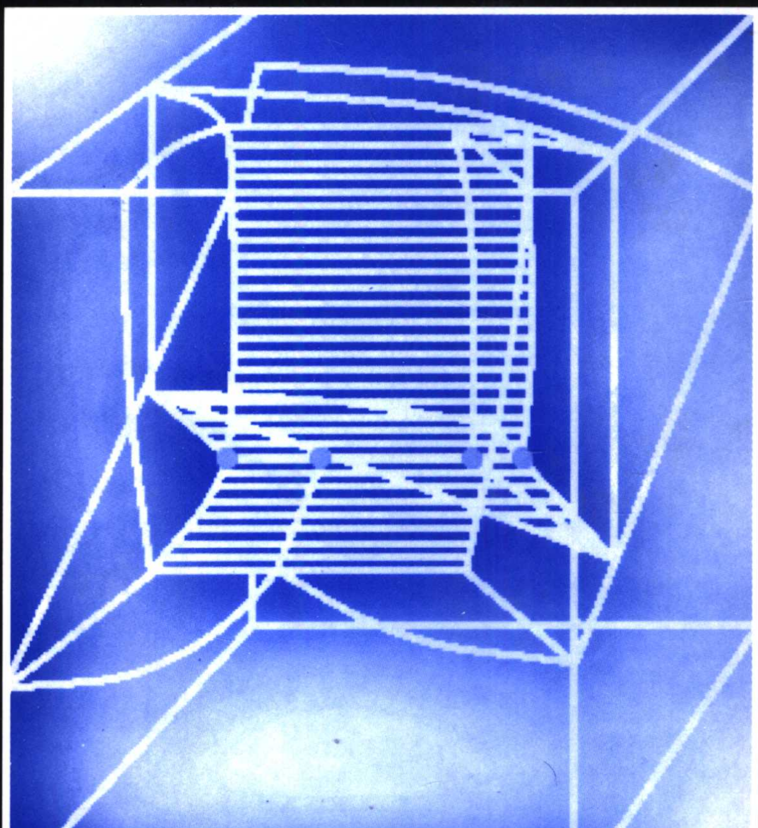
THERMODYNAMICS IN MATERIALS SCIENCE



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PREFACE

In his classic paper in 1883 J. Willard Gibbs completed the apparatus called phenomenological thermodynamics that is used in engineering and science to describe and understand what determines how matter behaves. This work is all the more remarkable in the light of the enormous expansion of our knowledge in science and technology in the twentieth century. During the last century hundreds of books have been written on thermodynamics. In most cases these texts were directed at students in a particular field. Thermodynamics plays a key role in chemistry, physics, chemical engineering, mechanical engineering, engineering science, biology, and materials science and engineering. Each presentation offered its own slant for its intended audience. Several of these texts are classics that have endured for decades experiencing many revisions and many printings.

An author who undertakes an introductory text in thermodynamics in the face of this history had better be:

a. Sure of his or her subject, and

b. Have something unique to say.

After teaching introductory thermodynamics to materials scientists for nearly three decades at both the graduate and the undergraduate levels, I am convinced that the approach used in this text is both unique and in many ways better than those available elsewhere.

Thermodynamics in Materials Science is an introductory text, intended primarily for use in a first course in thermodynamics in materials science curricula. However, the treatment is sufficiently general so that the text has potential applications in chemistry, chemical engineering, and physics, as well as materials science. The treatment is sufficiently rigorous and content sufficiently broad to provide a basis for a second course either for the advanced undergraduate or at the graduate level.

Thermodynamics is a discipline that supplies science with a broad array of relationships between the properties that matter exhibits as it changes its condition. All of these relationships derive from a very few general and pervasive principles (the laws of thermodynamics) and the repetitive application of a very few very general strategies. It is not a collection of independent equations conjured out of misty vapors by an all-knowing mystic for each new application. There is a structure to thermodynamics that is both elegant and, once contemplated, reasonably simple.

The approach that undergirds the presentation in this text emphasizes the connections between the foundations and the working relations that permit the solution of practical problems. In this emphasis, and in its execution, it is unique among its competitors. This difference is crucial to the student seeing the subject for the first time.

