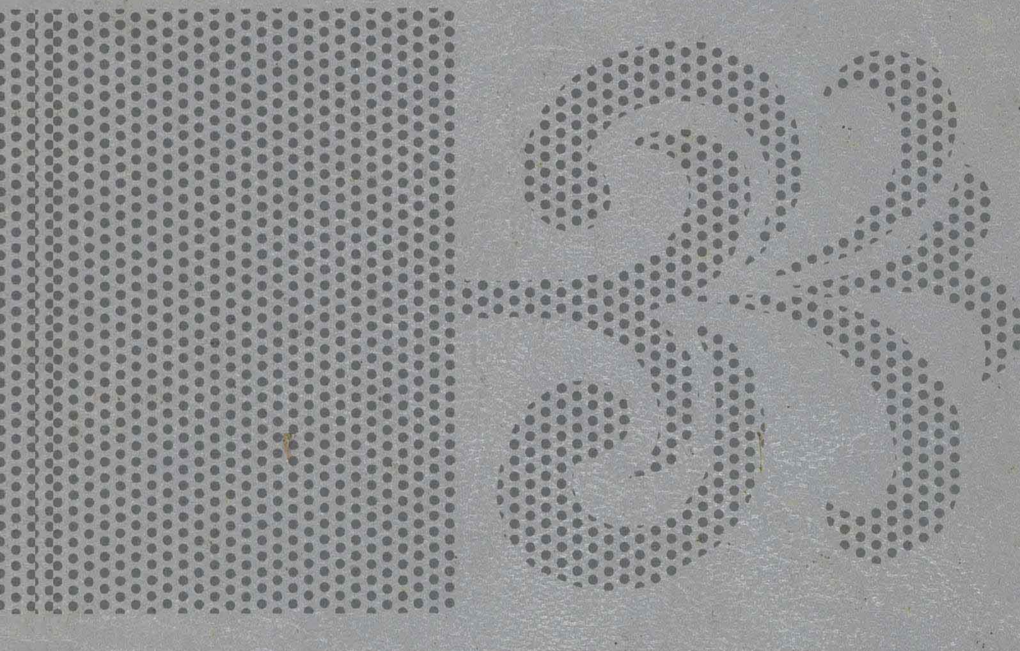
THERMODYNAMICS



KENNETH WARK

THERMODYNAMICS

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PREFACE

This edition retains the format of a dual system of units found in the third edition. Example problems, assignment problems at the end of each chapter, and data in the appendices are presented in both metric (SI) and English engineering (USCS) units. In general, problems are stated in one set or the other, but units are not mixed. Consequently, the text may be used exclusively in SI or USCS units. In addition, both sets of units may be emphasized by the proper choice of problem assignments. The problems for each chapter are grouped into specific topics and are identified by an appropriate title. This should make it easier for an instructor or student to choose problems for study. As in the preceding edition, any example problem, assignment problem, or table in the appendix which employs metric data is designated by the symbol M after the number. Metric pressure units in this edition include both the bar and the megapascal, while metric specific volume data appear primarily in either cubic centimeters per gram or cubic meters per kilogram.

As in preceding editions, the introductory concepts of the second law may be approached from either a macroscopic or microscopic viewpoint in this edition. If a statistical introduction is desired, in place of the macroscopic approach, the first five chapters should be followed by Chap. 9. An alternative is to use Chap. 9 as a supplement to Chap. 6 if desired.

On the basis of classroom experience a number of basic changes have been made in the general layout of the text. Subject matter has been carefully examined for changes which might aid in the clarification of material. In some instances this has led to the elimination or addition of a substantial amount of material within a section. Chapters 9, 12, and 13 of the third edition have remained essentially intact, while Chap. 10 on the applications of quantum-statistical mechanics has been entirely removed. This latter material is probably better covered by a separate course in statistical thermodynamics for those with a specific need for information in this area. Chapter 10 in this edition now involves transient flow analysis formerly presented at the end of Chap. 5. Chapter 8, on the concept of availability, has been completely rewritten and tested in the classroom on the senior level. Problems involving the application of availability concepts to engineering systems appear in later chapters.

