TREATISE

ON

THERMODYNAMICS

BY

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TRANSLATED WITH THE AUTHOR'S SANCTION

BY

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Translator's Notice

The modern developments of Thermodynamics, and the applications to physical and chemical problems, have become so important, that I have ventured to translate Professor Planck's book, which presents the whole subject from a uniform point of view.

A few noes have been added to the present English edition by Professor Planck. He has not found it necessary to change the original text in any way.

To bring the notation into conformity with the usual English notation, several symbols have been changed. This has been done with the author's sanction. Here I have followed J. J. van Laar and taken Ψ to signify what he calls the *Planck'sches Potential, i.e.* the thermodynamic potential of Gibbs and Duhem divided by $-\theta$.

Professor Planck's recent paper, "Über die Grundlage der Lösungstheorie" (Ann. d. Phys. **10**, p. 436, 1903), ought to be read in connection with his thermodynamical theory of solution.

I am indebted to Herren Veit & Co., Leipzig, for kindly supplying the blocks of the five figures in the text.

A. O.

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Preface

The oft-repeated requests either to publish my collected papers on Thermodynamics, or to work them up into a comprehensive treatise, first suggested the writing of this book. Although the first paln would have been the simpler, especially as I found no occasion to make any important changes in the line of thought of my original papers, yet I decided to rewrite the whole subject-matter, with the intention of giving at greater length, and with more detail, certain general considerations and demonstrations too concisely expressed in these papers. My chief reason, however, was that an opportunity was thus offered of presenting the entire field of Thermodynamics from a uniform point of view. This, to be sure, deprives the work of the character of an original contribution to science, and stamps it rather as an introductory text-book on Thermodynamics for students who have taken elementary courses in Physics and Chemistry, and are familiar with the elements of the Differential and Integral Calculus.

Still, I do not think that this book will entirely supersede my former publications on the same subject. Apart from the fact that these contain, in a sense, a more original presentation, there may be found in them a number of details expended at greater length than seemed advisable in the more comprehensive treatment here required. To enable the reader to revert in particular cases to the original form for comparison, a list of my publications on Thermodynamics has been appended, with a reference in each case to the section of the book which deals with the same point.

The numerical values in the examples, which have been worked, as applications of the theory, have, almost all of them, been taken from the original papers; only a few, that have been determined by frequent measurement, have been taken from the tables in Kohlrausch's "Leitfaden der praktischen Physik." It should be emphasized, however, that the numbers used, notwithstanding the care taken, have not undergone the same amount of critical sifting as the more general propositions and deductions.

Three distinct methods of investigations may be clearly recognized in the previous development of Thermodynamics. The first penetrates deepest into the nature of the processes considered, and, were it possible to carry it out exactly, would be designated as the most perfect. Heat, according to it, is due to the definite motions of the chemical molecules and atoms considered as distinct masses, which in the case of gases possess comparatively simple properties, but in the case of solids and liquids can be only very roughly sketched. This kinetic theory, founded by Joule, Waterston, Krönig and Clausius, has been greatly extended mainly by Maxwell and Boltzmann. Obstacles, at present unsumountable, however, seem to stand in the way of its further progress. These are due not only to the highly complicated mathematical treatment, but principally to essential difficulties, not to be discusses here, in the mechanical interpretation of the fundamental principles of Thermodynamics.

Sich difficulties are avoided by the second method, developed by Helmholtz. It confines itself to the most important hypothesis of the mechanical theory of heat, that heat is due to motion, but refuses on principle to specialize as to the character of this motion. This is a safer point of view than the first, and philosophically quite as satisfactory as the mechanical interpretation of naure in general, but it does not as yet offer a foundation of sufficient breadth upon which to build a detailed theory. Starting from this point of view, all that can be obtrained is the verification of some general laws which have already been deduced in other ways direct from experience.

A third treatment of Thermodynamics has hitherto proved the most fruitful. This method is distinct from the other two, in that it does not advance the mechanical theory of heat, but, keeping aloof from definite assumptions as to its nature, starts direct from a few very general empirical facts, mainly the two fundamental principles of Thermodynamics. From these, by pure logical reasoning, a large number of new physical and chemical laws are deduced, which are capable of extensive application, and have hitherto stood the test without exception.

This last, more inductive, treatment, which is used exclusively in this book, corresponds best to the present state of the science. It cannot be considered as final, however, but may have in time to yeild to a mechanical, or perhaps an electromagnetic theory. Although it may be of advantage for a time to consider the activities of nature–Heat, Motion, Electricity, etc.–as different in quality, and to suppress the question as to their common nature, still our aspiration after a uniform theory of nature, on a mechanical basis or otherwise, which has derived such powerful encouragement from the discovery of the principle of the conservation of energy, can never by permanetly repressed. Even at the present day, a recession from the

assumption that all physical phenomena are of a common nature would be tantamount to renouncing the comprehension of a number of recognized laws of interaction between different spheres of natural phenomena. Of course, even then, the result s we have deduced from the two laws of Thermodynamics would not be invalidated, but these two laws would not be introduced as independent, but would be deduced from other more general propositions. At present, however, no probable limit can be set to the time which it will take to reach this goal.

<div align="right">THE AUTHOR.</div>

BERLIN,

   April, 1897

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Part I

Fundamental Facts and Definitions

Chapter 1. Temperature

§1. The conception of "heat" arises from that particular sensation of warmth or coldness which is immediately experienced on touching a body. This direct sensation, however, furnishes no quantitative scientific measure of a body's state with regard to heat; it yeilds only qualitative results, which vary according to external circumstances. For quantitative purposes we utilize the change of volume which takes place in all bodies when heated under constant pressure, for this admits of exact measurement. Heating produces in most substances an increase of volume, and thus we can tell whether a body gets hotter or colder, not merely by the sense of touch, but also by a purely mechanical observation affording a much greater degree of accuracy. We can also tell accurately when a body assumes a former state of heat.

§2. If two bodies, one of which feels warmer than the other, be brought together (for example, a piece of heated metal and cold water), it is invariably found that the hotter body is cooled, and the colder one is heated up to a certain point, and then all change ceases. The two bodies are then said to be in *thermal equilibrium*. Experience shows that such a state of equilibrium finally sets in, not only when two, but also when any number of differntly heated bodies are brought into mutual contact. From this follows the important proposition: *If a body, A, be in thermal equilibrium with two other bodies, B and C, then B and C are in thermal equilibrium with one another.** For, if we bring A, B, $andC$ together so that each touches the other two, then, according to our supposition, there will be equilibrium at the points of contact AB and AC, and, therefore, also at the contact BC. If it were not so, no general thermal equilibrium would be possible, which is contrary to experience.

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*As is well known, there exists no corresponding proposition for electrical equilibrium. For if we join together the substances Cu|CuSO$_4$aq.|ZnSO$_4$aq.|Zn to form a conducting ring, no electrical equilibrium is possible.