

Book Review: *Modern Thermodynamics: From Heat Engines to Dissipative Structures*

Modern Thermodynamics: From Heat Engines to Dissipative Structures.
Dilip Kondepudi and Ilya Prigogine, Wiley, West Sussex, 1998.

This book is divided into five sections: Historical Roots; Equilibrium Thermodynamics, Fluctuations and Stability; Linear Nonequilibrium Thermodynamics; and Order Through Fluctuations. The first two sections are intended as a text for an introductory course in thermodynamics and the last three for an advanced undergraduate or graduate course. Although there are many admirable aspects of this book, I feel that it would not be suitable as a text for an undergraduate or a graduate course. It does make informative and enlightening reading for workers in the field.

My objections to the first part of the book concern a number of careless and imprecise statements. For example: the definition of the calorie on p. 10 does not specify whether the measurement is to be made at constant volume or pressure; the non-operational concept of partial pressure is introduced on pp. 12, 13; not all gasses obey the law of corresponding states as is stated on p. 21; the expression for pV work given on pp. 41 and 42 does not emphasize the fact that the pressure is the external pressure and only for reversible processes is that equal to the pressure of the system; there is no thermodynamic definition of reversible processes presented; Eq. (3.4.16) is always valid for closed systems if it is assumed that all states can be connected by reversible processes; the expressions for G and H given on pp. 127–131 again do not discriminate between the external pressure and the pressure of the system. We emphasize to our students in elementary thermodynamics that when taking partial derivatives it is just as important to specify what variables are to be held fixed as to specify those that vary. Particularly, in the treatment of multicomponent systems in Chapter 5 there is confusion in this text. Two examples of that are the definitions of the chemical potential, μ_k , in Eq. (5.1.4) and Eq. (5.1.7). In Eq. (5.1.4), μ_k should be defined as the partial derivative of G with respect to N_k , the number of moles of species k , at constant T , p and the number of moles of

all other species. In Eq. (5.1.7) it is not all clear what should be held fixed to make the equation valid. It is stated on p. 154 that the heat capacity at constant volume is independent of T which is not true in general. There is no treatment of real gas mixtures. On p. 176, it is stated that phase transformations are caused by heat though they can also be caused by changing the pressure, for example. In the discussion of the Gibbs Phase Rule there is no distinction drawn between species and components and in fact Eq. (7.2.1) is valid whether or not there are chemical reactions in the system if C is the number of components. The chapters on solutions, chemical transformations, and systems in external fields are well done.

It may seem that many of the objections that have been raised above are trivial, but an introductory course in thermodynamics has to be precisely done or else the students will be confused and unable to apply what they have learned.

There are some nice features to these introductory chapters. I particularly enjoyed the historical vignettes. The fact that many of the results given are essentially valid for nonequilibrium systems in which a local temperature can be defined is emphasized and not discussed in most texts.

Part III on Fluctuations and Stability contains chapters on Gibbs Stability Theory, Critical Phenomena and Stability and Fluctuations based on Entropy Production. It is generally successful though I wonder why there are no cross terms in Eq. (12.4.10) between δT and δV for example. At MIT, the material on Gibbs stability theory is presented in the elementary thermodynamics course.

Part IV on Linear Nonequilibrium Thermodynamics is in general well presented although much less complete than the classic text by de Groot and Mazur. There is mention of the formalism of "extended thermodynamics" and I missed having the authors comment on the validity and applicability of that formalism. In Chapter 17 on Nonequilibrium Stationary States there is no mention of the unexpected properties of these states which have long range correlations.

Finally, Part V has chapters on Nonlinear Thermodynamics and Dissipative Structures. Since the authors, and particularly the senior author, have contributed significantly to this field, I expected more insightful discussions. The subject is certainly presented in an adequate fashion.

Despite my comments, I enjoyed reading this book and recommend it to workers in the field if not to neophytes.

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