

Chapter 1

About This Book

Put yourself in the mindset of a 19th-century scientist—austere, heavily-bearded (see Appendix A), and intently focused on the “new” science of thermodynamics. One of your main practical motivations is *steam engines*—i.e., cylinders, pistons, boilers and the like—and specifically, how to improve their performance. It was in this engineering context that the field was born.

Very quickly, however, the importance of thermodynamics in many other areas became widely recognized. It even gained a strong foothold in the popular culture and imagination of the day (see Appendix B). Today, thermodynamics has developed into a cornerstone subject for virtually every discipline of science and engineering.

Simply put, thermodynamics is the science that addresses how matter behaves at the *macroscopic* scale (i.e., at the ordinary scale of everyday human experience), and also how this behavior relates to the *molecular* scale (i.e., of individual molecules, nanoparticles, etc.). As such, it is a subject of profound practical as well as fundamental importance.

Thermodynamics is used, for example, to characterize the properties of new materials developed for specific applications—from hydrogen cars to wind turbines to fabrics. Machines built to provide mechanical work, to condition air, or to perform computations, all rely on thermodynamic principles to maximize their efficiency. Likewise, these same thermodynamic principles govern a great many processes observed in nature: from the smallest nanodevices to the whole universe itself; from ultrafast chemical and photophysical reactions to “ultraslow” geological transformations.

But our job here is not really to explain to you how important thermodynamics is to your chosen discipline, nor to try to convince you that it’s “cool.” Our job is to lay a solid conceptual foundation for the subject, by clearly explaining and defining the core concepts (see Section 1.3), and clarifying the subtle—even insidious—distinctions that arise. As when building any stable edifice, success with thermodynamics, both in the classroom and in professional practice, requires a solid foundation. This means attaining both a conceptual and practical mastery of the fundamentals of the subject.

It was not called “classical thermodynamics” just yet...



From the Texts: Some authors prefer the terms “*macro*” or “*bulk*.”



From the Texts: Some authors prefer the terms “*micro*” or “*nano*.”

not to mention the bioenergetics of living organisms, lying somewhere in the middle...



From the Texts: Your primary textbook is there to do that.

Such study may not seem fun and exciting, and at first glance may even appear extraneous to your chosen discipline. Don't be fooled. Whatever your field of study, a careful consideration of the fundamentals early on in your thermodynamics (or related) course will generally lead later on to smoother sailing, less head-banging, and ultimately, better grades.

1.1 Who Should Use This Book?

As might be imagined, the various disciplines that train their students in thermodynamics tend to emphasize quite different aspects of this important subject. Despite this variety, the core thermodynamics concepts are the same across all disciplines; it is this common core that serves as the focus of this book.

As a general rule, if you are taking a thermodynamics or related course, and your primary textbook is listed either on p. xv of the Textbook Guide section, or on the companion website, then you are a good candidate for this supplement. (See the Preface for some specific examples of good candidates.)

If you are an undergraduate chemistry or physics major, then this book is very well suited for your "Physical Chemistry" or "Thermal Physics" course, respectively. Graduate students in these disciplines who are preparing for their cumulative or qualifying examinations may also find the book to be of benefit, as will premed students preparing for the MCAT.

Chemical engineering majors typically take two semesters of "Chemical Engineering Thermodynamics." This book may help such students, with regard to their understanding of concepts such as free energy and fugacity that play a vital role in phase and reaction equilibria, and in chemical yields. Other engineering majors typically take a one-semester "Engineering Thermodynamics" course. The more highly motivated graduate and graduate-school-bound engineering students may also find the molecular description of entropy useful, particularly as a direct connection with macroscopic entropy is provided here.

Undergraduate geoscience students might use this book in conjunction with their "Geochemistry" course. However, it is probably better suited for graduate students taking a "Chemical Thermodynamics for Geoscientists" course. Likewise, biological science students might find it useful as part of a "Physical Chemistry for Biological Sciences" course, particularly vis-à-vis the discussion of free energy.

Whether assigned as required reading for a specific course, or purchased voluntarily as supplemental reading, this book is primarily intended for students. That said, instructors may also find the material useful for lecture preparation and course development. Being a supplement, use of this book need not necessitate revision of an existing lesson plan—unlike, say, a change of primary textbook.



On the Website:

<http://www.conceptualthermo.com>

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Finally, we note that various ebook formats are also available; consult the website for details.



