Thermodynamics of Natural Systems

Second Edition

Thermodynamics deals with energy levels and the transfer of energy between states of matter, and is therefore fundamental to many branches of science. This new edition provides a relatively advanced treatment of the subject, specifically tailored to the interests of the Earth sciences.

The first four chapters explain all the necessary concepts of thermodynamics, using a simple graphical approach. Throughout the rest of the book the author emphasizes the use of thermodynamics to construct mathematical simulations of real systems. This helps to make the many abstract concepts accessible. Many computer programs are mentioned and used throughout the text, especially SUPCRT92, a widely used source of thermodynamic data. Links to useful information sites and computer programs as well as problem sets with detailed answers for instructors are available through http://www.cambridge.org/0521847729.

Building on the more elementary material in the first edition, this textbook will be ideal for advanced undergraduate and graduate students in geology, geochemistry, geophysics and environmental science.

Greg Anderson has been Professor of Geochemistry at the University of Toronto for 35 years and is the author of three textbooks on thermodynamics for Earth scientists: *Environmental Applications of Geochemical Modeling* (2002), *Thermodynamics in Geochemistry* (1993) and *Thermodynamics of Natural Systems* (1995). In 2000 he was awarded the Past President's Medal by the Mineralogical Association of Canada for contributions to geochemistry.

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To my dear wife,
Khodjasteh Hedjran Anderson
who made it all possible.

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Preface

Based on inadequate evidence, my own experience, I venture to suggest that the most avid readers of textbooks are the writers of textbooks. This is because writers have to make many choices in presenting any subject, and it is natural to wonder how others have done it. Naturally, after extensive reading, every writer concludes that he or she can do it better in some respect, otherwise why do it?

It usually is not difficult to find reasons to think that one can do it better. For one thing, science has become highly specialized, and there are many such specialized subjects which use thermodynamics in their special ways. For another thing,

> Almost all books on thermodynamics contain some errors which are not purely typographical (Reiss, 1965, Preface, p. ix.)

and so authors, myself included, write books which avoid those errors, and commit different ones.

This book is written for people more or less like myself; those interested primarily not in chemistry but in some aspect of Earth science, especially an aspect involving aqueous solutions. The level of presentation is difficult to define. The book includes almost all the material from the first edition, which was intended as an introduction for second year undergraduates, so selected portions might still be used at that level. However, it now also includes much of the material from a previous book by Dave Crerar and me[1] so it is now suitable for a more advanced course for senior undergraduates or graduate students. All this material has been rewritten and expanded with many examples.

Using thermodynamics and understanding it are two different things, and most of the difficulty in writing about the subject lies in explaining the fundamentals. Just where do all these differential equations come from, and why are such strange concepts useful in real life? There is a persistent trend among authors to see thermodynamics as an experimental science, understood by considering engines, salt solutions, rocks, and so on. In my view it is not. It is a

[1] Anderson and Crerar (1993).

bunch of mathematics, as are all the great theories of physics and chemistry, and the data serve as mathematical variables. The fact that pure mathematics often has relevance to our complex world is an amazing fact, often commented on by philosophers of science. In the first four chapters I try to use this approach to understanding thermodynamics by emphasizing the difference between real systems and our thermodynamic simulations of real systems. A central feature of this is the concept of constraints, introduced by Schottky in 1929 but little used since then. However, this concern for a fundamental understanding of the nature of physical theory, including thermodynamics, does not extend very far. I omit several topics which are considered essential in books written for chemists, including Carnot cycles, temperature scales and absolute zero temperature, and details of the third law. This makes the presentation less than completely rigorous, but based on experience in teaching, I think it better suited to Earth scientists.

In the final chapter I discuss the application of thermodynamics and kinetics to the modeling of processes, but in fact any use of thermodynamics really involves modeling of real systems. I have however tried to be careful about using that term, in view of Leatherdale's observation:

> It is unfortunate that the literature on 'models' displays a bewildering lack of agreement about what exactly is meant by the word 'model' in relation to science. (Leatherdale, 1974, p. 41)

A word about notation. I have considered the IUPAC recommendations (Mills et al., 2001) for units and symbols, and have followed them in most cases. Where I have differed it has been a conscious decision. A list of symbols used with some comments appears in Appendix F.

I thank Edgar Froese for innumerable discussions on thermodynamics and his encouragement in pursuing the constraint idea, and especially for bringing to my attention the work of Schottky, and translating the material in Appendix G. Dr. Alan Harvey made several very useful suggestions on the section dealing with the equation of state for water. Ed Ghent kindly supplied a garnet analysis, and Alex Navrotsky straightened me out on a point in Chapter 14. Eric Reardon made many useful suggestions, especially in Chapter 15. Many conversations with Wayne Nesbitt about activity coefficients were very helpful. Discussions with Norm Evensen over many years about thermodynamics, science, and other things, have helped me in many ways.

I have tried to write the book I wish I had had as a student. It would have saved me a lot of time. I hope it proves useful for others.