PREFACE TO THE FIRST EDITION

A major challenge facing the world today is not the depletion of energy resources, but the continual destruction of availability (the ability to produce useful work) predicted by the second law of thermodynamics. One of the primary objectives of this book is to develop second-law concepts in parallel with those of the first law to help make the student feel as comfortable with the concept of availability as with the more familiar concept of energy.

To fulfill this objective, the concept of the general balance,

Inflow + Produced = Outflow + Stored + Destroyed

is introduced in the first chapter and immediately applied to the extensive properties of mass, momentum, energy, availability, and entropy. Although at this stage the student is unable to measure energy, availability, and entropy, the student will accept that they are properties to be developed in later chapters. Early introduction to these balances, and continued reinforcement in later chapters, provides the student with a unified structure that aids immensely in problem solving.

Another unique feature is that the basic principles involving mass, momentum, energy, availability, and entropy are each stated as restrictions on the "produced" and "destroyed" terms in the general balance equation. If we ignore relativistic effects, as we do in classical thermodynamics, mass, momentum, and energy can never be produced or destroyed. The second-law statement in this book is that availability *destruction* must be greater than or equal to zero (availability is never produced). The second law in terms of entropy is that entropy *production* must be greater than or equal to zero (entropy is never destroyed). These principles, first introduced in Chapter 1, are reinforced throughout the book.

The development of the second law of thermodynamics differs from the usual approaches. Availability is developed as a system property at the *start* of the discussion of the second law (Chapter 4). By studying a battery or fuel cell and then a cylinder with piston, the student is given a physical feeling for nonuseful work (expansion energy to push aside the atmosphere). The application of availability balances is quite acceptable to the student who has already been exposed to balances in general in Chapter 1, to mass balances in Chapter 2, and to energy balances in Chapter 3. Balances of mass, energy, and availability then lead to the entropy balance.

Once the second law is developed, it is emphasized throughout the remainder of the book. In Chapter 5 (cycles) second-law analysis is considered to be equally as important as traditional first-law analysis. Availability destructions in various cycle components are calculated from second-law balances (availability or entropy) to show where are the most important needs for cycle improvement. Second-law cycle efficiency is introduced to evaluate performance.

Chapter 6 (nonreacting mixtures) includes both first- and second-law analysis on a more equal basis than that found in other textbooks. For moist-air problems at atmospheric pressure, other texts rely on the psychrometric chart (which does not have a second-law content). In this book, moist-air tables that include entropy are provided instead of the psychrometric chart so that entropy balances are now as convenient to make as energy balances.

Standardized properties are used for first- and second-law analyses of reacting mixtures in Chapter 7. Standardized enthalpies are derived from heat-transfer measurements and first-law energy balances; standardized entropies are calculated from the third law of thermodynamics.

The use of *reaction coordinates* to describe reacting mixtures when there are more unknown coefficients in a chemical equation than there are atom species to balance is another unique feature of this book. Equilibrium theory is developed with reaction coordinates to describe mixture composition. Property tables are included for 11 common reaction products. These tables have been expanded to include a normalized Gibbs function to facilitate equilibrium calculations. Students are shown how to apply equilibrium theory to consider such pollution problems as soot formation and the formation of oxides of nitrogen.

In the past, the rough notes of the professor had to be refined by cutting, pasting, and then retyping. This laborious process discouraged a polished product until after the second edition. Today, by virtue of the computer, the process of editing and revising a set of notes is much more practical. This text began its life some 10 years ago on a computer with relatively complete style, examples, and problems. At that time, illustrations were done by hand, but as software improved, the task was taken over by the computer. Through the years, the comments of colleagues and students allowed continual changes, with new "editions" produced about once a year. This evolution paid attention to student comments on readability, on type and abbreviation styles, and to their requests for space for notes. As a consequence, wide margins were introduced for student notes, and for text illustrations and diagrams to avoid disrupting the text descriptions.

The major goal of this book is to teach introductory and applied thermodynamics to junior-level students in engineering. The book is not intended to be a reference source for the experienced engineer since additional data are far too great to include in a teaching text. Also, an overabundance of topics or material would detract from the teaching objective. Orderly problem-solving techniques, systems, property diagrams, and balances are stressed. Other problems give the student practice in drawing graphs, interpolation, computer programming, and numerical integration.

Although engineers are in the midst of switching to the SI unit system, it is too early to use exclusively SI units since much engineering still employs US (English) units. Both SI and US (English) units are included throughout the text. Dimensions and units are discussed in Appendix A and unit equivalents are provided. Appendix B gives thermodynamic property data in US units. Appendix C gives comparable thermodynamic property data in SI units.