All other chapters have been modestly or extensively revised. The ideal-gas material of Chap. 1 in the third edition now has been incorporated into the closed-system energy analysis of ideal gases in Chap. 3. The state postulate material formerly in Chap. 3 is now combined with the introduction to the first law for closed systems presented in Chap. 2. Introductory second law concepts involving Carnot heat engines and refrigerators which appeared early in Chap. 7 have been moved back to the end of Chap. 6. Chapter 17 has been split into two chapters, with the material on vapor power cycles remaining in this chapter, and that on refrigeration devices forming a new Chap. 18. Finally, based on items removed from other chapters and some new discussions, a new Chap. 19 covers some alternative and innovative energy conversion systems of current interest. This chapter is not all-inclusive, but simply contains discussions of some approaches to energy conservation and usage which are heavily based on thermodynamic analysis.

The problems carried over from the third edition have been carefully examined for their appropriateness. Data in problems have been altered, and problems have been dropped and others added. The large number of problems available should allow an instructor to select appropriate problems without repetition over several years.

The author is indebted to the students and faculty of the Mechanical Engineering School at Purdue University for their helpful input over the years. A special debt of gratitude goes to Dr. Peter E. Liley of this school, who has provided resource information for new and revised thermodynamic data which appear in the text.

Kenneth Wark

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CHAPTER

ONE

BASIC CONCEPTS AND DEFINITIONS

1-1 THE NATURE OF THERMODYNAMICS

Thermodynamics is a science which comprises the study of energy transformations and of the relationships among the various physical qualities, or properties, of substances which are affected by these transformations. Predictions of the physical properties of substances can be carried out either by analyzing the large-scale (gross) behavior of a substance or by statistically averaging the behavior of the individual particles which make up the substance. A thermodynamic analysis which is undertaken without recourse to the nature of the individual particles and their interactions falls into the domain of *classical thermodynamics.* This is the macroscopic viewpoint toward matter and its interactions, where the overall, large-scale effect is the focal point of interest. It requires no hypothesis on the detailed structure of matter on the atomic scale; consequently, the general laws of classical thermodynamics are not subject to change as new knowledge on the nature of matter is uncovered.

Another approach to the study of thermodynamic properties and energy relationships is based on the statistical behavior of large groups of individual particles. This method, founded on a microscopic viewpoint, is called *statistical thermodynamics.* It combines the computational techniques of statistical mechanics with the findings of quantum theory. The dual purpose of statistical thermodynamics is to predict and interpret the macroscopic characteristics of matter in equilibrium situations from their microscopic origins. It postulates that the values of macroscopic properties (such as pressure, temperature, and density, among others), which we measure directly or calculate from other measurements, merely reflect some sort of statistical average of the behavior of a tremendous number of particles. In present technology, where substances are employed under extreme ranges of temperature and pressure, the predictive methods of statistical thermodynamics are extremely important. In addition, the interpretive role of the microscopic approach is of value. For example, the interpretation in a microscopic context of a thermodynamic property called entropy frequently is helpful in increasing a student's understanding of this concept. This viewpoint of entropy is considered in Chap. 9. This theory also was helpful in the modern development of new, direct energy-conversion methods, such as thermionics and thermoelectrics.

Another independent approach to the analysis of particle behavior is the field of *kinetic theory*. This subject is the study of particle behavior based normally on newtonian mechanics, and requires a detailed knowledge of the interactions between particles. It is extremely useful in developing relations for the transport properties of rate processes, such as viscosity, thermal conductivity, and diffusion coefficients. Since it does not take into account the quantization of energy, it is not successful in predicting thermodynamic properties except in limiting cases. A third microscopic approach is *information theory*. Its applications to thermodynamics has been developed since the 1950s. It has made some important contributions to the interpretation of the macroscopic state of matter in terms of microscopic behavior.

Emphasis will be placed upon the macroscopic viewpoint in this text, with the statistical viewpoint playing a supporting role. There are several reasons for this. First of all, the solution of a great majority of thermodynamic problems requires an analysis only in terms of macroscopic variables. An understanding of the underlying mechanisms for the process in terms of particle behavior would not be necessary in these cases, nor especially beneficial. Second, classical thermodynamics is an easier, more direct approach to the solution of engineering problems, and often has fewer mathematical complications. It is somewhat more free of abstractions. Finally, it may be pointed out that macroscopic analyses in a number of instances have demonstrated what major area could be studied profitably by the methods of statistical mechanics.

1-2 ENERGY SOURCES AND CONVERSION EFFICIENCIES

One measure of a country's standard of living is gross national product (GNP). Worldwide data indicate that GNP is closely related to the energy consumption per capita in a particular country. Hence, the use of energy by industrialized countries is an important factor in their continued growth. In addition, the desire of underdeveloped nations to drastically improve their standard of living will lead to an increase in energy usage throughout the world, even if the growth rate of energy usage in developed countries were to approach zero. As a result, a great