

**THERMODYNAMICS, AN
INTRODUCTORY TREATISE
DEALING
MAINLY WITH FIRST PRINCIPLES
AND THEIR DIRECT APPLICATIONS**

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Thermodynamics, an introductory treatise dealing mainly with first principles and their direct applications by G. H. Bryan

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G. H. BRYAN

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B. G. TEUBNERS SAMMLUNG VON LEHRBÜCHERN
AUF DEM GEBIETE DER
MATHEMATISCHEN WISSENSCHAFTEN
MIT EINSCHLUSZ IHRER ANWENDUNGEN.
BAND XXI.

THERMODYNAMICS

AN INTRODUCTORY TREATISE DEALING MAINLY WITH
FIRST PRINCIPLES AND THEIR DIRECT APPLICATIONS

BY

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PREFACE.

When I accepted an invitation to write the article for the *Encyclopædic* on the General Foundations of Thermodynamics, it was understood that the article should deal, as far as possible, exclusively with the laws of thermodynamics and consequences immediately deducible from them, and that all properties of particular substances and states which depended partially on experimental knowledge or other hypotheses should be left for another article. I had long felt the want of a book in which thermodynamics was treated by purely deductive methods, and it has been my object in the following pages to develop the subject still more on this line than was possible in an article professing to be to some extent an exposition of the history and actual state of knowledge of the subject.

It cannot be denied that the perfection which the study of ordinary dynamics has attained is largely due to the number of books that have been written on *rational* dynamics in which the consequences of the laws of motion have been studied from a purely deductive stand-point. This method in no way obviates the necessity of having books on experimental mechanics, but it has enabled people to discriminate clearly between results of experiment and the consequences of mathematical reasoning. It is maintained by many people (rightly or wrongly) that in studying any branch of mathematical physics, theoretical and experimental methods should be studied simultaneously. It is however very important that the two different modes of treatment should be kept carefully apart and if possible *studied from different books*, and this is particularly important in a subject like thermodynamics.

In most text books the treatment of the first and second laws is based more or less on the historic order, according to which a considerable knowledge of the phenomena depending on heat and temperature preceded the identification of these phenomena with energy-transformations. For a logical order of treatment it is better to regard the laws of thermodynamics as affording definitions of heat and temperature, just as Newton's laws afford definitions (so far as definitions are possible) of force and mass. But in any case there is great danger of assuming some property of temperature without realising that an assumption has been made, and of this danger we have an excellent illustration in the assumption commonly made, but rarely if ever explicitly stated, that the temperature of a body at any point is the same in all directions.

To lessen such risks and at the same time to carry the deductive method further back it appeared to me desirable to adopt the principles of conservation and degradation of energy as the fundamental laws of

thermodynamics, and to deduce the ordinary forms of these laws from those principles. A paper was published by me on this subject in the Boltzmann *Festschrift*, and some criticisms on it sent to me by Mr. Burbury have led to a more extended examination of the foundations upon which thermodynamics rests. Degradation of energy in some form or other is a necessary consequence of *irreversibility* of energy phenomena. We therefore go still further back and assume the principle of irreversibility as our starting point. When an irreversible transformation takes place the number of subsequent possible transformations is thereby from the very nature of the case reduced and we thus have a *loss of availability* in its most general sense. When we want to identify the more and less available forms of energy with those forms of energy which we see around us, an appeal to experience is necessary. It is in fact possible to conceive a universe in which irreversible phenomena tend in a different direction to what they do in our own. A mere reversal of the whole of the phenomena of our universe would give us one example, and if we want another we should only have to imagine ourselves of molecular dimensions when we should find that the whole progress of irreversible phenomena (whether regarded statistically or otherwise) would assume an entirely different aspect to that to which we are accustomed. The laws of thermodynamics are thus restricted to phenomena of a *particular size* in the scale of nature, and the lower limit of size is about the same as the limit involved in the applications of the infinitesimal calculus to the physical properties of material bodies e. g. in hydrodynamics, elasticity and so forth. The term "differential element" is introduced in the present book to represent the smallest element which can be regarded, for the purpose of these applications, as being formed of a continuous distribution of matter, and the notion of temperature *at a point* is regarded as not more nor less justifiable than the corresponding conventions as to pressure and density at a point.