Most texts spend a significant quantity of print and students' time in presenting the laws of thermodynamics, and in laying out arguments that justify the laws and lend intuitive interpretation to them. This presentation is based upon the recognition that such diversions are generally a significant waste of time and effort for the student, and, what is worse, are usually confusing to the uninitiated. Worse still, students may be left with an inadequate intuition that merely serves to mislead them when they attempt to apply it to complex systems. Thermodynamics is fundamentally a rational subject, rich with deductions and derivations. Intuition in thermodynamics is not for the uninitiated.

Thus, the laws are presented as *fait accompli*: "great accomplishments of the nineteenth century" that distilled a broad range of scientific observation and experience into succinct statements that reflect how the world works. Best at this beginning stage that these laws be presented with clear statements of their content, without the perpetual motion arguments, Carnot cycles, and other intuitive trappings.

The most significant departure of this text from its competitors lies in the treatment of the concept of *equilibrium* in complex physical systems, and in the presentation of a *general strategy for deriving conditions for equilibrium* in such systems. A *general criterion for equilibrium* is developed directly from the second law of thermodynamics. The mathematical procedure for deriving the equations that describe the internal condition of a system when it is at equilibrium is then presented with rigor. It is the central viewpoint of this text that, since all of the "working equations" of thermodynamics are mathematical statements of these internal conditions for equilibrium, establishment of the connection between these conditions and first principles is crucial to the development of a working understanding of thermodynamics. Indeed, the remainder of the text is a series of applications of this general strategy to the derivation of the conditions for equilibrium in systems of increasing complexity, together with strategies for applying these equations to solve problems of practical interest to the student. With each increment in the level of sophistication of the system being treated, new parts of the apparatus of thermodynamics are introduced and developed as they are needed. The general strategy for getting to the working equations is the same for all of these applications. Thus, the connection to the fundamental principles is visible for each new development. Further, this connection can be maintained without introducing any mathematical or conceptual shortcuts. Repetition builds confidence; rigor builds competence.

One early chapter introduces the concepts of statistical thermodynamics. This subject is treated as an algorithm for converting an atomic model for the behavior of a system, formulated as a list of the possible states that each atom may exhibit, into values of all of the thermodynamic properties of the system. The strategy for deriving conditions for equilibrium applies in this case to the derivation of the Boltzmann distribution function, which reports how the atoms are distributed over the energy levels when the system attains equilibrium. The algorithm is then illustrated for the ideal gas model and for the Einstein model of a crystal. Statistical thermodynamics is used very little in subsequent chapters because the classes of systems that are the domain of materials science tend to be too complex for tractable treatment, much less for presentation to first-time students of the subject.

Most chapters contain several illustrative examples designed to emphasize the strategies that connect principles to hard numerical answers. Each chapter ends with a summary that reviews the important concepts, strategies, and relationships that it contains. Each chapter also ends with a collection of homework problems. Many of these are designed so that they are best solved using a personal computer; the astute student will find it useful to write some more general programs that can be used repeatedly as the level of sophistication increases. Examples and homework problems will be drawn more or less uniformly from the major classes of materials: ceramics, metals, polymers, electronic materials, and composites. This approach serves to illustrate the power of the concepts, laws, and strategies of phenomenological thermodynamics by demonstrating that they can be applied to all states of matter.

The experience gained in twenty-five years of teaching an undergraduate course in thermodynamics in materials science, together with more than fifteen years of teaching a graduate course in the same area, has resulted in an approach to the topic which is unique. This approach accents rigor, generality, and structure in developing the concepts and strategies that make up thermodynamics. Because the connections between first principles and practical problem solutions are clearly and sharply illuminated, the first-time student can hope not only to apply thermodynamics to the sophisticated kinds of system that are the bread and butter of materials science, but to understand their application.