For the convenience of the student and the instructor, the property tables in appendixes B and C have been made into a separate booklet. With the booklet, students are not forced to switch back and forth between the homework problem in the text and the tables at the back of the book when working problems. Instructors may give closed-text exams that need these tables. The dimensional/unit relations in Tables A.3 through A.6 are also in the booklet. Since this booklet does not come with the text, it must be purchased separately if desired. Contact the author for more details.

An effort has been made to use notation familiar to students from calculus (*e.g.*, Δ notation, area function) and from mechanics (*e.g.*, $\mathbf{F} = M\mathbf{a}$, no g_c), and that will be consistent with later courses (*e.g.*, q for heat-transfer rate). In many thermodynamic books m is the symbol for the mass in a system and $\dot{m}$ is the symbol for the rate of mass flow across a system boundary. Except for the special case of a system with a single entering mass flow stream and no mass flow leaving, this conflicts with the widely accepted notation that $\dot{x} = dx/dt$. Thus, mf, not $\dot{m}$, is the symbol for mass-flow rate in this book.

Another feature of this textbook is the inclusion of over 50 carefully selected photographs to provide additional information about the size and scope of thermodynamic applications in the real world. Detailed captions for the photographs contain interesting engineering data to illustrate what might be in store for a student entering the energy area.

In summary, this book gives a comprehensive treatment of the most important topics and concepts in thermodynamics. It attempts to fit in with the student's background in calculus and mechanics. By discarding old approaches to the second law and placing more emphasis on second-law analysis, the student should gain a much better understanding of thermodynamics than is usually obtained from other books.

ACKNOWLEDGMENTS FOR THE FIRST EDITION

This book reflects my own experiences in learning and teaching thermodynamics. I have been influenced by my teachers when I was a student; J. W. Bursik, N. P. Bailey, and F. J. Bordt at Rensselaer Polytechnic Institute; and by A. L. London, W. C. Reynolds, R. H. Eustis, S. J. Kline, and F. Bloch at Stanford University; and by discussions with colleagues R. A. Gaggioli and E. F. Obert at the University of Wisconsin–Madison.

Professors W. A. Beckman, G. L. Borman, H. T. Ceylan, J. F. Davis, F. T. Elder, D. E. Foster, C. P. Gupta, S. A. Klein, J. W. Mitchell, P. S. Myers, H. N. Powell, K. W. Ragland, and O. A. Uyehara used early versions of this text in their classes and provided valuable feedback. A special word of thanks should also be given to the many students who asked questions when something was not clear or made constructive criticisms to improve the text for future students.

The notes for the book were originally developed on a mainframe computer at Wisconsin. M. F. Ganter and J. J. Uicker were especially kind in providing programming advice, computer time, and file space. J. I. Fritz and D. L. Oppriecht at the Madison Academic Computing Center were very helpful in reproducing countless sets of notes in time for classes. Figure labels and equations that were not convenient to do on the computer were expertly typed by L. L. Litzkow.

A major change in the production of the notes for the book was made in 1985 with the switch to the Apple Macintosh computer and the Apple LaserWriter. The text processor was Microsoft Word. Apple’s MacDraw was used for the artwork. Art was added to the text files with Switcher and Multifinder.

Professors J. C. Bennett, Jr. (University of Connecticut), R. A. Gardner (Washington University), E. F. C. Somerscales (Rensselaer Polytechnic Institute), and E. M. Sparrow (University of Minnesota) provided valuable suggestions in the final review. I am also grateful for the comments of two anonymous reviewers.

The patience and understanding of my wife Susan and children Tim and Christy made late dinners and long nights and weekends of writing, drawing, proofreading, and editing more bearable.

PREFACE TO THE SECOND EDITION

There have been many thermodynamics textbooks published during the 50 years I have taught (and been taught) the subject. The basic approach has not changed much during this time. The concept of availability is mentioned in most of these books, but only as a "luxury" that can be easily omitted. Early in my career, as I grappled with how to present the second law to undergraduate students in their first course in thermodynamics, it became apparent to me that the concepts of useful work, availability and availability balances were very effective ideas that students could grasp.

I think the most helpful end result of the second law is the ability to make second-law balances (of availability and/or entropy) to calculate availability destruction. It became clear to me that the best way to reach this result was to focus on availability from the *start* of the second-law discussion rather than leave it as an afterthought with very little follow-up in later chapters. By using the general balance equation that

Inflow + Produced = Outflow + Stored + Destroyed

the basic principles regarding mass, energy, availability and entropy can all be stated in a similar manner. This eases the transition from mass and energy to availability and then to entropy.

