SIXTH EDITION

THERMODYNAMICS

KENNETH WARK, JR. / DONALD E. RICHARDS

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Kenneth Wark, Jr.
Purdue University

Donald E. Richards
Rose-Hulman Institute of Technology

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About the Authors

Kenneth Wark, Jr. received his B.S. and M.S. degrees in chemical engineering from Purdue University and the University of Illinois, respectively. He joined the faculty of mechanical engineering at Purdue after receiving his Ph.D. degree from that school. In addition to his primary teaching responsibilities in undergraduate and graduate courses in thermodynamics, he has been involved in courses in heat transfer, fluid mechanics, combustion, and design. He was one of the first recipients of the best teacher awards from the Purdue chapter of Tau Beta Pi. His experience outside of Purdue has involved work with the General Electric Company, Boeing Aircraft, Carrier Corporation, U.S. Steel (USX), Allison Division of General Motors, Atlantic-Richfield, Standard Oil of Indiana, NASA-Lewis Field, and the Dow Chemical Company. In addition to this text, Dr. Wark is the author of a graduate text *Advanced Thermodynamics for Engineers,* McGraw-Hill, Inc., New York, 1995, and is a co-author (with Dr. Cecil Warner and Dr. Wayne Davis) of *Air Pollution–Its Origin and Control,* Third Edition, Addison-Wesley, Reading, Massachusetts, 1998. Dr. Wark retired from Purdue in 1996.

Donald E. Richards is a Professor of Mechanical Engineering at Rose-Hulman Institute of Technology in Terre Haute, Indiana. He received B.S., M.S., and Ph.D. degrees in mechanical engineering from Kansas State University, Iowa State University, and The Ohio State University, respectively. Before joining Rose-Hulman, he was a member of the mechanical engineering faculty at The Ohio State University. Over the years, he has taught basic and graduate courses in thermodynamics, fluid mechanics, and heat transfer. In addition, he has taught courses in HVAC systems, heat exchanger design, second-law analysis, and turbomachinery. While at Ohio State, he was awarded the Charles F. MacQuigg Outstanding Teaching Award by the students of the College of Engineering. His research has focused on natural convection, augmentation of forced-convection heat transfer, and design of multi-fluid heat exchangers. At Rose-Hulman, he was team leader for a new sophomore engineering science curriculum that uses common concepts—system identification, conservation and accounting of extensive properties, constitutive relations, modeling, and mathematics—as a basis for engineering science education.

PREFACE

This introductory textbook in thermodynamics is designed for undergraduate students in the field of engineering. The primary objectives are to provide an understanding, and to exhibit the wide range of applicability, of the basic laws of thermodynamics and to present a logical development of the relationships among the physical properties of interest in the thermal sciences. The overall aim is to present thermodynamics as a science built upon a group of postulates and concepts which complement one another. An analysis becomes meaningful only through the application and interlocking of these ideas.

—Preface to *Thermodynamics* (1966) by K. Wark, Jr.

These words are as true today for the sixth edition of *Thermodynamics* as they were for the first edition published in 1966. However, changes in engineering students, engineering education, and the engineering profession over the last thirty years have lead to significant changes in how and what we teach. The sixth edition of *Thermodynamics* has been written to respond to these changes. The authors had two major goals during the preparation of this edition: to clarify further the important concepts and tools of thermodynamics, and to encourage students to develop good problem-solving skills. As a result, major portions of the first nine chapters have undergone considerable changes in writing and format.

In preparing the sixth edition of *Thermodynamics,* Prof. Wark was joined by co-author Prof. Richards from Rose-Hulman Institute of Technology. In addition to his teaching and research experience in the thermal sciences, Prof. Richards brings significant experience in the design and implementation of a new, innovative sophomore engineering science and mathematics curriculum, the Rose-Hulman/Foundation-Coalition Sophomore Engineering Curriculum. This integrated curriculum attempts to improve student learning by stressing an underlying framework—system identification, conservation and accounting of extensive properties, constitutive relations, modeling, and mathematics—as a common basis for engineering science education.

