A COURSE IN THERMODYNAMICS

Revised Printing

VOLUME I

Joseph Kestin

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BROWN UNIVERSITY

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Preface to the Revised Printing

THESE TWO VOLUMES (originally published by Blaisdell Publishing Company in 1966 and 1968) have met with, to me, very satisfactory reviews. However, my earlier hopes that the books could be used "to introduce the novice into the subject" have not been fulfilled. My professional colleagues tell me that the intensity of effort required on the part of young undergraduates to follow this course and, more importantly, the length of time needed for it cannot be fitted into the curriculum. The trend, clearly visible in the early sixties, toward wider and deeper coverage of the fundamental subjects has by now reversed itself and the tendency is to be selective as well as economical of time. On the other hand, I received information from many sides to the effect that the "Course" has found acceptance as supplementary reading and as a basis for a variety of courses for graduate students.

The present is a straightforward reprint of the original version with as many printing errors corrected as my generous readers and I could spot over the years. And the problems for Volume I, originally published as a separate booklet, have been included in the volume itself. If I had to write a new book at this stage, I would probably compress the contents and remove the chapters on statistical thermodynamics (now revised and expanded into *A Course in Statistical Thermodynamics*, written with J. R. Dorfman and published by Academic Press in 1971), giving increased emphasis to irreversible processes, especially those in continuous systems. It is gratifying to me that the two concepts whose importance is being increasingly recognized, namely that of an accompanying equilibrium state (called "local state" and introduced on page 211 of Volume I) and of entropy production (first defined in an elementary though rigorous way on page 587 of Volume I) are fully covered, and that the relation between entropy production and dissipation (also called work "lost") is both recognized and used fully throughout, and particularly in Chapter 24 of Volume II on irreversible processes.

Due to a concatenation of circumstances beyond my control, these two volumes have not been easily accessible to potential readers for some time. I am, therefore, grateful to the publishers and in particular to Mr. W. Begell, president of Hemisphere Publishing Corporation, for his efforts on my behalf and for his generous decision to reprint both volumes.

J. KESTIN

Preface

IN RECENT YEARS, it has become customary to apologize for presenting the academic community with a new book on thermodynamics. The number of new textbooks on this subject has indeed been great and I, like my predecessors, feel that I must justify my efforts to my readers by the hope that I succeeded in anticipating and in answering questions which have not been anticipated and answered elsewhere.

The purpose of this book is frankly pedagogical, and I would like to think that it can be used to introduce the novice into the subject and to accompany him to a point when he feels that he understands the foundations and has acquired an appreciation of its power, its universality as well as of its limitations. Although it endeavors to speak to beginners, it makes no concessions as far as rigor is concerned and attempts to preserve a logical deductive sequence.

The education of engineers has undergone a deep transformation during the last decade, and it is, therefore, understandable that present-day textbooks must differ radically from those of the quite recent past. The scientific basis of this education has broadened, and more importance is attached to depth of understanding. The education of a modern engineer no longer proceeds along several clearly demarcated and isolated grooves, but aims at presenting the scientific basis of engineering in as unified a way as may be possible. Much public discussion has been spent on the desirable extent of courses in thermodynamics, on the role of statistical concepts in it and on the desirability of introducing the study of irreversible processes in continuous systems. The present book contains the author's views on these controversial topics in a detailed manner. In fact, so much detail has been given that it was found necessary to split the work into two volumes, of which this is the first, it being hoped that the sequel can be put into the hands of the reader with a minimum of delay.

The textbook has not been designed for a specific course of well-defined duration. Rather, it attempts to set out the experimental basis of the subject of classical thermodynamics and the generalizations which can be formulated from it in a connected way. I would like to think that I successfully avoided circular arguments as well as non sequiturs, and that I reduced anticipatory statements to a minimum. In addition, an attempt has been made to demonstrate the wide applicability of thermodynamics to a multitude of systems, emphasis being placed on the fact that the study is not restricted to systems characterized by only two independent parameters of state. Chapters 7 and 8 provide the necessary descriptive background for a physical understanding of a variety of systems, starting with the conventional pure substances, inclusive of heterogeneous systems and mixtures, galvanic and fuel cells, and so on. Beyond this, special attention is devoted to solid rods stressed elastically as well as plastically including the phenomena of creep and relaxation, and to interactions which occur through the intervention of gravitational, electrostatic, and magnetostatic fields. It is believed that the latter topics have received a more thorough treatment on an elementary level than has been available hitherto. In this manner, I hope to establish in the students' minds a clear link between thermodynamics and the parts of the curriculum which deal with mechanics, fluid mechanics, solid mechanics, and electromagnetic theory. In particular, the study of pure substances includes the often unappreciated limiting case of a gas whose properties are approximated by those of an incompressible fluid. These two chapters somewhat disrupt the continuity in the exposition of the Zeroth, First, and Second Laws of thermodynamics, but I have decided to tolerate the interruption in order to furnish the student with a set of clear physical ideas for future use.

Chapter 1 devotes a good deal of space to the study of systems of units and dimensions, it being recognized that an ability to work with a large variety of them is essential in our times. Although the MKSA system of units is favored, the view is taken that the use of quantity equations makes it unnecessary to work with a narrowly defined set of units and to become enmeshed in it.