Availability is central in the unique development of the second law in this book. The second-law statement that availability destruction must be ≥ 0 is not an "add on" in this book. It replaces both the Kelvin-Planck and the Clausius statements which then follow from availability and energy balances and the statement that availability destruction < 0 is not possible.

Chapter 1 prepares students by introducing systems (closed and open), balances (rate and increment) and the symbols that will be used to make balances. The basic principles are stated.[1] An understanding of availability is not needed at this point, but will come later after additional experience with mass and energy balances has been obtained. Chapter 2 treats mass balances along with property evaluation and process representations. Energy balances and the energy analysis of engineering components are presented in Chapter 3. The concepts of availability and availability balances then follow smoothly in Chapter 4. Mass, energy and availability balances also lead to entropy balances in Chapter 4. Second-law balances (availability and/or entropy) continue to be used in chapters 5 (cycles), 6 (nonreacting mixtures) and 7 (reacting mixtures). It is difficult to avoid the concept of availability in this book.

[1] Momentum is also included in Chapter 1, but is not of primary interest in this book.

Although the primary purpose of this book is to present a different approach (and emphasis) to the second law, it was also an opportunity to improve upon the notation used in other books. This book makes an effort to use meaningful notation that is consistent with calculus and other courses taken by students. As a result, the notation in this book varies somewhat with other books as shown in the following table:

Quantity	Myers	Others
Mass of a system	M	m
Mass-flow rate	mf	$\dot{m}$
Work flow during time interval dt	dW	δW
Work-transfer rate at an instant	w	$\dot{W}$
Work flow during time interval Δt	ΔW	W
Heat flow during time interval dt	dQ	δQ
Heat-transfer rate at an instant	q	$\dot{Q}$
Heat flow during time interval Δt	ΔQ	Q
Specific availability of a system	a	ϕ
Specific availability of a flow stream	af	ψ

Four of my concerns about notation in other books are:

1. The use of m for system mass and $\dot{m}$ for mass-flow rate is not consistent with usage in other courses since, as used in thermodynamics, $\dot{m} \neq dm/dt$.

2. One book states that

$$W = \int_1^2 \delta W$$

but explains why the value of the integral is not $W_2 - W_1$. Also, the use of δ instead of d in the integrand puzzles students since this (to the best of my knowledge) is never found in calculus books. The present book avoids these concerns by defining a *work function* $W(t)$ at time t as

$$W(t) = \int_{t'=0}^{t'=t} w(t')\,dt'$$

where $w(t')$ is the instantaneous work-transfer rate at time t'. It then follows directly from calculus that the work transfer during Δt is given by

$$\int_{t'=t}^{t'=t+\Delta t} w(t')\,dt' = \int_{t'=0}^{t'=t+\Delta t} w(t')\,dt' - \int_{t'=0}^{t'=t} w(t')\,dt' = W(t+\Delta t) - W(t) = \Delta W$$

Thus, it makes sense to use $w(t)$ for the work-transfer rate at time t and ΔW for the difference in the work function between time t and time $t + \Delta t$ or the amount of work transfer during time increment Δt. Similar comments apply for $q(t)$ and ΔQ.

3. The use of q instead of $\dot{Q}$ is common in heat-transfer textbooks. The use of w instead of $\dot{W}$ is then consistent with using q instead of $\dot{Q}$.

4. The use of a for specific availability of a system and af for specific availability of a flow stream is much easier for students to remember than ϕ and ψ.

To use this book effectively, instructors should be prepared for and receptive to a different approach to the second law. They should be willing to treat availability and entropy balances as being just as important as mass and energy balances. It is also helpful for students if instructors use the notation in the book.

As was the case with the first edition, the major focus of the second edition of this book is still on engineering students taking their first course in thermodynamics. Therefore, the book focuses on thermodynamics from the standpoint of balances of mass, energy, availability and entropy. This methodology is reinforced throughout the book and therefore the student will become comfortable with using these balances as tools to solve an array of problems. In addition to balances, the book emphasizes process sketches (primarily T-v and T-s diagrams) to display process paths. Careful attention is paid to units both in the layout of the tables of unit conversions and in all computations.

Effective coverage of the material in this book requires two semesters. The topics are discussed in a logical order; it should not be necessary to jump back and forth between different sections nor omit major sections. Troublesome areas have been anticipated and explained in some detail. Excess material, more appropriate for a graduate course, is not included.

