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.

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