It is a pleasure to acknowledge the help of Heather Klugerman who provided advice in the more sophisticated aspects of word processing involved in putting together this text. Pamela Howell proofread the manuscript with remarkable skill before it was submitted to the publisher. David C. Martin, University of Michigan, and Monte Pool, University of Cincinnati, offered many helpful comments and suggestions while reviewing the manuscript. My thanks to the many students, both graduate and undergraduate, who for many years encouraged me to undertake this text. Finally, I am grateful to my wife, Marjorie, who sacrificed many evenings, weekends, and vacations as I disappeared into the den to work on the project.

Robert T. DeHoff

CONTENTS

CHAPTER 1

INTRODUCTION

What determines how matter behaves?

This question has been at the core of scientific enquiry since man became curious about his environment. As the human experience unfolded, answers to this question were first shrouded in mysticism. Occasional flashes of insight flared in the mist, parting it, only to be engulfed again in the fog. Scientific understanding of this question began to emerge when Sir Francis Bacon suggested that we *examine* the behavior of matter in our attempt to explain its behavior, rather than accepting mystical explanations handed down from the ancients. Acceptance of the notion of experimental science required several centuries to digest, and clear demonstrations that this approach to the question in fact works by an ever increasing number of protagonists such as Copernicus, Kepler, Galileo, and ultimately Isaac Newton.

By the nineteenth century this *mechanical* description of the behavior of matter was well established, but it was also becoming evident that this view was incomplete. Mechanics recognized that the behavior of matter could be described in terms of two fundamental ideas, one associated with the *motion* of matter and the other associated with its *position* in a potential field. These rudimentary notions were formalized as *kinetic energy* and *potential energy*. However, experimental studies of the behavior of matter made it clear that the condition of matter in a system could be influenced by factors *besides* its motion and position.

The most obvious of these influences is formulated in the concept of *heat*. Once the idea of temperature appeared and was quantified, it became clear that the aspect of the system behavior indicated by temperature could be altered for matter at rest in its surroundings. Thus, some influence beside kinetic and potential energy could change the condition of matter.

It also became evident that a system could be made to expand and contract by supplying or removing heat. This motion is such that some of the parts enclosing a system could be put to use to do work previously done by men or beasts of burden, for example, to raise water from a well. The idea of *pressure* inside such a system served to quantify this aspect of the behavior of matter. These mechanical effects could, like heat, be made to occur without moving the center of mass of the system, and thus were influences not included in a picture restricted to kinetic and potential energy.

The realization that these various influences could be converted from one form to another set the groundwork for a general description of the behavior of matter. The heat from the fire in a rudimentary steam engine could be converted into the work of expanding the steam in a piston, which could in turn be converted into the work of raising a weight in a gravitational field. It was noted that the mechanical work done by a boring tool in making a cannon made the barrel hot. The observation that heat from the fire was produced by matter conversions, recognized to be chemical changes, added yet another class of influences capable of altering the condition of matter at rest. The notion evolved to an understanding that these influences were all different manifestations of the same thing.

In its origins, *thermodynamics* focused upon the most rudimentary effects beyond kinetic and potential energy: mechanical work derived from expansion and contraction of the system, and heat. In practical settings these effects were primarily viewed in terms of understanding how transfers of heat influenced matter. Since in mechanics, the description of the motion of matter was called dynamics, it was reasonable to refer to this developing field as *thermodynamics*.

As the field evolved it gradually grew in scope to encompass *all* of the influences that could affect the condition of matter, and all of the interrelations that could exist among these influences. Eventually, that expansion in scope came to embrace not only thermal, mechanical, and chemical effects, but also the original influences of mechanics including kinetic energy and the complete set of potential energies that physics enumerates: gravitational, electrical, magnetic, and body forces.

The development of the thermodynamic view of what determines how matter behaves reached a pinnacle in 1883 with the publication of J. Willard Gibbs' classic paper, "On the Equilibrium of Heterogeneous Substances." In this single publication Gibbs completed the apparatus of thermodynamics, providing the formalism that has come to be accepted as the basis for the description of all phenomena that influence the condition of matter. With the exception of atomic energy, which essentially adds a term to the apparatus, and was of course unknown to him, Gibbs set out the general principle for determining the equilibrium condition of matter of arbitrary complexity, defined all of the properties necessary for the description of the state of matter at rest and in equilibrium, and laid out the strategy for computing changes in the state of matter that occur when it is taken through processes of arbitrary complexity. During the past century many of the most widely used textbooks in thermodynamics are, as they are intended by the authors to be, elaborations of Gibbs' classic paper. This text is no exception.