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1.2 Philosophy of This Book

This book is a *supplement*, and decidedly *not* a comprehensive, standalone thermodynamics textbook. As such, the focus is on developing (fairly) precise definitions of the key concepts used in the field, as well as on pointing out common misconceptions, so as to make the subject easier to understand. We thus leave the splashy color graphics—together with a description of the latest “sexy” applications—to your primary textbook, and instead concentrate here on a clear presentation of the core ideas. The premise is that a solid conceptual understanding of the core principles will lead to a better understanding of the subject—and ultimately to greater practical success, e.g., in solving problems. For problems, the main goal is to convey a sense of how these should be initially conceptualized and approached—rather than to work through many detailed examples from start to finish, as you can no doubt already find in your primary textbook. Again, the aim is to complement, rather than to replace, the latter.

In the interest of clarity, this book does not include many formal mathematical proofs as such, but tends to rely instead on intuitively plausible arguments. The level of rigor is presumably appropriate for most disciplines at the introductory level. At the least, it should serve to get students past the dangerous practice of just “plugging in the formula” *without really understanding when or why it applies*—which is a major goal of this book.

In any case, a more rigorous treatment would require *statistical mechanics*—an advanced field lying for the most part beyond the scope of this book. It is true that we do rely on a molecular, or statistical, viewpoint, in the development of some of the important core concepts—notably energy and entropy (see Section 1.3). We do so, however, only to the extent necessary to clarify a conceptual understanding of these vitally important thermodynamic quantities. Most other quantities are derived directly at the macroscopic scale.

1.3 Four Core Concepts of Thermodynamics

Science is—well—an “exact science,” and so meaningful scientific discourse depends vitally on knowing precisely what one is talking about. Even so, science often commandeers words and phrases from imprecise, everyday usage—words such as “energy,” for instance.

This practice presents both a benefit and a hindrance. On the one hand, it provides us with intuition about the meaning of new scientific terms. On the other hand, it can limit our thinking, or bias us towards certain expectations that are ultimately unwarranted. This situation pervades science in



From the Texts



From the Texts: A good source of worked problems is *Schaum's Outline of Thermodynamics*, whether for *Engineers* or *With Chemical Applications* (McGraw-Hill).

if not *the* major goal...

though this book could serve as a useful primer for a statistical mechanics-based course...

For additional discussion on the difference between macroscopic and molecular scales, see Chaps. 2 and 3.

general, but it is *especially* true of thermodynamics. Here, the main concepts can be subtle and confusing—and even inconsistent or ill-defined, historically speaking.

We therefore rely on *definitions*, to clarify the precise meaning of terminology. Here is the first definition that we will encounter in this book, the definition of a definition:

Definition 1.1 *A definition is a complete specification of what something is.*

A central goal of this book is to provide unambiguous definitions—together with an intuitive understanding—of four core concepts in the field of thermodynamics. These are: *equilibrium*, *energy*, *entropy*, and *free energy*. Note that there are also four Laws of Thermodynamics, which more or less correlate to the four core concepts. This book is also divided into parts, one of which is also dedicated to each of the four core concepts. Each of these concepts will be properly defined in due course; in the meantime, a very brief introduction is presented here.

- equilibrium** The word “equilibrium” has certain connotations that are fairly appropriate with regard to its thermodynamic usage. One thinks of stillness and stability. *Do not*, however, imagine that the molecules in an equilibrium system are stationary [*Don’t Try It !!*]. Indeed, molecules in “still” air, for example, move approximately as fast as those in an intense tornado.
- energy** This is the most important quantity in all of science. In thermodynamics, though, the term has at least three distinct meanings (see Chapter 5). One must therefore be careful about which kind of energy—and energy conservation—one is talking about.
- entropy** This term does not get used so much in everyday speech—or rather, did not, before thermodynamics entered the popular culture (see Appendix B). In this context, “entropy” often suggests “chaos” or “disorder.” Within thermodynamics, it remains the most confusing and least understood concept, by far. Suffice it to say that a major goal of this book is to explain clearly and precisely what entropy actually is.
- free energy** Often described as the “energy available for useful work,” free energy (and its engineering cousin, exergy) is the determining factor underlying much of what occurs naturally in the world. Conceptually, it can be described as follows:

$$\text{free energy} = \text{energy} - \text{entropy} \quad (1.1)$$

Thus, free energy implies a *tension* or competition between energy and entropy—these being the two primary forces that drive natural processes forward. Note that free energy can be—and often is—*negative*.

1.4 How to Use This Book

As this book is a supplement, it should be used differently from a textbook. To begin with, it is not expected that you should read the *entire* book, nor should you necessarily read it in the order presented. If it is required reading for a thermodynamics course, your instructor will sort out the details of what you should read, and when. If you have purchased this book on your own, then you should read whichever sections seem appropriate, or otherwise strike your fancy. Note that there is a lot of cross-referencing, so that if at any point you need something from earlier in the book, you will generally be directed there.

