Preface

The present work is based on our two previous books published in Polish and entitled (in English translation): *Thermodynamics for chemists, physicists and engineers* [6] and *Thermodynamics by exercises* [7]. The first one, besides the part devoted to the fundamentals of phenomenological thermodynamics and its application to phase transitions and chemical reactions, contains also an introduction to statistical thermodynamics written by Alina Ciach. The second book is a collection of exercises on thermodynamics together with their solutions, which correspond to the material presented in [6]. The motivation for writing of these books was the lecture on thermodynamics with the elements of statistical mechanics, given by us at the College of Science, which was a part of the physical chemistry course for the 2nd year undergraduate students. Presently the College of Science forms the department of mathematics and science at the University of Cardinal Stefan Wyszyński in Warsaw, but originally it was established due to the initiative of a few research institutes of the Polish Academy of Sciences, including the Institute of Physical Chemistry where we are employed, and still benefits from their scientific and research potential. Because of large diversity of research carried out in the institutes of the Polish Academy of Sciences, the studies in the College of Science are of interdisciplinary character. Therefore the course of thermodynamics differs from traditional courses of this subject at the physics or chemistry departments. In spite of many excellent textbooks in this field it was difficult to find one, at rather an elementary level, whose scope would correspond to the material lectured by us. This fact inclined us to write a textbook adapted to our needs. However, in the course of writing, we decided that if we extended somewhat the scope of the book, it could also be useful for the Ph.D. students in our institute, who after the second year of studies are obliged to pass an examination on physical chemistry, which is roughly at the level of P.W. Atkins' book [1].

The present book is not simply a compilation of [6] and [7], since we have introduced many significant changes and improvements. Moreover, as we did not want the book to grow in size too much, we decided to limit its scope to phenomenological thermodynamics. To facilitate its use, we have highlighted in the text the postulates and laws of thermodynamics, as well as the most important definitions

and conclusions. Mathematical digressions are included in the main text, instead of appendices, as we think that the formalism used in thermodynamics should be treated as its integral part. We pay special attention to the compatibility of definitions, terms, units and notation used in our book with the recommendations of the International Union of Pure and Applied Chemistry (IUPAC) [4].

The book is divided into three parts. At the end of each chapter, there are exercises whose solutions are given at the end of the book. The first part, consisting of five chapters, contains the postulates and laws of phenomenological thermodynamics together with examples of their application. In Chaps. 2 and 3, we introduce and discuss the basic concepts and quantities, such as the equilibrium state, parameters and functions of state, thermodynamic process, pressure, temperature, internal energy, heat and chemical potential, relying mainly on the reader intuition. Writing Chaps. 4 and 5, we were inspired with Callen's book [3]. Chapter 4 is mainly devoted to entropy and the second law of thermodynamics and to the conclusions following from that law. In Chap. 5, we discuss the thermodynamic potentials and natural variables, and also the conditions of intrinsic stability for a pure substance. Less advanced readers can skip the last point.

The second part is devoted to application of thermodynamics to phase transitions in pure substances (Chap. 6) and in mixtures (Chaps. 8 and 9); Chap. 7 is an introduction to thermodynamics of multicomponent systems. In Chap. 6, we give general classification of phase transitions and a few examples of first order and continuous transitions. In the rest of the book, however, we restrict ourselves to first order transitions. The concept of ideal mixture is introduced in Sect. 7.5. Less advanced readers can skip Sects. 7.2 and 7.6. The discussion of phase transitions in mixtures is limited to the case of two-component systems. In Chap. 8, we discuss the phenomena that can be explained by the model of ideal mixture. Non ideal mixtures are considered in Chap. 9. In this case, we study the simplest extension of the ideal mixture model called the simple solution. To understand the whole material presented in this chapter the reader who skipped Sects. 7.2 and 7.6 should return to them. However, less advanced students can skip the formal part of Chap. 9 and concentrate on the phase diagrams presented.

In part three, we consider thermodynamic systems in which chemical reactions occur. Chapter 10 concerns reactions between electrically neutral compounds. The law of mass action, which follows from the condition of chemical equilibrium, is derived for a mixture of ideal gases. Therefore the material presented in this chapter should be understood also by less advanced students. Chapter 11 concerns electrochemical systems, in which chemical reactions occur between ions. Our main aim was to show that due to a chemical reaction a system can perform work other than the mechanical one, which in the framework of thermodynamics can be explained by means of a reversible cell. This chapter is mainly for more advanced graduate students.

We know from our own experience that for the second year students the concepts of the differential and differential form are rather difficult. Since these concepts are crucial for the whole course of thermodynamics, we have tried to explain them in a simple way without going into mathematical details. The second crucial mathematical concept, which is used to introduce the thermodynamic potentials, is the

Legendre transformation. Obviously one can define enthalpy or the Helmholtz or Gibbs free energy without any reference to that concept. On the other hand, we think that it is easier to understand properly the meaning of natural variables of a thermodynamic potential in terms of the Legendre transformation, which was shown in an elegant way by Callen [3].

The exercises together with solutions are to help the readers to evaluate their understanding of the material learned. We believe that our book can be useful both for the students of physics, especially for those who want to extend their knowledge in the direction of physical chemistry, and for the students of chemistry who can treat it as a part of the physical chemistry course. Also students of some engineering departments or biology may use it.

Although the subject of our book is phenomenological thermodynamics, in a few places we refer to statistical mechanics. To the readers who wish to learn more about this important branch of science we recommend the classical books [8] and [14]. From among other books on thermodynamics, physical chemistry and chemistry used by us, we recommend references [9], [15], [13], [1] and [11], and for advanced readers also [5], [10] and [12]. References [16] and [2] can serve as an introduction to the field of phase transitions and critical phenomena.

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