It is, however, in connection with entropy and with thermodynamic equilibria and stability, that the present method of treatment is found to be the most advantageous. A controversy on entropy between English mathematicians, physicists and electrical and other engineers took place in England in 1903 at the instigation of Mr. Swinburne, an electrical engineer, who defined entropy by means of what he called "incurred waste". In the present book it is shown that if entropy be defined in terms of increase of unavailable energy this definition will apply not only in the case of entropy imparted to a system by heat conduction but also in the case of entropy produced by the irreversible changes within a system, of which a number of simple illustrations are given.

Moreover the available energy method possesses considerable advantages in the treatment of thermodynamical equilibria. If we assume that in a state of equilibrium the available energy of a system is a minimum it follows immediately that the conditions of equilibrium can be deduced from the equations of reversible thermodynamics and that it is only when the stability of the equilibrium is discussed that recourse must be had to the inequalities of irreversible thermodynamics.

The old and defunct caloric theory has left us an inheritance in the terms "heat" and "quantity of heat" the vagueness of which does much to cause confusion in the study of thermodynamics. The quantity of heat which one body receives from or imparts to another is a perfectly definite conception, and throughout this book the symbols dQ and dq refer to this quantity of heat thus received from without by a whole body or system and a unit mass respectively. It was my original intention not to consider any other kind of quantity of heat. But there are many intrinsically irreversible phenomena of common experience such as the flow of viscous liquids, in which it is usual to regard work as being converted into heat in the interior of a system, moreover in many such cases it is possible to assign a perfectly definite meaning to the "quantity of heat" so generated. It appeared desirable for several reasons to discuss examples of such transformations at some length and in these examples the so-called quantity of heat generated internally by the irreversible transformation of work has been denoted by dH or dh , and the total quantity of heat gained, according to this stand-point viz. $dQ + dH$ for the entire system or $dq + dh$ for unit mass, has been denoted respectively by $d\Omega$ or dq . This convention sometimes enables the increase of entropy to be put into the form of $d\Omega/T$ or dq/T when the expressions dQ/T and dq/T are inapplicable.

Into the difficulties connected with the extension of thermodynamic formulæ to irreversible processes, some insight is afforded notably at the end of Chapter XI. Even the simple statement that we may put $dq = l_e dv + \gamma_e dT$ cannot be admitted without due reserve when irreversible changes are taken into account. The method of treatment given in the section referred to is not the only one that could be proposed and it may be said with considerable justification that the truth or otherwise of any proposed formula in irreversible thermodynamics depends largely on the particular interpretation which is assigned to the symbols in that formula. In the controversy of English engineers on entropy already referred to much importance was attached to the question whether dQ/T did or did not always represent the change of entropy, and from what we have said either party had considerable justification for believing himself to be right according to his own particular interpretation of dQ .

A few words must be said as to the order of treatment in this book, as this is a very important point. The deductive method here proposed is not started till Part II (Chapter IV). This chapter might well be taken as the starting point of a course of lectures given to a class of students who are already familiar with the elements of thermodynamics, and it was my original intention to place it at the beginning of the book. But it appeared that the necessarily somewhat philosophical discussion of Chapters IV—VIII hardly made a sufficiently easy starting point for a beginner, and moreover it is important in building up a theory that the main facts for which that theory has to account should be prominently borne in mind. Accordingly Chapters I, II contain a general sketch of the most important facts and definitions of thermodynamics as based on experience; Chapter I containing definitions of the

principal thermal magnitudes, such as specific heat and latent heat, and Chapter II containing a brief summary of the conventional or "classical" treatment of the first and second laws. In these chapters no attempt has been made to define heat and temperature, or to aim at anything like a complete or rigorous discussion. Chapter III contains the matter included in my *Encyklopädie* article under the heading "Change of the Independent Variable". It was difficult to find a suitable place for this subject matter in any sequence but its present position was chosen as the best. The formulae there discussed are immediate deductions from the principles of the differential calculus, which are in no way dependent on the dynamical theory of heat; they would be equally true on the old caloric hypothesis; and for this reason they would be out of place in Part II. It is important that such formulae should be kept apart from formulae which are properly described as thermodynamical. The formulae of Chapter III are not practically required before Chapter XI.

In Part III, which deals with particular systems, the discussions are confined as far as possible to direct consequences of the principles of Thermodynamics.

Mr. Ferguson, B. Sc. has kindly assisted in revising the manuscript and proofs.

July 1906.

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