To help you identify which sections of your primary text correspond to specific chapters of this book, please refer to the maps given at the start of each chapter, and on the website. Likewise, the Terminology and Notation Key on p. xviii of this book will sort out any differences in that regard, that might otherwise lead to confusion. Also, don't forget to register on the website, which will open up many more resources to you for free, including textbook-specific materials.

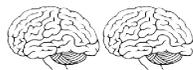
With the exception of this Introduction and the Appendices, in which we deliberately indulge ourselves a bit, the chapters tend to be short and to the point. Generally, the most important or fundamental material is presented towards the front of each chapter, whereas the more advanced or esoteric material is found in the later sections. Sometimes, *marginal notes* will be used to warn you that such material is being approached. In general, marginal notes refer to the period, comma, or italicized word(s) in the line of the main body of text corresponding to the first line of the marginal note.

Your conceptual muscles will also be stretched, in special **To Ponder...** areas. Here is the first To Ponder, referring to Definition 1.1, as presented in Section 1.3:



▷▷▷ **To Ponder...** Definition 1.1 allows for the possibility of multiple definitions for the same thing—provided that all such definitions are equivalent. Does this mean that the definition of “definition” could itself have multiple forms?

Occasionally, you will also encounter the dreaded, *double* brains:



▷▷▷ **To Ponder...at a deeper level.** These areas are reserved for the most advanced material, often relying on such subjects as statistical mechanics or quantum mechanics that may lie well beyond the level of a traditional introductory thermodynamics course. Enter at your own risk! Or, work with a study buddy—two brains are better than one!



On the Website:

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such as this one...

Thus, this marginal note refers to “note,” whereas the marginal note above refers to “*marginal notes*”.

There are also special **Try It!!** areas:



▷▷▷ **Try It!!** Flip through this book and you will find a number of these, encouraging you to conduct various “experiments” or exercises, and exhorting you to look certain things up in your primary textbook.

Also, because students of thermodynamics tend to make the same kinds of mistakes, special warnings are presented in the **Don't Try It!!** areas:



▷▷▷ **Don't Try It!!** Here, we warn you about the most common pitfalls that you should try your best to avoid. Heed our advice, and don't become another statistic!

Likewise, we also offer you useful, practical advice, in their own special **Helpful Hint** areas:



▷▷▷ **Helpful Hint:** Be sure to consult these for useful tips to use when solving thermodynamics homework problems and exercises—tips that you may or may not find in your primary textbook.

Material that (for the most part) can be read independently of the main body of text is sectioned off into gray-boxed areas that we refer to simply as *boxes*. These include examples, derivations, highlights, mathematical discussion, etc. The first box in this book appears on p. 13, with the title, **EXAMPLES: Law vs. Model**. Note that the term “box” refers only to *gray* boxes, and never to the special icon areas discussed above.

though technically, these also have a box around them...

One of the most confusing aspects of thermodynamics study is that many of the equations that one encounters apply only in certain situations. Such *conditional equations* are presented in this book using special formatting. Consider the example below:

$$\text{February has 29 days.} \quad [\text{leap year}] \quad (1.2)$$

The square brackets to the right of the equation indicate the conditions under which it applies.



▷▷▷ **Don't Try It!!** Don't bother trying to memorize all of the conditional equations in this book. This is useless unless you also memorize all of the conditions—and anyway, there are simply far too many of them!



▷▷▷ **Helpful Hint:** In contrast, you *should* memorize the *definitions* of thermodynamic quantities—which according to Definition 1.1, must hold true *always*. You can then derive specific conditional results directly from the definitions, as needed.

In this book, quantities are underlined when defined.

We conclude this Introduction with a discussion of two “catch-phrases” that you will see repeated from time to time throughout this book, describing two principles that are useful to keep in mind.

▷▷▷ **Science Doesn’t Care.** This means that the natural world does not care about how easy or hard it is for us to understand it; it does what it does, regardless. One has to understand science on *its* terms, and not the other way around. Often, this means undermining our own preconceived notions about how things ought to work. On the other hand...

▷▷▷ **It’s OK to be Lazy.** You may have been taught that preconceived notions are a bad thing, but at least they provide a starting point. Rather than completely reinvent the wheel at every turn, scientists *often* borrow ideas from one area to apply to another. And why not, provided that it works? (though be wary of when it *doesn’t* work...) It is important to realize that such a practice is not “cheating,” and should not be considered shameful.

Note that we are *not* talking about the kind of laziness that might lead one to wait until the last possible moment before starting homework assignments or exam study ... As in most fields, success in thermodynamics usually follows from steady, consistent, and disciplined effort.

Isn’t that a preconceived notion of its own?

The practice of borrowing terminology from everyday speech is one such example.

Economy of thought and action is a virtue, not a vice, and well worth trying to master early in life.