What determines how matter behaves?

The answer to this question can be presented on a variety of levels of sophistication. The first is *phenomenological thermodynamics*, the primary subject of this text, which focuses upon the phenomena that matter can experience as exposed by experimental observation. This level of description of the behavior of matter seeks a complete enumeration of all the kinds of behavior that are possible, and all the observed relationships that exist among the various classes of behavior. It is unnecessary to know the nature of the constitution of matter in order to apply this level of description; it is only necessary to know what phenomena are possible. For example, in order to predict the change in volume that a system experiences when its temperature is raised, it is only necessary to measure the coefficient of thermal expansion for that substance. It is not necessary to explain why that particular substance has the value of the coefficient of expansion that it has in comparison with other systems; it is sufficient to have measured it experimentally.

The second level of sophistication in answering the fundamental question is *statistical thermodynamics*. This level attempts to explain why different substances have different values of their properties, and, indeed, to predict the values of their properties from a knowledge of the *structure* of matter. In its most rudimentary form, which is the kinetic theory of gases, this description begins with the assumption that matter is composed of atoms that are particles of a known mass and with a known distribution of velocities. As our breadth of experimental knowledge expanded, it became clear that these aspects of the behavior of matter required a more comprehensive view of its structure. The atom itself has an internal structure composed of a nucleus and surrounding electron cloud. The nucleus has a structure, as does the electron cloud. The atoms arrange themselves into molecules with a molecular structure that dictates much of their chemical behavior. In most solids, the atoms or molecules form a regular crystal structure. The crystal structure has defects that play a dominant role in some of its properties. The crystals fit together to form the *microstructure* of the system. Each level in this hierarchy of structures has an influence on the behavior of matter. It is the bold goal of the statistical thermodynamics of matter to explain, and ultimately predict, its properties and behavior from a knowledge of its structure.

A third, more sophisticated and more fundamental level of answer to the basic question, seeks to explain why the structure of atoms and molecules is as it is observed to be. *Quantum mechanics* formulates descriptions of isolated single atoms, as well as ensembles of atoms in molecules, liquids, and crystals, that yield predictions of the electronic structure. The spatial distribution of the electron cloud provides the basis for computing some subset of the properties of the system, which may then be tested more or less directly by experiment.

The practical everyday encounters with the question, "What determines how matter behaves?" are best handled with phenomenological thermodynamics. This apparatus is capable of describing the behavior of very complex systems that may experience very complex processes. The more fundamental understanding, embodied in statistical thermodynamics, provides the basis for generalizing our understanding of the behavior of matter. However, since the formalism is complicated, its application is limited to relatively simple systems. The computations of quantum mechanics are extremely involved and lengthy, severely restricting their application in practice. With the exception of Chap. 6, Statistical Thermodynamics, this text presents the practical apparatus of phenomenological thermodynamics formulated by Gibbs.

Because it explains what determines how matter behaves in the most complex kind of system, thermodynamics lies at the foundation of materials science. More than any other branch of science and engineering, materials science requires the full breadth of the thermodynamic apparatus. An understanding of how microstructures of materials evolve, a prerequisite for controlling the properties of materials, begins with the phase diagrams of these multicomponent, multiphase systems. Chemical reactions with the environment may limit the useful lifetime of a material at high temperatures, or in other situations may be used to protect a material during processing. Adsorption and capillarity effects are key factors in determining the development of microstructures. Electrochemical behavior may degrade a material by corrosion, or it can be used to protect or even purify it. Thus the full apparatus of phenomenological thermodynamics presented in this text finds application in materials science presented at the undergraduate level.

Ultimately, the most profound formulation of the question, "What determines how matter behaves?" enters the realms of philosophy, metaphysics or theology. Some of the brightest minds in human science have illuminated the sharp outlines and internal structure of the stuff of which the universe is made and the mechanism that operates it. The light of reason has penetrated deeply into the structure but the ultimate foundation remains shrouded in mysticism.

