JOHN P. O'CONNELL · J. M. HAILE

THERMODYNAMICS

Fundamentals for Applications

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J. P. O'Connell
University of Virginia

and

J. M. Haile
Macatea Productions

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To Verna and Tricia

If it were easy … it cannot be educational.
In education, as elsewhere, the broad
primrose path leads to a nasty place.

Alfred North Whitehead
"The Aims of Education," in
Alfred North Whitehead, An Anthology,
F. S. C. Northrop and M. W. Gross, eds.,
Macmillan, New York, 1953, p. 90.

remarkable things
occur in accordance with Nature,
the cause of which is unknown;
others occur contrary to Nature,
which are produced by skill
for the benefit of mankind.

Mechanica, Aristotle (384–322 BCE)

Many scholars doubt that the *Mechanica,*
the oldest known textbook on engineering,
was written by Aristotle. Perhaps it was written
by Straton of Lampsacus (a.k.a. Strato Physicus,
died c. 270 BCE), who was a graduate student
under Aristotle and who eventually succeeded
Theophrastus as head of the Peripatetic school.

PREFACE

Thermodynamics is fundamental and applicable to all technical endeavors. Its two brief laws provide a complete basis for establishing the states of pure substances and their mixtures. It shows us the directions in which those states tend to change when systems are prodded by external forces. It provides a secure foundation for scientific investigations into all forms of matter. It reveals constraints on interconversions of heat and work, on separations of components from solutions, and on ultimate extents of chemical reactions. It can guide screening for feasibility of alternative processes, and when a design has been selected, it can contribute to the optimization of that design.

Although thermodynamics describes natural phenomena, those descriptions are in fact products of creative, systematic, human minds. Nature unfolds without any explicit reference to energy, entropy, or fugacity; these are unnatural concepts created by humans. Nevertheless, the complexities observed in Nature can be organized by appealing to thermodynamic methodology. With proper understanding, generalized thermodynamic techniques can be used to deal effectively with many aspects of reality. But to gain that understanding, thermodynamics must be studied in a systematic way that uncovers its structure and economy.

Thermodynamic ideas originated almost 200 years ago, but the subject continues to evolve. Although some claim that "there is nothing new in thermodynamics," scholars still find challenges in its abstractness, rigor, and universality. They debate the "best" ways to phrase its basic principles and to identify the limits of its application. In addition, much current work seeks to extend thermodynamics into new domains of technological development. For example, modern computers enable us to test models at every level of complexity. As a result, thermodynamics is now being used to an unprecedented extent as a basis for creating models that can correlate and predict natural phenomena. In many applications, experimental data are being replaced by modeling and simulation of thermodynamic properties.

But in spite of all this, we have come to the realization that the full power of thermodynamics can be used to advantage only after its foundations are fully assimilated. So in this text we concentrate on fundamentals, rather than modeling, with the belief that a deeper knowledge of the basics will enhance your ability to combine them with models when you need to apply thermodynamics to practical situations.

Over our years of teaching, we have identified three common attitudes that many students bring to an advanced study of thermodynamics. One is "I don't like this stuff, it's too abstract, it's not engineering, so I'll get by as best I can." This attitude springs from frustration with an earlier exposure to the material—an incomplete or misleading experience, often exacerbated by a weak background that cannot support the development of a sound logical structure. These frustrations must be confronted and relieved, if the student is to become self-reliant with thermodynamic concepts and proficient in their use. Self-reliance and proficiency require care, maturity, and intelligence. For these students, a major objective of an advanced course is to overcome confusion and antipathy from earlier exposures, while fully integrating the concepts, knowledge, and procedures. This is a demanding but essential exercise because only then can a learner see full relevance, make prudent applications, and have a satisfying learning experience.

A second attitude stands diametrically opposed to the first: "This stuff is ok; it's just calculus plus reasoning, I could learn it if I really wanted to." With this attitude, students read the text and, feeling quite comfortable, turn the page; but later they have difficulty applying what they've read. Their knowledge is superficial. Perhaps these students delude themselves because the logic of thermodynamics seems relatively straightforward compared to the subtleties encountered when trying to apply that logic in realistic situations. To combat this attitude, we have tried to go well beyond simple derivations of relevant thermodynamic relations; you may find the ratio of words-to-equations much higher here than in many texts. We do not avoid discussing the exceptions, the special cases, the constraints, the limiting behaviors that must be addressed to reach deeper understandings. Nor do we demure from making subjective judgments about relative importance, about issues to be confronted in choosing from among alternatives, about the levels of approximation that can apply to the problem at hand. These kinds of issues constitute a large part of engineering practice, and thermodynamics provides a rich and varied environment in which to develop appreciation for and skill in dealing with such issues—thermodynamics can foster the development of sound engineering judgment.

