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Equilibrium Thermodynamics

 Springer

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to my beloved wife
Tânia

Preface

If a birth date could be assigned to the science of thermodynamics, it would certainly be the day of publication of the Clausius article on the first and second law of thermodynamics, occurred in 1850. Independently, these two laws were also laid by Kelvin. Both authors arrived at the two fundamental laws of thermodynamics relying on the ideas of Carnot on the operation of heat engines and on the work of Mayer and Joule on the mechanical equivalent of heat. Subsequently, the thermodynamic theory received contributions from other authors including Maxwell and Helmholtz. We point out the fundamental contribution of Gibbs whose formulation of the thermodynamics on the basis of the convexity properties of the thermodynamic potentials is that we follow in this book starting from Chap. 3.

By its origin thermodynamics is closely related to the study of heat engines and thermodynamic processes. However, the science of thermodynamics should also be understood as the study of thermodynamic properties of substances. In this book, we adopt the point of view according to which thermodynamics is concerned with the study of macroscopic properties obtained from macroscopic laws. This does not mean that the laws of thermodynamics can not be obtained from microscopic laws. We just understand that this task belongs to the domain of another discipline, the statistical mechanics.

In the first two chapters of this book we use the thermodynamic processes to introduce the first law of thermodynamics, which we call Joule principle, and the first part of the second law of thermodynamics, which we call Carnot principle, which allows us to define the absolute temperature and entropy. In Chap. 3 we present the principle of maximum entropy as introduced by Gibbs, which corresponds to the second part of the second law of thermodynamics. This principle leads to the convexity of thermodynamic potentials, studied in Chap. 4 along with the Legendre transformations. Chapter 5 is reserved for the analysis of the consistency of equations of state and Maxwell relations. The Nernst-Planck principle, which is the third law of thermodynamics, is presented in Chap. 6.

This book treats not only the fundamental principles of thermodynamics but also the thermodynamics of phase transitions and critical phenomena observed in various types of systems. Initially, we study the transitions between ordinary phases,

solid, liquid and vapor, in pure substances and in binary mixtures. We then examine the transitions of the order-disorder type in binary alloys and then pass to the study of phase transitions in magnetic systems, that include the ferromagnetic and antiferromagnetic materials, and in dielectrics.

The chapter on the Gibbs phase rule and the structure of the phase diagrams of multicomponent systems is based on the work of Griffiths and Wheeler. The study of criticality is done in accordance with the view that the systems have universal behavior in the critical region and can be described by the scaling theory introduced by Widom. In the study of phase transitions and criticality we use equations of state that are introduced ad hoc and whose most notorious example is the van der Waals equation. Such equations, in spite of being different, describe the same critical behavior if they have the same symmetries. This universal behavior can be understood by the Landau theory of phase transitions, also described in this book.

Other topics studied in this book include the thermodynamics of solids, liquid crystals, thermal radiation and thermochemistry. We examine the structural phase transitions and the phase transitions occurring between the mesophases of liquid crystals. In the study of thermal radiation we arrive at the Planck distribution by a thermodynamic reasoning. The last chapter concerns the equilibrium thermodynamics of chemical reactions.

São Paulo, Brazil
May 2013

Mário J. de Oliveira

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