which depends eventually on nothing other than the existence of a certain symmetry group.

In carrying out this work I have benefited greatly from discussions with many past and present members of the Natural Philosophy Department at Glasgow University. I should like to mention expecially Dr. W. K. Burton and Dr. G. Wyllie whose constant interest and helpful criticism have been a source of continual encouragement. I am indebted to Professor E. A. Guggenheim for his careful study and

criticism of an early version of the work and to Professor J. C. Gunn for his encouragement and advice. Dr. Burton read the manuscript and the proofs and made many valuable suggestions and corrections. Mr. A. McKerrell devoted much time to a detailed study of the work at proof stage; because of his efforts there are substantially fewer errors and obscurities in the text. To all these people I should like to express my warmest thanks.

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INTRODUCTION

A FAMILIAR way of introducing the concept of absolute temperature in elementary expositions of thermodynamics is through the consideration of a Carnot cycle, in which a reversible heat engine operates between two heat reservoirs at different temperatures. This approach reveals clearly the essential nature of absolute temperature and has immediate physical appeal. The derivation of the concept of entropy, on the other hand, depends on considerations of a mathematically much more sophisticated nature, so that the physical significance of this concept remains initially relatively obscure. However, once the *existence* of entropy has been established it is possible to clarify its physical meaning by showing how a reversible heat engine may be used to measure entropy directly. Thus if we allow the engine to operate between a hot body A and a heat reservoir at, say, 0°C—call this process β—then the loss of entropy of A is proportional to the gain in energy (E calories, say) of the heat reservoir, no matter what the temperature difference between the initial and final states, A_1 and A_2, of A may be.

Indeed we obtain in this way not merely a simple means of measuring entropy changes but the basis of a new way of defining entropy, based on a measure of the "irreversibility" of a natural process. Thus if α denotes the process which consists in the dissipation of mechanical energy in A until its state is changed from A_2 to A_1, and γ a process in which 1 cal of mechanical energy is dissipated in a heat reservoir at 0°C, then α followed by the *reversible* process β, described above, is evidently equivalent in its ultimate effect to the dissipation of E calories in the heat reservoir — a process which may be denoted by $E\gamma$. This leads one to regard α and $E\gamma$ as "equally irreversible" and so to define the *irreversibility* $I(\alpha)$ of α to be E times that of γ. The irreversibility of γ may be assigned arbitrarily. [$I(\gamma) = (1/273)$ cal/deg will yield the customary scales of entropy and temperature.] Having thus defined the irreversibility of each process α of the above type, one can then define entropy in terms of irreversibility in exactly the same way as internal energy is defined in terms of work in the discus-

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sion of the first law of thermodynamics [see, for instance, Pippard (1957) or Zemansky (1957)].

With this approach to entropy it is not necessary to define absolute temperature by means of a Carnot cycle; instead it can be obtained from entropy by a process of differentiation, just as entropy is usually obtained from temperature by integration.

We thus obtain a way of introducing entropy which is physically very satisfying, since it emphasises the essential property of entropy: that its increase measures the irreversibility of a process. However, this approach is not entirely satisfactory from a logical point of view, since it still depends on the qualitative concept of temperature (through the use of a heat reservoir) and also on the possibility of making quantitative comparisons of energy changes (in the measurement of E).

It is possible to overcome both these disadvantages. First observe that β is equivalent in its ultimate effect to α *reversed* followed by $E\gamma$, so that the fact that β can occur may be described by saying that $E\gamma$ can "drive α backwards". Now, let α_1 and α_2 be any two natural processes and suppose that we can tell by experiment whether or not α_1 can drive α_2 backwards. Such an experiment determines whether or not the relation $I(\alpha_1) \geqq I(\alpha_2)$ holds. If it does, we can then test the relation $I(\alpha_1) \geqq 2I(\alpha_2)$ by seeing whether α_1 can drive α_2 backwards *two times in succession*, and so on. In this way it is possible, by a sequence of such experiments, to determine *with arbitrary accuracy* the ratio $I(\alpha_1)/I(\alpha_2)$. If we fix a scale of irreversibility by assigning arbitrarily the irreversibility of a single natural process, then that of every other process can be determined by experiment. We can then proceed to derive the concepts of entropy and temperature in the same way as before.

