Principles of Thermodynamics

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Dedicated to my beloved brother Stuart,

whose brilliant life ended too soon.

Preface

Once upon a time there were Giants, with names like Joule, Maxwell, Carnot, Clausius, and Thomson (Lord Kelvin). They lived during a time, called the Industrial Revolution, when labor-saving machines were being developed to greatly expand the productive capabilities of humankind. In the never-ending attempts to improve the performance of these machines, the Giants were led to profound considerations of the fundamental limits of energy conversions. Starting with some simple observations, they developed the science of thermodynamics. This science deals with energy and its capabilities and transformations. Later, Boltzmann—another Giant—connected thermodynamics to the microscopic world of atoms and molecules, while Prigogine extended thermodynamics to deal with non-equilibrium systems.

The purpose of *Principles of Thermodynamics* is to convey the powerful ideas of the Giants to advanced undergraduates, beginning graduate students, and interested scientific readers at an appropriate mathematical level, enlightening this audience to the wide variety of problems for which a thermodynamic perspective is useful. In this volume, I have chosen to express the laws of thermodynamics in terms of simple principles, self-evident from everyday experience. For example, the second law—the cornerstone of any presentation of thermodynamics—is stated as "in any real process there is net degradation of energy." I believe this approach is much more comprehensible than that based on machines, used by the Giants.

Since mathematics is the language of thermodynamics, there are many equations in this book. However, the mathematics used is no more complicated than necessary. Facility with differentiation and integration at the level of a first-year course in calculus is assumed and a few relationships from multivariable calculus are used repeatedly. All the reader has to know about this subject, however, is presented in Appendix A. Although the mathematically advanced reader can skim over this, it remains as a handy reference for any question that arises on multivariable calculus.

Principles of Thermodynamics should be accessible to scientifically literate persons who are either learning the subject on their own or reviewing the material. At Emory University, this volume forms the basis of the first semester of a one-year sequence in physical chemistry. Problems and questions are included at the end of each chapter. Essentially, the questions test whether the students understand the material, and the problems test whether they can use the derived results. More difficult problems are indicated by an asterisk. Some problems, marked with an M, involve numerical calculations that are most easily performed with the use of a computer program such as Mathcad or Mathematica. A brief survey of some of these numerical methods is included in Appendix B, for cases in which the programs are unavailable or cumbersome to use.

Thermodynamics deals with relations between properties of materials and changes of these properties during processes. Some knowledge of specific properties is thus necessary before beginning a discussion of thermodynamics. This is the purpose of Chapter 1, which deals with some of the properties of gases and other materials. In Chapter 2, after defining terms and introducing the zeroth and the first law, conservation of energy is applied to a number of processes. In Chapter 3, the quality of energy is used as the basis for introducing entropy and the second law, which determines the direction of spontaneous processes and equilibrium. In Chapter 4, entropy is placed on an absolute basis with the third law, which involves low-temperature systems. The advantages of analyzing processes using free-energy functions are then introduced.

Chapter 5 gives a microscopic-world explanation of the second law, and uses Boltzmann's definition of entropy to derive some elementary statistical mechanics relationships. These are used to develop the kinetic theory of gases and derive formulas for thermodynamic functions based on microscopic partition functions. These formulas are applied to ideal gases, simple polymer mechanics, and the classical approximation to rotations and vibrations of molecules.

In Chapters 6, 7, and 8, the thermodynamic framework is successively applied to phase transformations of single-component systems, chemical reactions, and ideal solutions. Included are discussions of the thermodynamics of open systems, the phase rule, and colligative properties. Chapter 9 gives the framework for discussing nonideal multicomponent systems and describes a variety of phase diagrams of such systems. In Chapter 10, the discussion is extended to ionized systems, including galvanic cells. Chapter 11 deals with surface effects in both single- and multicomponent systems, including adsorption. Finally, in Chapter 12 the thermodynamics of open systems is applied to systems at steady state undergoing dissipative process. Although several applications of this material are considered, the aim is to give the reader the tools needed to approach the extensive literature on this subject. The material in Chapter 12 is not covered in the physical chemistry sequence, but is assigned as outside reading for outstanding students.

Principles of Thermodynamics is both compact and rigorous; almost all results are "derived." Most of all, this book tries to convey the beauty of one of the most impressive triumphs of the human mind—the application of deductive reasoning from a few simple postulates, resulting in the development of a myriad of relationships useful in just about every branch of science.

Many thanks are given to Professor C. G. Trowbridge of Emory University and Professor Wentao Zhu of Tsinghua University, Beijing, for reading parts of the manuscript. More than anyone, I thank my wife, June, for her encouragement and understanding throughout the protracted period it took to write this book.

Myron Kaufman

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