Thermodynamics of the Earth and Planets

This textbook provides an intuitive yet mathematically rigorous introduction to thermodynamics and thermal physics focused on the rich variety of planetary processes. It demonstrates how the workings of planetary bodies can be understood in depth by reducing them to fundamental physics and chemistry.

The book is based on two courses that the author has taught for many years at the University of Georgia. It offers a strong "first-principles" theoretical foundation in classical thermodynamics, yet it also provides many examples of numerical calculations, including a large number of *Maple* procedures that the reader can use and modify, limited only by their interests and imagination. The book assumes that the reader is proficient in calculus and introductory college physics, chemistry and Earth science. All required material beyond this is introduced in the book. The book also includes a large number of bibliographic references and suggestions for further study. There are many "Worked Example" boxes interspersed in the text, and end-of-chapter exercises, which in many cases expand upon the topics covered in the worked examples. Worked solutions to the problems are provided online. The book also includes Software Boxes, which show the reader how to implement numerical solutions to many of the problems, using *Maple*.

As well as being an ideal textbook on planetary thermodynamics for advanced students in the Earth and planetary sciences, it also provides an innovative and quantitative complement to more traditional courses in geological thermodynamics, igneous and metamorphic petrology, chemical oceanography, mineral deposits, planetary geology and planetary atmospheres. In addition to its use as a textbook, it is also of great interest to researchers looking for a "one-stop" source of concepts and techniques that they can apply to their research problems.

- Ties together the physics and chemistry of planetary systems into a single textbook.
- Emphasizes first principles and foundations.
- Contains rigorous mathematical derivation of ALL results.
- Applications and examples are drawn from many different branches of Earth and planetary sciences.
- Contains many worked numerical examples and end-of-chapter problems.
- Includes many downloadable *Maple* routines, explained in Software Boxes.

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Preface

My first words when meeting a new class at the beginning of every semester, whether an introductory physical geology course or a graduate seminar, are always more or less the same: "*Geology does not exist* !". Some students start frantically going over their schedules, wondering whether they are in the right room, but most of them just stare at me, wondering whether I am a lunatic. While they do this I explain that what I meant was that the Earth and other planets are complex systems in which every process can, and must, be dismantled until we can understand it in terms of the simplest possible physics and chemistry. This does little to put them at ease, but over the course of the first few weeks of class many of them come to understand what I mean, and even to agree with it.

This brings me to the several reasons why I decided to write this book. First, although a few good textbooks on thermodynamics applied to Earth systems are available, I find that none of them goes into the fundamentals of thermodynamics with the depth that I am convinced is necessary. Rather, they tend to discuss the foundational principles of thermodynamics on a "need to know" basis. My approach is exactly the opposite: build a solid understanding of the foundations of thermodynamics first, and explain everything else in terms of this understanding. Second, many students in Earth and Planetary Sciences have a tendency to think of our science as standing in splendid isolation of the fundamental sciences, and of the laws of nature that they have painstakingly codified. Yet ultimately everything is physics, and must be understood as such. Third, there is too much of a terrestrial emphasis in all current books on thermodynamics for Earth and Planetary scientists. The diversity of bodies and environments in the Solar System provides a wealth of opportunities to demonstrate the unifying explanatory power of thermodynamics. To name just a few, why not look at cryolavas in Triton and brines on the Martian surface as examples of eutectic melting? At methane–ethane fractionation in Titan's atmosphere and Fe–Ni fractionation during crystallization of planetary cores as examples of binary $T-X$ loops? At the conditions in the Martian mantle to discuss equations of state for solids and the concept of thermal pressure? Or at the evolution of atmospheric composition while making atmospheric mass and gravitational acceleration, and therefore pressure, adjustable parameters? You will find these and other unusual examples in this book. Finally, I think that in order to be complete and useful, a textbook must not only cover the fundamental principles but also show the *full* details of how those fundamental principles and mathematical relationships are converted to numerical results. In this book I show the derivation of every single equation that is used to obtain numerical estimates, and in those cases in which the equations cannot be solved by hand I include open *Maple* procedures that you are free to use, modify and expand as far as your interests and abilities will take you.

