

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

$$\text{Inflow} + \text{Produced} = \text{Outflow} + \text{Stored} + \text{Destroyed}$$

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 $\text{C}(\text{solid})$. 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 $\text{C}(\text{gas})$, 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@enr.wisc.edu*.

ACKNOWLEDGEMENTS FOR THE SECOND EDITION 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.