The virtue of this approach to entropy is not only that it is independent of the concepts of temperature and energy, but that it is actually independent of any quantitative concepts at all. For it presents the measurement of entropy as resulting from a sequence of experiments of a qualitative nature, the result of each experiment being simply *yes* or *no*.

It is natural, having obtained such a direct approach to entropy involving only concepts of a qualitative nature, to ask whether it would not be possible to give a similar treatment of the concept of energy. Such a treatment would presumably be applicable to other "conserved" quantities also, among which we may consider, in particular, *inertial mass*.

This particular example has been discussed by Weyl [Weyl (1949), § 19] who presents it as the prototype of a general process of measurement. For the measurement of mass, he observes, two properties alone suffice. First, a method of *qualitative comparison* or *ordering:* if two bodies moving in opposite directions with equal speeds collide and adhere, then the body whose direction of motion is unchanged has the greater mass; secondly, a process of *addition:* if two bodies are united, the mass of the whole is the sum of the masses of the parts. Thus, granted these two possibilities, we may compare quantitatively the masses of two bodies A and B by making, for an increasing sequence of values of m and n, a qualitative comparison of the mass of mA (an object made by uniting m replicas of A) with that of nB.

That this description of the measurement process does not only apply to mass can be seen by considering other examples. Thus it is possible to *weigh* accurately even with a bad (i.e. non-linear) spring balance, provided only that the moving parts do not stick: the *ordering* of weights is here determined by the pointer readings, the process of *addition* is provided by placing together on the scale-pan the two bodies concerned. Similarly, we can measure the *duration* of an event— for instance, the swing of a pendulum—in virtue of the fact that we can qualitatively *compare* durations (by initiating the two events together and observing which is completed first) and *add* durations (the sum of the durations of two events being that of the event which is obtained by causing the two to occur consecutively). For example, to compare the periods of two pendulums we might note that m swings of the first had a duration between that of n and $n + 1$ swings of the second, making an observation of this type for an increasing sequence of values of m. Lastly, it is significant that even the method of measuring *irreversibility*, described above, illustrates the same principle: we can qualitatively *compare* irreversibilities by seeing which of two processes will drive the other backwards; and we can *add* irreversibilities, the sum of the irreversibilities of two natural processes being that of a process which consists of the two occurring consecutively.

With these thoughts in mind let us now return to the question of the measurement of *energy.* We observe that the objects to which we wish to assign an energy are *systems,* or, more precisely, *states* of systems. We are thus led to consider whether there exists, in the set $\mathscr{S}$ of all states of all systems, (a) a process of *addition,* and (b) a relation of *order.* But this is indeed the case: we can consider the *sum* of two states a and b of systems A and B to be the state obtained by

taking A and B together as a single system and supposing the two
parts of this system to be in the states a and b respectively; and
we can regard a state a as being *greater than* a state b if a is the
sum of b and some other state c. (Notice that this relation of order is
not a new concept but is *derived* from the process of addition.) The
only essential difference between this case and the previous examples
is that the relation "greater than" is not a "simple ordering" but
only a "partial ordering": that is to say, it can be that, given two
states a and b, neither of the relations "a is greater than b" and "b is
greater than a" holds. It turns out, however, that, as in the case of
simple ordering, a real-valued quantity Q can still be defined which
(a) is determined by the concepts of order and addition alone, (b) is
additive when states are added, and (c) has the property that whenever
a state a is greater than a state b then $Q(a) > Q(b)$. But this quantity
is no longer unique; indeed, there exists a whole set of such quantities.
However, this is just what we require: for, in general, energy is not
the only conserved quantity; for instance, the amounts of a number
of "chemical species" may well also be present as additive and con-
served quantities.