SIGNIFICANT FEATURES OF THE NEW EDITION

Problem Solving Approach. The authors believe that students need to do more than just "plug-and-chug" solutions using predigested equations from the textbook. As an antidote to this approach, this text provides students with repeated opportunities to develop the necessary equations from general principles by explicitly applying modeling assumptions in the context of a specific problem. In this approach, the emphasis shifts from remembering specialized equations to learning how to pick a system and apply basic modeling assumptions. A specific problem solving methodology is proposed and used for both the example problems and the solutions manual.

Sign Convention for Work and Heat Transfer. One of the constants in this text over the years has been its use of a consistent sign convention for energy transfer by work and heat transfer, i.e., work and heat transfers into a system are positive as written in the energy balance. Once again we have retained this sign convention. The specific sign convention adopted for any term in the energy balance is arbitrary and often dictated by history. At one time work and heat transfer were treated as separate, unrelated concepts that came together in an energy balance. When they were treated as separate concepts, having a different sign convention for each was reasonable. Since steam engines required heat input and did work, it seemed reasonable that heat *input* and work *output* should both be positive.

Today, these two concepts have been unified and are both recognized as *energy transfer mechanisms.* Although we still hear that "work is done" and "heat is added," we now speak about "energy transfer by work" and "heat transfer of energy." Because of this, the authors continue to believe that a consistent sign convention based upon the direction of energy transfer is preferable. Our sign convention, that energy transfer into a system by work and heat transfer are both positive, is consistent with a student's earlier experience in physics, chemistry, and mechanics. This approach is also consistent with current efforts in engineering education to help students integrate material across traditional course boundaries by stressing the similarities between the basic conservation laws of mass, energy, net charge, and momentum plus the accounting principle for entropy.

Entropy Production and the Second Law of Thermodynamics. In recent years there has been an increased emphasis on the concept of entropy production or generation as a tool to help students understand the directional nature of the second law of thermodynamics. The authors applaud this change and have increased the use of the entropy accounting equation or balance as a tool for solving problems.

The development of second law relations (Chap. 6) has undergone extensive changes. The role of internal reversibility and irreversibility are emphasized in the early development, rather than total reversibility. This approach enhances the later introduction to entropy generation (production). To supplement the classical approach based on the Kelvin-Planck statement of the second law in Sec. 6-5, the authors have included in Sec. 6-6 an alternate development of the second law based upon a postulational approach. This approach parallels the development of the first law in Chap. 2 and begins with a statement about entropy transport by heat transfer and entropy production for a closed system. Instructors are encouraged to decide which approach meets their goals and then only assign either Sec. 6-5 or 6-6 to their students. Either approach leads directly to the control-volume entropy balance that then serves as the primary tool for applying the second law throughout the text, including Chaps. 10 and 13, and Chaps. 15, 16, and 17 on cycle analysis. An improved discussion of the loss of work potential associated with heat transfer and the calculation of entropy production in simple, cyclic devices ends Chap. 6.

Changes from the Fifth Edition

Specific major changes are listed and discussed below.

1. *Problem solving methodology.* In this edition, the problem solving methodology is introduced in Chap. 1 and used fully beginning with the examples in Chap. 2. The *Solution* of any example problem generally consists of five parts entitled: *Given, Find, Model, Strategy,* and *Analysis.* The *Strategy* section appears in the first eight chapters and asks the student to outline in words a proposed sequence of steps for solving the problem before they begin the *Analysis.* A four- or five-step approach appears in all examples for which it is appropriate throughout the text. A schematic of the system includes all the important input data, and the system boundary is designated by a dashed line. A similar methodology appears in other texts including two thermal science texts written by fellow members of the School of Mechanical Engineering at Purdue University, those by R. W. Fox and A. T. McDonald and by F. P. Incropera and D. P. Dewitt.