Throughout the book I try to emphasize the importance of physical intuition and mathematical rigor, and of striking a balance between the two. The book is organized in 14 chapters, some of them more orthodox than others. The table of contents is fairly self-explanatory, but I wish to highlight some points. The First Law is introduced in Chapter 1, but only after a lengthy discussion of conservation laws in general, and other associated concepts. At the end of Chapter 1 there is a discussion of the nature of planetary materials that I believe can be found nowhere else. The Second and Third Laws must wait until Chapter 4, as Chapter 2 focuses on energy conservation, and the discussions of energy dissipation and thermodynamic cycles in Chapter 3 lead more or less naturally to the need for the Second Law. Thermodynamic potentials, including Gibbs free energy, are introduced in Chapter 4 in a mathematically formal way, i.e. I first demonstrate (rigorously) the properties of the Legendre transform, and only then apply it to derive the various thermodynamic potentials. There is no other way that makes sense. Chapter 2 is a thorough quantitative presentation of all sources of planetary internal energy. I know of no comparable treatment anywhere else. Chapter 3 covers heat diffusion and advection in planetary bodies; it is not intended to substitute the various excellent textbooks that are available on this topic (cited in Chapter 3), but rather as a complement that may add some new twists to this fundamental field. The way I define activity in Chapter 5 is unusual, and owes not a small amount to Guggenheim's unique insight, but it is in my view the most mathematically appealing way of doing it (you may feel Guggenheim's presence in this statement too). Discussion of non-ideal activity is focused chiefly on the concept itself, and on the computational difficulties associated with its mathematical representation. There is simply no space to delve in detail into the huge fields of solution theory in crystals (Chapter 5), fluids (Chapter 9), melts (Chapter 10) and electrolyte solutions (Chapter 11), but I hope that I provide enough background for students to be able to jump directly into the relevant research literature. The equations needed to calculate phase boundaries are developed in full and implemented in a series of progressively more complete *Maple* procedures (Chapters 1, 5, 6, 7, 8 and 9). Feel free to use "black box software" if you wish, but first make sure that you understand where those results come from. I have tried to emphasize the concept of universality of critical behavior by highlighting the similarities among critical mixing phenomena (Chapter 7), lambda phase transitions (Chapter 7) and the critical point of fluids (Chapter 9), without using the word "universality" nor introducing the concept of critical exponents. The interested students should be able to pick it up from here. I emphasize the use of non-dimensional variables as much as possible, including in unusual contexts such as discussion of critical mixing and solvi (Chapter 7), high pressure and temperature behavior of solids (Chapter 8), critical phenomena in fluids (Chapter 9), concentration of non-equilibrium atmospheric species (Chapter 12) and energy dissipation by planetary differentiation (Chapter 2). I have done my best to lay out in simple yet rigorous mathematical terms the sometimes confusing topics of equations of state for solids and thermal pressure (Chapter 8); again, I know of no comparable treatment elsewhere. There is a full discussion of the calculation of species distribution in fluids, both by chemical equilibrium and by Gibbs free energy minimization, including the derivation of all necessary equations and the accompanying implementation in *Maple* (Chapter 9) – I hope that this will demystify what is no more than relatively simple algebra. Chapter 10 is a somewhat unusual take on igneous petrology. My debt to the work of M. Hirschmann, P. Asimow and E. Stolper should be evident here, but I hope to have added some new insights especially with regards to volatile-fluxed melting. I present "toy models" of ozone depletion (Chapter 12) and greenhouse warming (Chapter 13) as applications of chemical kinetics and radiative heat transfer, respectively. Chapter 12 also contains an introduction to non-equilibrium thermodynamics, that I hope to be able to expand upon in the not too distant future. Finally, there is a simplistic but, I believe, fundamental discussion of the origin of life in Chapter 14.

All chapters contain Worked Examples. These are also a fundamental part of the text. Do not skip them, or you will miss explanations and discussions that are not repeated elsewhere. There are also Boxes that contain accessory material that may be skipped without loss of continuity, but to which you should return at some point to clarify the contents of the main text. Finally, there are Software Boxes that contain generally succinct documentation for the *Maple* procedures that can be downloaded from the book's website. I plan on updating and adding to these procedures periodically, and any additional documentation or (inevitable) corrections will also be posted on the website. Please feel free to contact me with suggested changes or additions to the *Maple* library. If you use any of these procedures in published work please cite this book as reference. All figures in this book are my original artwork, and were designed to match specifically the associated content in the text – in fact, in not a few occasions the text was written around the figure. I think that this makes the content much more understandable.

Mike Roden read some of the text and made perceptive comments that I did my best to incorporate. Matt Lloyd at Cambridge was instrumental in getting this project started. I wish to express my gratitude to him and all his staff for their support, encouragement, patience and understanding in the face of missed deadlines. In particular, I wish to thank Assistant Editor Laura Clark, Production Editor, Emma Walker and Copy-editor Beverley Lawrence. My wife Marta has been more patient throughout this project than I have any right to expect, and our son Javier has contributed to it more than he knows – all my love to both of you! Writing this book took about three years and would have been impossible without the company and encouragement offered by our cats, Kali and Watson (to the memory of both of whom I dedicate this book), Ajax, Marx and Engels, and Leonidas and Dottie.