Taking these considerations together with the earlier remarks on
irreversibility, we come to recognise the possibility of defining con-
structively an entropy function and a set of conserved quantities (like
energy)—which we shall call *components of content*—in terms of
just two purely qualitative concepts: first, the operation of forming
the sum $a + b$ of two states a and b (from which we can *derive* the
procedure for adding processes); and secondly, the property of a
process of being natural, or, which is the same thing, the relation
between two states a and b that there exists a natural process leading
from a to b—we denote this relation by $a \rightarrow b$.

Naturally, the implementation of this programme will be possible
only if certain conditions are satisfied. The appropriate form for these
conditions is by no means evident, but it is clear that, in any case, they
can involve only the operation of addition of states and the relation $\rightarrow$
between states, for the derivation of entropy and components of con-
tent is to be effected by experiments which refer to these concepts
alone.

What one must do, then, is to seek a set of conditions which on the
one hand are physically acceptable and on the other hand lead, in
the above way, to the existence of entropy and "sufficiently many"
components of content. This task can be simplified by first writing

down such properties of + and → as appear physically obvious. (For instance, it is clear that addition of states is associative and commutative.) Then, by exploring the consequences of these conditions, one can discover in what respects they are inadequate, and add further conditions to make up the deficiencies.

When a suitable set of conditions has been obtained, the final theory can, if desired, be presented as follows. First, taking the chosen set of conditions as *axioms*, one develops a purely mathematical theory in which the terms *state*, +, →, *entropy*, *component of content*, and so on, appear as mathematical objects *without any physical connotations*. One can then attach to this exposition a "text" explaining the physical meaning which is to be assigned to the various terms employed. In principle, it is sufficient that the text should assign meanings only to the *primitive* terms *state*, +, and →, for every other term in the theory is derived from these, its physical meaning being thus determined by its definition. Such a formulation presents thermodynamics as *the science of "state"*, +, *and* → : that is, it shows thermodynamics to consist exactly of those assertions which have an experimental meaning for an observer who can appreciate, in the physical world, only these three concepts. We call such an observer a *primitive observer* for thermodynamics.

The fulfilment of this programme is our ultimate goal in this book. Chapter 1 begins with an analysis of the conditions which should be satisfied by a "good" physical theory. This analysis is necessary in order to justify the claim that a treatment of thermodynamics on the above lines is "more satisfactory" than previous formulations of the subject. Following this, the primitive concepts (state, +, and →) on which the theory is based are introduced and *rules of interpretation* for these concepts are given. The chapter concludes with the introduction of a provisional set of axioms expressed in terms of these concepts alone.

In Chapters 2–6 the consequences of these axioms are derived, following the lines explained above. The work culminates in the following theorem (Theorem 6.2.3):

There exists an additive function of state S, called the entropy, and a set of additive functions of state, called components of content, such that, for any states a and b, a → b if and only if $S(a) \leq S(b)$ and $Q(a) = Q(b)$ for every component of content Q.

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This theorem shows that all the information obtained in the (quali-
tative) experiments of a primitive observer can be expressed in quanti-
tative terms: namely, in terms of the values of the entropy and of the
components of content for the various states concerned.

However, all is not well: in Chapter 7 it is shown by examples that
the definitions of "entropy" and "component of content" admit, as
well as the desired quantities, certain functions which are, in a physical
sense, so "discontinuous" that no physicist would accept them. An
analysis of the situation suggests certain modifications in the axioms,
through which a satisfactory form of the theory is obtained.

In Chapter 8 the situation is consolidated and the way prepared
for further work. It is shown how the states can be conveniently
"plotted" in a "thermodynamic space" in which the components of
content and the entropy serve as coordinates; and we study, in particular,
the special case (which always arises in practice) in which this space is
finite-dimensional. The chapter concludes with a commentary, addressed
to the mathematician, on some mathematical aspects of the theory.