2. *Introduction to property data.* In earlier editions, the chapter on ideal gas relations preceded a general discussion of the PvT behavior of substances. In this edition, a general discussion of the properties of a pure, simple-compressible substance appears first (Chap. 3) and now includes a discussion of the Tv diagram. There also is an enhanced discussion of data acquisition and evaluation and of reference states and reference values for tabular data. Chapter 4 then presents two important property models that represent actual behavior under restrictive conditions: the ideal gas and the incompressible substance models. The use of the compressibility chart is also presented here as a method to estimate PvT properties when experimental data are not available and to gauge when the ideal-gas relations are appropriate.
3. *Introduction to the second law.* In Chap. 7 the evaluation and use of the entropy function and entropy generation (production) has now been divided into closed-system analyses followed by steady-flow applications, similar to the energy analyses in Chaps. 3 through 5. The use of the increase in entropy principle has been de-emphasized with preference given to entropy production as a guideline to reversibility and irreversibility. The relation between actual and reversible work is developed early in the chapter, and the chapter concludes with polytropic, steady-state work.
4. *Simple cycles introduced early.* There is now a discussion of simple steam power cycles and refrigeration cycles at the end of Chap. 5 on steady-state systems. This new material serves two purposes. First, it shows the reader applications where several pieces of steady-state equipment operate in series. Second, knowledge of the equipment arrangements for several simple cycles enhances the discussion on cycle performance introduced immediately in Chap. 6 in conjunction with the development of second law theorems. This approach has been class tested over several semesters. Preceding the problems covering these simple cycles in Chap. 5 are other problems that illustrate the use of two pieces of equipment in series.
5. *Choice of units.* This edition continues the use of both SI and English (USCS) units. Early in the text both sets of units are employed in examples, but after Chap. 2 the example problems are predominantly in SI units. Both sets of units are used individually in the problems at the end of each chapter. In the sixth edition, the problems in SI units are 60 to 65 percent of the total in a given chapter. Data in SI units appears in Appendix A-1, where all tables and figures are numbered consecutively from 1 to 32. Data in USCS units appears in Appendix A-2, where tables and figures are numbered from 1E to 26E. In the appendices, data for refrigerant 134a (R-134a) replaces data for refrigerant 12 (R-12), and the tables of specific heat data for liquids and solids now appear as A-4 and A-4E. Former Table A-32M listing the logarithms of the equilibrium constant now appears as Table A-24, immediately following enthalpy of formation data. Also, former Tables A-4M and A-4 for the specific heat data of gases are now Tables A-3 and A-3E, respectively. Other tables are found in their former positions. Finally, data for the specific volume are now reported in m^3/kg (or L/kg) in SI tables.
6. *Assigned problems.* Unlike the fifth edition, problems in the sixth edition are not separated into two distinct groups depending on the type of units required. Problems in SI and USCS are intermingled and numbered consecutively, although problems on a given topic will appear together, regardless of the units. Problems involving USCS (English) units are now marked by a capital E after the number, while problems in SI units are unmarked. A new group of problems have replaced a sizable fraction of those in the fifth edition, while some older problems have been upgraded in terms of data and questions. The problems at the end of the chapters now total over 2000. Throughout the text the problems are divided into sections separated by headers that indicate the subject matter, as was done in the fourth edition.
7. *Parametric and design problems.* A group of problems entitled "Parametric and design studies" appears at the end of the application chapters, namely, Chaps. 10 and 13 through 17. Some of the design-oriented problems have been used in the second semester course in thermodynamics at Purdue University, and one

author (Ken Wark) wishes to acknowledge these contributions from a number of his faculty colleagues. These problems are more easily solved by means of a software package that contains property data, such as the EES program described below.

