

Heat, Thermodynamics, and Statistical Physics

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Heat,
Thermodynamics,
and
Statistical Physics

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Preface

This text is intended for junior or senior students interested in physics, chemistry, and engineering. The aim is to provide a background of the experimental as well as the theoretical growth of the study of the thermal properties of matter. During long experience in teaching thermodynamics, the author has become more and more impressed with the desirability of integrating the study of matter in bulk (thermodynamics) with an introduction to the molecular, or statistical, study of matter (statistical physics). The present work has grown out of a senior year's course devoted to such a program. It is, of course, necessary to develop the bulk view first, to the point where the student begins to think in this new (and often rather baffling) way. However, a great deal of the beauty and power of the subject is lost if it is not followed immediately by the molecular approach, with all the insight it gives into the problems discussed.

In general, then, the first fourteen chapters of this book deal with thermodynamics, and the remaining five with statistical physics. The role of entropy, a central one, serves as a major link between the two concepts. Many, for example, will wish to follow Chapter 9 (on entropy) with Chapter 15 (on entropy and probability).

The chapters on thermodynamics pay particular attention to the question of independent variables and their proper selection, introducing and applying extensively a Jacobian scheme for systems of two or more variables, and emphasize thermodynamic methods and the use of curve differentials in the treatment of heat and work. The chapters on statistical physics are concerned with kinetic theory, statistical mechanics, the uses of statistical physics in determining thermodynamic functions, and various applications. Throughout, the author defines both heat and work added to a system as *positive*. Although thermodynamics arose from the historic interest in engines as sources of external work, the usual convention is almost as confusing and unnecessary as calling paper money positive and coins negative in preparing a bank balance.

The examination of such large topics as thermodynamics and statistical physics puts great strain on any notation. Even with upper-case, lower-case,

and script letters, the combined Latin and Greek alphabets are inadequate. It has accordingly been expedient, but without undue violence to long-established conventions in mechanics and atomic and molecular spectroscopy, to present many symbols in multiple contexts. Thus, to mention only one case, the overworked S does duty for entropy, the S state, and the total spin quantum number of the atom. Subscripts and superscripts make many symbols self-explanatory and therefore prevent ambiguity.

Although this book is designed for a year's course, it can readily be adapted to a semester's course by suitable omissions and curtailment. For a one-semester course, the author suggests the following chapters: 1, 2 (Secs. 2.1 to 2.9), 4, 5, 6 (with the omission of Sec. 6.8 through 6.11), 7 (Secs. 7.1 to 7.11), 8, 9, 11, 12, 15, and as much of 16 and 17 as time permits. Conceivably a class might cover 60% of the text in one semester.

The author owes much to the standard works on thermodynamics, especially the books of Epstein, Roberts and Miller, and Zemansky in thermodynamics and of Mayer and Mayer and Fowler and Guggenheim in statistical mechanics. It is a pleasure to express thanks to my wife, who typed the entire manuscript and helped prepare the drawings, and without whose efforts the book might never have been completed. My colleague David Park read several of the later chapters and gave excellent criticism and advice. The staff of the library of Williams College was most helpful in locating hard-to-find journals. Last but not least, the author is grateful to the President and Trustees of Williams College for granting a sabbatical leave that enabled him to finish the manuscript at this date.

FRANZO H. CRAWFORD

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The subject of thermodynamics, which is concerned with the study of heat, energy, and the relations between them, is a branch of physics. It is based on the fundamental laws of mass, energy, and entropy. The first of these is due largely to the efforts of James Prescott Joule (1818-1889) and James Joule (1818-1889). The second is due to the contributions of Rudolf Clausius (1822-1888) and Hermann von Helmholtz (1821-1894). It is generally a special formulation of the law of the conservation of energy. The second law derives from the work of Rudolf Clausius (1822-1888), Auguste Comte (1822-1889), and Lord Kelvin (1824-1907). Although it has many formulations, it deals primarily with the nature of heat as the conversion of heat into work.

There have been many developments in the study of these laws and generally of these laws have been very rapidly extended. The first and second laws, in particular, have an increasing number of applications throughout the subjects of physics and chemistry. They deal with applications not only to the study of steam engines and turbines but also to the study of jets and rockets. They have not only the high-velocity aerodynamics and the general theory of rockets and jets but also in the wide field of the production and study of very low temperatures. Other applications include the theory of electric cells, thermodynamic processes, the study of gas mixtures, and heat conduction. The understanding of these and many other subjects of chemical engineering theories depends on the use and interpretation of these laws.

1.2 Large-Scale or Macroscopic View

The two basic laws of thermodynamics are primarily empirical laws. Their truth depends on direct observation of the macroscopic behavior of matter which is subject to various experiments and processes. These processes deal with the properties of macroscopic systems such as volume, length, pressure, and