THERMODYNAMICS AND INTRODUCTORY STATISTICAL MECHANICS

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To Cecelia
. . .and to William, Diane, Richard, Nancy, and Carolyn

CONTENTS

PREFACE

This book is based on a set of lecture notes for a one-semester first-year chemistry graduate course in *Thermodynamics and Introductory Statistical Mechanics*, which I taught at Florida State University in the Fall of 2001 and 2002 and at various times in prior years. Years ago, when the University was on the quarter system, one quarter was devoted to Thermodynamics, one quarter to Introductory Statistical Mechanics, and one quarter to Advanced Statistical Mechanics. In the present semester system, roughly two-thirds of the first-semester course is devoted to Thermodynamics and one-third to Introductory Statistical Mechanics. Advanced Statistical Mechanics is taught in the second semester.

Thermodynamics is concerned with the macroscopic behavior of matter, or rather with processes on a macroscopic level. Statistical Mechanics relates and interprets the properties of a macroscopic system in terms of its microscopic units. In this book, Thermodynamics was developed strictly from a macroscopic point of view without recourse to Statistical-Mechanical interpretation, except for some passing references to fluctuations in the discussion of critical phenomena. Both Thermodynamics and Statistical Mechanics entail abstract ideas, and, in my opinion, it is best not to introduce them simultaneously. Accordingly, the first 12 chapters (Part I) deal exclusively with Thermodynamics; Statistical Mechanics is only then introduced.

Thermodynamics, unlike some other advanced subjects in Physical Chemistry, does not require complicated mathematics, and for this reason the subject is often thought to be "easy." But if it is easy, it is *deceptively* *easy*. There are subtleties and conceptual difficulties, often ignored in elementary treatments, which tend to obscure the logical consistency of the subject. In this book, conceptual difficulties are not "swept under the rug" but brought to the fore and discussed critically. Both traditional and axiomatic approaches are developed, and reasons are given for presenting alternative points of view. The emphasis is on the logical structure and generality of the approach, but several chapters on applications are included. The aim of the book is to achieve a balance between fundamentals and applications.

In the last four chapters of the book, which are devoted to Statistical Mechanics, not much more can be hoped to be accomplished than to cover, from an elementary point of view, the basics. Nonetheless, for some students, especially those who are not physical-chemistry majors, it is essential that simple statistical-mechanical applications be included, thus acquainting students with some working knowledge of the practical aspects of the subject. Among the applied statistical-mechanical topics are numerical calculations of entropy and other thermodynamic functions, determination of equilibrium constants of gases, and determination of heat capacity of solids.

Although all fundamental equations are developed from first principle, my treatment is more advanced than what some students are likely to have been exposed to in elementary discussions of thermodynamics. This book is designed as a one-semester course, useful both to students who plan to take more advanced courses in statistical mechanics and students who study this as a terminal course.

An essential feature of this book is the periodic assignment of homework problems, reflecting more or less the content of the topics covered. Ten typical problem sets are included in Appendix I and their solutions in Appendix II.

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Bruno Linder

CHAPTER 1

INTRODUCTORY REMARKS

Thermodynamics, as developed in this course, deals with the macroscopic properties of matter or, more precisely, with processes on a macroscopic level. Mechanics (especially quantum mechanics) is concerned with molecular behavior. In principle, and in some limited cases, the molecular properties can be calculated directly from quantum mechanics. In the majority of cases, however, such properties are obtained from experimental studies such as spectral behavior or other devices, but the interpretation is based on quantum mechanics. Statistical mechanics is the branch of science that interconnects these seemingly unrelated disciplines: statistical mechanics interprets and, as far as possible, predicts the macroscopic properties in terms of the microscopic constituents.

For the purposes of the course presented in this book, thermodynamics and statistical mechanics are developed as separate disciplines. Only after the introduction of the fundamentals of statistical mechanics will the connection be made between statistical mechanics and thermodynamics. As noted, the laws of (macroscopic) thermodynamics deal with *processes* not *structures.* Therefore, no theory of matter is contained in these laws. Traditional thermodynamics is based on common everyday experiences. For example, if two objects are brought in contact with each other, and one feels hotter than the other, the hotter object will cool while the colder one will

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heat up. Because thermodynamics is based on the common experience of macroscopic observations it has a generality unequaled in science. “Classical Thermodynamics,” Einstein remarked, “. . . is the only physical theory of universal content . . . which . . . will never be overthrown” (Schilpp, 1949).

1.1 SCOPE AND OBJECTIVES

Class make-up varies greatly. Some students take this course as part of one-year course, in preparation for a comprehensive or preliminary exam, required for a Master’s or Ph.D. degree. Others sign up because they heard it was a “snap” course. Still others take it because they think, or their major professor thinks, that it may help them in their research. A course designed to satisfy all students’ aspirations is difficult, if not impossible. A suitable compromise is one, which provides a reasonable balance between *fundamentals* and *applications*, which is the aim of this book.

1.2 LEVEL OF COURSE

Most students are likely to have had previous exposure to thermodynamics in some undergraduate course, such as physical chemistry, physics, or engineering. The present course is intended to be more advanced from the standpoints of both *principles* and *applications.* The emphasis is on the logical structure and generality of the subject. All topics of interest cannot possibly be covered in a semester course; therefore, topics that are likely to have been adequately treated in undergraduate courses are skipped.

1.3 COURSE OUTLINE

The idea is to proceed from the *general* to the *particular.* The following outline suggests itself.

Part I: Thermodynamics

- *A. Fundamentals*
  1. Basic concepts and definitions
  2. The laws of thermodynamics
     - *2.1 Traditional approach*
     - *2.2 Axiomatic approach*
  3. General conditions for equilibrium and stability

B. Applications
1. Thermodynamics of (Real) gases, condensed systems
2. Chemical equilibrium
    2.1 Homogeneous and heterogeneous systems
    2.2 Chemical reactions
3. Phase transitions and critical phenomena
4. Thermodynamics of one- and two-dimensional systems
    4.1 Film enlarging
    4.2 Rubber stretching

Part II: Introductory Statistical Mechanics

A. Fundamentals
1. Preliminary discussion
2. Maxwell-Boltzmann, Corrected Maxwell-Boltzmann Statistics
3. Partition Functions
4. Thermodynamic connection

B. Applications
1. Ideal gases
2. Ideal solids
3. Equilibrium constant
4. The bases of chemical thermodynamics

In addition, mathematical techniques are introduced at appropriate times, highlighting such use as:

1) Exact and inexact differentials (Section 3.3)
2) Partial Derivatives (Section 3.6)
3) Pfaffian Differential Forms (Section 4.6)
4) Legendre Transformation (Section 5.1)
5) Euler's Theorem (Section 5.7)
6) Combinatory Analysis (Section 13.5)

1.4 BOOKS

Because of the universality of the subject, books on Thermodynamics run into the thousands. Not all are textbooks, and not all are aimed at a particular discipline, such as chemistry, physics, or engineering. Most elementary chemical texts rely heavily on applications but treat the fundamentals lightly. Real systems (real gases, condensed systems, etc) are often not treated in any detail. Some books are strong on fundamentals but ignore applications.

Other books are authoritative but highly opinionated, pressing for a particular point of view.

Two chemical thermodynamics books, which discuss the fundamentals in depth, are listed below.

1. J. de Heer, *Phenomenological Thermodynamics*, Prentice-Hall, 1986.
2. J. G. Kirkwood and I. Oppenheim, *Chemical Thermodynamics*, McGraw-Hill, 1961.

Other books that may provide additional insight into various topics are listed in the Annotated Bibliography on page. . . .

PART I

THERMODYNAMICS