

# Modern Thermodynamics with Statistical Mechanics

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# Preface

Thermodynamics is not the oldest of sciences. Mechanics can make that claim. Thermodynamics is a product of some of the greatest scientific minds of the 19th and 20th centuries. But it is sufficiently established that most authors of new textbooks in thermodynamics find it necessary to justify their writing of yet another textbook. I find this an unnecessary exercise because of the centrality of thermodynamics as a science in physics, chemistry, biology, and medicine. I do acknowledge, however, that instruction in thermodynamics often leaves the student in a confused state. My attempt in this book is to present thermodynamics in as simple and as unified a form as possible.

As teachers we identify the failures of our own teachers and attempt to correct them. Although I personally acknowledge with a deep gratitude the appreciation for thermodynamics that I found as an undergraduate, I also realize that my teachers did not convey to me the sweeping grandeur of thermodynamics. Specifically the simplicity and the power that James Clerk Maxwell found in the methods of Gibbs were not part of my undergraduate experience. Unfortunately some modern authors also seem to miss this central theme, choosing instead to introduce the thermodynamic potentials as only useful functions at various points in the development.

I introduce the combination of the first and second laws and then the complete set of the potentials appears in chapter four. The remainder of the text is then built on the potentials. Before discussing modern laboratory measurements, for example, I show that the fundamental quantities sought in the laboratory are those which are required for determining the potentials.

The question of how to present our microscopic understanding of matter in a thermodynamics course confronts the author of any text. Presently the subjects of thermodynamics and statistical mechanics are a seamless whole [cf. [154, 155]]. I believe that we should try to convey that to our students without recourse to probability arguments. And so I have elected to present statistical mechanics as an integral part of the text. I begin with a chapter that takes the reader as far as we can go with simple models of molecules. Then I present ensemble theory as succinctly and simply as I am able, with the seamless connection to thermodynamics. Because of the

modern work in Bose Einstein Condensation and in astrophysics, I then added a chapter on quantum statistical mechanics.

Because of its importance in modern applications I have chosen to treat irreversibility and the ideas of Ilya Prigogine. This provides a logical transition into the application of thermodynamics to chemical reactions. And irreversibility is at the center of all of biophysics.

I have used irreversibility as a step to considerations of stability and then to chemical equilibrium, solutions, and the equilibrium of heterogeneous systems. As a physicist I have also looked at chemical reaction rates and transition state theory. TST is a very interesting branch of theoretical physics. I encourage any physicist considering this text to not disregard this chapter.

This text is intended to be used as an introduction to modern thermodynamics and statistical mechanics. I believe it has the depth that can be appreciated without the extreme length to which many textbooks have gone. Consistent with this I have limited the exercises at the end of chapters. The exercises I have used are not intended to teach methods of solution nor are they intended as drill. Some are even intended as vehicles for investigation.

I suspect that my interests as a physicist will be apparent. My original training as an engineer, however, has led me to believe that applications only follow from understanding. Thermodynamics is subtle.

As an author I owe deep debts of gratitude to many that I can never hope to repay. I encountered the beauty and subtlety of thermodynamics first from Jerzy R. Moszynski. I was privileged then to work with David Mintzer and Marvin B. Lewis, from whom I gained an understanding of statistical mechanics and kinetic theory. I am also very grateful to generations of students who have helped this text emerge from my efforts to introduce them to thermodynamics. In an evaluation one student remarked that you have to work to hang on, but if you do the ride is worth it. I am also grateful to those who have been personally involved in the writing of this book. My wife, Betty Jane, has provided patience, understanding, and support, without which this book never would have been written. And Thomas von Foerster read and commended on the first drafts of almost all of the chapters. His critique and insistence have been invaluable.

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