The study of temperature, energy, and entropy with the aid of the three laws of thermodynamics is based on the mathematical properties of differential forms, and interpretations in terms of vector fields are used freely, because most contemporary students of engineering are familiar with them from their studies of mechanics. The First Law is first formulated for closed, uniform systems and then extended to the cases of open and continuous systems. Thus the student is introduced early to the essential concepts which he will require for the understanding of continuum (so-called irreversible) thermodynamics, and this has enabled me to include the study of various physical fields in a natural way. In order to prepare the ground still further, a distinction is made between quasistatic reversible and quasistatic irreversible processes in addition to the presentation of irreversible processes whose rates may not be infinitesimal.

The Second Law is presented in the manner of Clausius and Planck as well as in the manner of Carathéodory, Chapter 10 being devoted to the latter.

The last three chapters explore the consequences of the Second Law both for the derivation of relations between properties and fundamental equations of state, and for the introduction of the concepts of entropy production and maximum work. A formulation for open systems and the introduction of the chemical potential are also included.

Statistical concepts are used only when I thought that their inclusion contributes to a deeper understanding of the subject, but this has been done sparingly and heuristically only.

I am aware that I produced a discursive and occasionally repetitious volume. No real apology is made for that, because I believe that the modern tendency for shortening and compression has gone too far. Often it is preferable to study a more leisurely exposition rather than to grapple with an incomplete presentation over and over again, and most of us learn by repetition anyway. Certain basic ideas must be examined from different angles for clarification, and certain illustrations can well be used in several contexts.

Very few universities can devote enough time to a first course in thermodynamics in their curricula to allow them to expound the subject to the extent presented in this book. Instead of attempting to make the selection for them, I have deliberately included more than can be reasonably covered in one course. I trust that each instructor will not find it difficult to emphasize the aspects which he considers important and hope that the book can be used again in a second, deeper study. At the same time the student will not be left with the erroneous impression that the subject can be fathomed in all its profundity in a single pass and will be left with something which he can turn to later if a greater mastery of thermodynamics appears to him desirable.

The absence of tables may prove somewhat disconcerting to students, but they will find them all at the end of Volume II when it becomes available.

In concluding this preface I think that I ought to give expression to the admiration which I feel for a number of classical authors whose writing influenced me in my attempt to reorganize the subject for a new presentation. My interest was first aroused when I worked on the translation of Professor E. Schmidt's *Thermodynamics* about twenty years ago. I think that his book contains an excellent presentation of the more detailed engineering applications of the subject. At about that time I was deeply influenced by M. Planck's *Theory of Heat* and J. H. Keenan's *Thermodynamics*. Somewhat more recently, my work on the translation of A. Sommerfeld's magnificently concise *Thermodynamics and Statistical Mechanics* and my study of A. H. Wilson's book of the same title clarified to me the connection between the macroscopic and microscopic points of view. The fundamental simplicity of structure of the subject was revealed to me in H. B. Callen's *Thermodynamics*, and M. W. Zemansky's well-known textbook continuously served as a model of simplicity combined with accuracy. As I was preparing the present manuscript I was presented with a set of galley proofs of Howard Reiss' forthcoming *Methods of Thermodynamics* which contains a concise exposition of a point of view that I find very close to my own.

My colleagues R. Di Pippo, H. Reiss, V. L. Shah, J. H. Whitelaw, and R. Wood helped me greatly in reading the proofs and I wish to thank them for their time and effort. Mr. Di Pippo was also very helpful with the preparation of the illustrations, tables, list of symbols, and the index, and Mr. Wood gave me invaluable help in selecting and classifying problems for inclusion and in outlining solutions. Mrs. Judi Bardsley patiently and competently typed several versions of the manuscript.

J. KESTIN

Contents

CHAPTER 1

Definitions and Basic Concepts

1.1 The scope and methods of thermodynamics

The science of thermodynamics is a branch of physics. It describes natural processes in which changes in temperature play an important part. Such processes involve the transformation of energy from one form to another. Consequently, thermodynamics deals with the laws which govern such transformations of energy.

The student will recall that in the elementary presentation of the subjects of mechanics, electromagnetism, and fluid mechanics, it was tacitly assumed that the processes under consideration occurred at constant temperature and that the transformation of mechanical or electrical energy into heat was largely ignored. Thus, in the study of friction, the considerations were restricted to the calculation of the forces acting on bodies and only seldom was an attempt made to take into account the loss of mechanical energy, kinetic or potential, suffered by a body in the presence of friction. The study was mainly concentrated on *conservative systems* in which the sum of kinetic and potential energy remained constant, that is, to systems in which the amount of *mechanical* energy was conserved.

Experience teaches that real phenomena in mechanics are always accompanied by friction, that the flow of electric currents is always accompanied by the evolution of Joule heat, and so on. In general, all real phenomena in nature involve some *energy dissipation*. The subject of thermodynamics recognizes this fact and studies its consequences and to this effect makes a careful distinction between reversible and irreversible processes (Section 4.6). The systematic distinction between these two kinds of processes is one of the most characteristic and important features of thermodynamics.

Thermodynamics is firmly based on experiment. It is developed, principally, from four fundamental so-called *laws of thermodynamics*: the Zeroth Law (Section 2.3), the First Law (Section 5.3), the Second Law (Sections 8.2 and 9.1) and the Third Law (Volume II). Each of these laws constitutes an axiomatic generalization obtained on the basis of experience. In addition, as will be carefully pointed out in this exposition, it will be necessary to accept the validity of certain other generalizations, all of them based on experimental facts; in view of their more restricted scope, these additional principles are not given the rank of laws of thermodynamics.

It is essential to realize that the laws of thermodynamics cannot be directly and exhaustively verified by suitable experiments. They always represent bold generalizations obtained on the basis of restricted experiments and their truth is ascertained by inference, that is, from the fact that of all the consequences derived from them, none have failed to be verified experimentally.