A third attitude that some students bring to a graduate course can be characterized by thoughts like these: "Where is the equation to solve this problem? Where is the example that shows me how to solve this problem? Where is the solution manual that shows me whether my numerical answer is correct?" Too many students confuse problem solving with studying; too many think the objective in solving a problem is to get a number, so they can move on to the next problem. Too many believe the book, or some book somewhere, has all the answers. In writing this text, we have made determined efforts to subvert these attitudes: we present relatively few worked examples and our examples are not like the problems at the ends of chapters. Many of our problems are not answered with a number, and in many others, the student is to explain or compare or discuss the numbers that have been obtained. Following the advice of master teachers and our own experience, we do not provide a solution manual for the problems.

In solving problems, we expect students to always begin by articulating a general statement or equation that can be expected to apply to nearly any situation; examples include the first and second laws. We call these the *always true*, and we expect students to memorize a small select set of *always true* relations, for at least one of them will apply to any situation. Hence, thermodynamics always gives a starting point for problem solving. In contrast, students are not expected to memorize equations that represent models—except, of course, for very simple ones, like the ideal gas. This approach encourages students to deploy the full power of thermodynamic deduction. It also motivates students to distinguish models from the few really important concepts that apply in most situations. When encountering this approach for the first time, some students become impatient or disdainful. But most grow to appreciate that there are clear rules for distinguishing those few *always true* relations that are to be memorized from those many *always true* relations that can always be derived when needed, just as there are clear rules for distinguishing the *always true* from models, which are always special cases.

But problem solving is only one part of an engineering education, and somehow, in the continuing efforts to convert engineering students into effective problem solvers, more important and rewarding aspects of learning have been ignored: the delight of discovery, the satisfaction of grasping an intricate and convoluted argument, the stimulation from contributing to a wide-ranging enquiry in a scholarly atmosphere. With much of the earlier computational burden now relieved by computers and software, it might be expected that the imbalance of problem solving against deeper understandings would be redressed. But the reality is otherwise, for too often in today's scholasticism, computers have been adopted as tools for even more elaborate problem solving, widening the gulf between computation and thought. This book is an attempt, however modest, to bridge that gulf.

The material in this book is developed for beginning graduate students in chemical engineering, and the needs of those students are, in our view, best served if we focus on macroscopic thermodynamics. In this book, models and molecular concepts are confined to illustrations and brief discussions; nevertheless, studied thoroughly, this material alone is sufficient for a full semester course. Alternatively, to create time to study contemporary applications from other sources, certain chapters (such as 0–6) could be covered less thoroughly or selected sections (some in Chapters 8, 9, 11, and 12) might be omitted. However, because we build a logical structure in a systematic fashion, familiarity with the content of the early chapters is essential if you are to fully comprehend the development and applications presented in later chapters.

Students best overcome misconceptions and grow to reliable, efficient practice when studying with a master teacher. Such study can be enhanced by a textbook that stimulates deeper explorations of the material. Our goal is that this text will stimulate students and their instructors to dig deeper, so they begin to appreciate the distinctive structure of thermodynamics, to become effective in its use, to enrich their vision of Nature's unity and diversity, and to enhance their professional proficiency.

ACKNOWLEDGMENTS

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The page design, composition, and layout for this book were done by Macatea Productions (www.macatea.com).

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INTRODUCTION

You are a member of a group assigned to experimentally determine the behavior of certain mixtures that are to be used in a new process. Your first task is to make a 1000-ml mixture that is roughly equimolar in isopropanol and water; then you will determine the exact composition to within ±0.002 mole fraction. Your equipment consists of a 1000-ml volumetric flask, assorted pipettes and graduated cylinders, a thermometer, a barometer, a library, and a brain. You measure 300 ml of water and stir it into 700 ml of alcohol—Oops!—the meniscus falls below the 1000-ml line. Must have been careless. You repeat the procedure: same result. Something doesn't seem right.

At the daily meeting it quickly becomes clear that other members of the group are also perplexed. For example, Leia reports that she's getting peculiar results with the isopropanol-methyl(ethyl)ketone mixtures: her volumes are *greater* than the sum of the pure component volumes. Meanwhile, Luke has been measuring the freezing points of water in ethylene glycol and he claims that the freezing point of the 50% mixture is well *below* the freezing points of both pure water and pure glycol. Then Han interrupts to say that 50:50 mixtures of benzene and hexafluorobenzene freeze at temperatures *higher* than either pure component.

These conflicting results are puzzling; can they all be true? To keep the work going efficiently, the group needs to deal with the phenomena in an orderly way. Furthermore, you want to understand what's happening in these mixtures so that next time you won't be surprised.

0.1 NATURAL PHENOMENA

These kinds of phenomena affect the course of chemical engineering practice. As chemical engineers we create new processes for new products and refurbish old processes to meet new specifications. Those processes may involve mixing, separation, chemical reaction, heat transfer, and mass transfer. To make homemade ice cream we mix fluids, promote heat transfer, and induce a phase change, without worrying much about efficiency or reproducibility. But to design an economical process that makes ice