CHAPTER 2

THE STRUCTURE OF THERMODYNAMICS

Thermodynamics is rooted in logic and reason. At its foundation are a very few, very general, and therefore very powerful principles: the Laws of Thermodynamics. From these few principles can be deduced predictions about the behavior of matter in a very broad range of human experience. This structure can be visualized as an inverted pyramid with the laws at the apex and the consequences or deductions expanding upward and outward as the range of applications is developed. An understanding of how matter behaves in every situation rests directly upon these laws.

In their simplest and most general form the laws apply to the universe as a whole:

1. There exists a property of the universe, called its *energy*, which cannot change no matter what processes occur in the universe.
2. There exists a property of the universe, called its *entropy*, which can only change in one direction no matter what processes occur in the universe.
3. A universal absolute temperature scale exists and has a minimum value, defined to be *absolute zero*, and the entropy of all substances is the same at that temperature.

More precise mathematically formulated statements of the laws are developed in Chap. 3.

In practice the focus of thermodynamics is on a subset of the universe, called a *system*, Fig. 2.1. In order to apply thermodynamics, the first step is to identify the

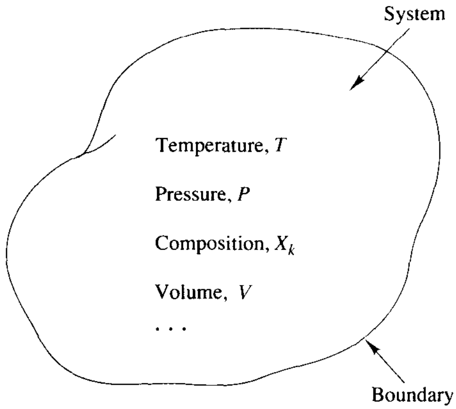

FIGURE 2.1
The subset of the universe in focus in a particular application of thermodynamics is usually called the *system*. At any given instant of observation, the condition of the system is described by an appropriate set of *properties*. Limitations on changes in these properties are set by the nature of its *boundary*.

subset of the universe that encompasses the problem at hand. It is necessary to be explicit about the nature of the contents of the system, and the specific location and character of its boundary.

The condition of the system at the time of observation is described in terms of its *properties*, quantities that report aspects of the condition of the system such as its temperature, T, its pressure, P, its volume, V, its chemical composition, and so on. As the system is caused to pass through a *process*, its properties experience changes, Fig. 2.2. A very common application of thermodynamics is the calculation of the changes in the properties of a specified system as it is taken through some specified process. Thus, an important aspect of the development of thermodynamics is the deduction of *relationships* between the properties of a system. Changes in some properties of interest, such as the entropy of the system can be computed from information given or determined about changes in other properties of the system such as temperature and pressure.

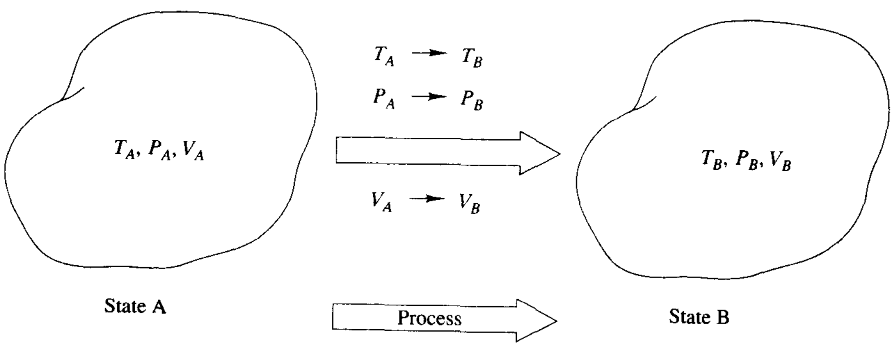

FIGURE 2.2
A *process* is a change in the condition or state of the system. Properties change from their values in some initial state A to some final state B.