In a one-semester treatment, the cuts would have to be substantial or the pace of the course would be too fast for good understanding. One of the features of the book is the development of the second law based on balances of availability and entropy in Chapter 4 and the use of these balances throughout chapters 5, 6 and 7 to solidify the concepts. First- and second-law balances are purposely intermingled in chapters 5, 6 and 7 to give them equal emphasis. Omitting the second-law analysis in chapters 5, 6 and 7 would circumvent one of the objectives of the book—to place second-law balances on an equal footing with first-law balances.

The first edition, also developed on a Macintosh computer, suffered from two nontraditional features; equation formatting and font selection. It has been 18 years since the first edition was published. There have been many improvements during this time that permit self-publishing a more polished final book than was readily possible with the first edition. *MathType* is now available for conventional typesetting of equations; built-up equations are now possible and are used in the second edition. A more conventional font (Times) is now used. The page layout capability of *Word* has improved and *Word* can now handle significantly larger files. File storage is no longer limited to 400 K floppy disks.

Art work in the second edition has also improved. *Canvas 9* has more features than were available in desktop drawing programs in 1989. The use of shading gives more clarity to the illustrations. Color is still not used in order to keep production costs down.

The preparation of plots (to scale) has been greatly simplified by the use of *Engineering Equation Solver* (*EES*)[2] software written by Professor S. A. Klein. *EES* contains a wealth of thermodynamic property functions. The properties of air in appendixes B•5 and C•5 were replaced by values obtained from *EES* and include c_v and c_p rather than P_r and v_r so that the tables are more useful. The R-12 properties in appendixes B•6 and C•6 were replaced by the properties of R-134a from *EES* to be more relevant to modern vapor-compression technology.

Although *EES* was used in the preparation of the second edition, it is not required by those using the book. Most of the problems in the book do not need a computer in order to solve. Many of the problems, for which a computer would be helpful, can be solved using other software. However, for problems involving properties of multiphase substances, *EES* is very helpful because it eliminates property look-up in tables and interpolation.

2 Klein, S. A.: *EES-Engineering Equation Solver*, F-Chart Software, www.fchart.com.

Another improvement over the first edition is a more streamlined development of the concept of availability flow due to heat flow in Section 4•2. Specifically, only one theorem must be proved instead of the three that were previously required.

A major change in the second edition is the presentation of chemical equilibrium. Other thermodynamics textbooks mention either maximizing entropy or minimizing the Gibbs function but then go on to develop the idea of the equilibrium constant. I have always found the concept of the equilibrium constant difficult to teach and understand. In most books, only relatively simple examples are provided (*e.g.,* determining the equilibrium composition of a mixture of CO_2, CO and O_2). This was also the approach used in the first edition of this book. In the second edition, however, students reach the point where they can, for example, calculate the equilibrium composition resulting from a reaction of C_8H_{18} and air in which the products include O_2, N_2, CO_2, CO, H_2O, H_2, OH, NO, NO_2, CH_4 and C(solid). The oxides of nitrogen and soot (particulates) are pollutants that should be of interest to today's students.

The presentation of chemical equilibrium in this book eliminates reaction coordinates and equilibrium constants. The Gibbs function is minimized using calculus and element potentials. A brief review of the calculus required to find constrained extremes of functions using Lagrange multipliers has been added to Appendix A. Although the mathematical details of the presentation may not be of much interest to students, the end result is very helpful. Appendix F now contains an *EES* program, *EQUIL11*, that can be modified to calculate the equilibrium composition of mixtures of the above 11 products or simplified to handle fewer species. Four additional species, O, N, H and C(gas), have been added in appendixes B•8 and C•8 so that students can be asked to create *EQUIL15* from *EQUIL11* to further expand their understanding of reacting mixtures.

If you have questions, concerns or suggestions regarding the content of this book, you can contact the author via email at: *myers@engr.wisc.edu.*

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The interest in resurrecting the first edition for use by present-day students shown by Professor G. F. Nellis provided additional incentive for me to continue editing and then to publish the second edition of the book.

I am indebted to Professor S. A. Klein for writing and continuously updating *EES*. The thermal-property and plotting capabilities of *EES* were invaluable in preparing the second edition. Unit checking was added to force students pay more attention to units.

J. Rhoades and M. Smith at Thomson-Shore gave valuable guidance in file preparation and other book-production concerns.

I am also grateful to my wife, Susan, for allowing me to devote so much time during "retirement" to complete and publish the second edition.