It was pointed out, earlier in this introduction, how, given the con-
cepts of entropy and energy, one can define absolute temperature.
In the general theory it is not possible to do exactly this, since there
is no way of distinguishing any particular component of content as
the energy. (Such a distinction can be made only by reference to the
properties of a particular system. See Chapters 11 and 12.) But we can
define a set of quantities, called *components of potential*, which play
roughly the same part for the various components of content as tempe-
rature does for energy. This is done in Chapter 9, but only with the
aid of certain *ad hoc* assumptions of the nature of "differentiability".
In Chapter 10, however, it is shown that it is possible to proceed, to
a considerable extent, without any such assumptions.

In the next three chapters we discuss a number of examples which
illustrate the application of the theory in some typical cases. Our pur-
pose here is to demonstrate clearly that these are indeed special cases
of the above theory and, in particular, to show explicitly that the
thermodynamic properties of such systems could in fact be determined
experimentally by a primitive observer. These chapters also serve to
clarify the physical significance of certain new theoretical concepts
which have been introduced. Chapter 13 concludes by showing why
a system which exhibits *hysteresis* is not amenable to treatment by
classical thermodynamics: in such a case one of the axioms is not
satisfied.

The remaining three chapters of the book stand rather apart. They are concerned with the effect of *symmetry* in a thermodynamic system. The consequences of symmetry in mechanics, and, in particular, in quantum mechanics, have been much studied, and group-theoretic methods, which are the mathematical embodiment of symmetry, form one of the most important tools in modern quantum theory. But the consequences of symmetry in thermodynamics have received little attention. The abstract nature of our formulation of thermodynamics makes it ideally suited for such an analysis. Our principal aim, which is carried through in Chapter 16, is the study of the thermodynamic consequences of the symmetry imposed by special relativity. As a preparation for this we consider first (Chapter 14) the thermodynamics of systems which move in accordance with Newtonian mechanics, showing, for example, that a system in equilibrium rotates uniformly as a rigid body. In this discussion we appeal, from time to time, to Euclidean geometry and classical mechanics.

In Chapter 15 a rigorous general treatment of symmetry is initiated. We first prove that the assumption of a set of equivalent observers implies the existence of an abstract *symmetry group* $\mathscr{G}$, and show how an observer can determine the nature of this symmetry group by a method which depends only on the possibility of communication between the observers. We then consider the thermodynamic implications of symmetry, showing that they can all be expressed in terms of a certain *representation* of $\mathscr{G}$.

In Chapter 16 the particular case in which $\mathscr{G}$ is the symmetry group of special relativity (the inhomogeneous Lorentz group) is treated in detail. We obtain results similar to those applying in the Newtonian case. Again, a centre of mass, which moves uniformly, can be defined, and it can be shown that a system in equilibrium rotates uniformly "as a rigid body" in a precisely defined sense. The concept of temperature can be defined *locally* in such a rotating system, but the temperature is no longer uniform; it increases with distance from the axis. These results are of some interest for their own sake, but what is of principal importance is that *their derivation is entirely independent of geometry and mechanics*; all the concepts involved are defined in purely thermodynamic terms: that is, ultimately in terms of the primitive concepts "state", $+$, and $\rightarrow$ alone.

There are three appendixes. Appendix A consists of a concise formal presentation of the mathematical part of the new formulation of thermodynamics. Apart from establishing various theorems which

are quoted without proof in the body of the book, its function is to demonstrate explicitly the complete separation of mathematics and physics which is achieved in this formulation. Some mathematical results needed in this appendix are derived in Appendix B.

Appendix C is an addendum to Chapters 15 and 16. In these chapters it was shown that the thermodynamic effect of a symmetry group $\mathscr{G}$ could be expressed in terms of a real representation of $\mathscr{G}$. In Appendix C it is shown, by reference to the principles of quantum mechanics, that this representation is not arbitrary, being in a sense uniquely determined by the abstract group $\mathscr{G}$ itself.