8. *Computer-aided solutions.* Solutions to typical problems in the text have been developed using a software package called EES (Engineering Equation Solver) and are available on an EES Software Problems Disk. Problems included on the problems disk are usually example problems and are denoted in the text with a disk symbol. By using example problems, students can clearly see the differences between hand and computer-aided solutions. Each fully-documented solution is an EES program that is run using the EES engine. These programs illustrate the use of EES and help the student master the important concepts without the computational burden previously required with hand calculations. This type of program is extremely useful in parametric studies as well as for open-ended design problems.
9. *Learning aids.* For emphasis, all basic equations and other important relations are now enclosed in a box, and fundamental terms appear in boldface type when they are defined. In addition to the discussion in the text, important concepts are stressed using notes in the margin and in critical thinking or concept questions (marked by a capital C) at the beginning of the problem sections of the first eight chapters. These questions may be assigned or used for class discussion. Finally, a brief summary has been added at the end of each chapter containing the basic equations and property relations developed for that topic. Equations for specialized applications do not appear in the summaries.
10. *Use of figures.* As a result of the amplification of the problem-solving approach in the sixth edition, the number of figures in the text has increased threefold. There are now about 200 figures which are used in the problem-solving methodology described in item (1) above, and the total number of figures is now around 450.
11. *Availability (exergy) and irreversibility.* The introduction to the concepts of availability and irreversibility, introduced in Chap. 9, has been substantially revised. The major results are now used in the analysis of power and refrigeration cycles (Chaps. 15–17) and of chemically reactive systems (Chap. 13).
12. *Chemical equilibrium.* In Chap. 14 the equations for chemical equilibrium have been changed to include a K_0 quantity based on the standard-state Gibbs function change and a K_p term based on ideal-gas partial pressures.
13. *Advanced energy systems.* Chapter 19 in the fifth edition contained discussions on advanced and innovative energy systems such as fuel cells, combined cycles, cogeneration, and geothermal and ocean thermal-energy conversion systems. In the sixth edition, these topics have been moved to Chaps. 14, 16, and 17, where they tie more directly to the basic theory and practice to which they are related.
14. *Arrangement of advanced topics and applications.* An area of difference between thermodynamic textbooks is the placement of material on gas mixtures, generalized thermodynamic relationships, combustion, and chemical equilibrium (Chaps. 10–14) versus power and refrigeration cycles (Chaps. 15–17). Some other texts reverse this order. Should the instructor desire a different sequence, there is no conflict in using this text if the chapters on cycle analysis are assigned first.

SUPPLEMENTS

A **Solution Manual** showing the complete solution to each problem is available; however, solutions to parametric and open-ended design problems are not provided. In addition, adopters of the text may obtain an **Instructor's Resource CD** of selected figures and tables from the text. A **Tables and Figures Supplement** containing information from the two appendices is also available in the format used for the fifth edition.

EES (Engineering Equations Solver) is a general program that solves algebraic and initial-value differential equations. EES can also do optimization, parametric analysis, and linear and nonlinear regression and provide publication quality plotting capability. EES has an intuitive interface that is very easy to master. Equations can be entered in any form and in the most efficient manner. The EES engine is available to adopters of the text with the Problems Disk. The book is available with or without the EES Problems Disk. Faculty interested in using the book with the Problems Disk should notify their local WCB/McGraw-Hill representative to obtain information on obtaining the EES engine that drives the Problems Disk.

EES is particularly useful in thermodynamics problems since most property data needed for solving problems in these areas are provided by the program. For example, the steam tables are implemented such that any thermodynamic property can be obtained from a built-in function call in terms of any other properties. Similar capability is provided for all substances. EES also allows the user to enter property data or functional relationships with lookup tables, with internal functions written with EES, or with externally compiled functions written in Pascal, C, C++, or Fortran. Interesting practical problems that may have implicit solutions are often not assigned because of the mathematical complexity involved. EES allows the user to concentrate on concepts by freeing him or her from mundane chores.

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