

# Chapter 1

## Introduction

Physical chemistry deals with general properties common in different materials despite their chemical diversity. Properties referring to materials stored in a container – i.e., materials “at rest,” without temporal changes – have a special importance. These materials are told to be in an “equilibrium state” and are described by the science called *thermodynamics*. Equilibrium states can be very different depending on the circumstances; thus, one of the major aims of thermodynamics is to quantitatively characterize materials within different conditions and the changes accompanying their transition to a new state. The term “thermodynamics” has a historical origin. At the beginning of the nineteenth century, there was an attempt to understand the underlying principles of the efficiency of steam engines already in operation. The basic problem of the investigations was the transformation of heat into mechanical work. The Greek word *θερμη* [therme] means hotness (heat), while another Greek word, *δυναμις* [dynamis] means the ability to act (power). Putting the two words together expressed the basic direction of this research. (The branch of mechanics dealing with movements is also called dynamics, originating from the same Greek word. Based on this, some authors criticize the name thermodynamics and propose *thermostatics* instead, as the underlying Greek word (*στασις* [stasis] = state) refers more directly to equilibrium states. These critics are not really relevant since actual names of branches of science are arbitrary, having a historical origin.) The term “thermodynamics” survived, even though this science explains a lot more than the efficiency of heat engines.

There are other branches of physics dealing with the characterization of equilibria; mechanics with equilibria of mechanical interactions, electrostatics with that of electric interactions, magnetostatics with that of magnetic interactions, and the calculations of interaction energies. Thermodynamics includes all these interactions but includes in addition the influence on interaction energies of the state of “hotness” (or coldness) of matter. It will be clear from molecular (or statistical) thermodynamics that the temperature-dependent energy involves changes in the molecular modes hidden at the macroscopic level. These molecular modes cannot be observed directly by measuring macroscopic quantities only, but the consequences of their changes are accessible for macroscopic observations.

Thermodynamics differs basically from other branches of physics by considering this *thermal energy* and other *thermal properties*.

*Chemical thermodynamics* – in addition to what physicists and civil engineers usually learn as thermodynamics – deals with materials and properties where the chemical composition and its change are especially important. Quantitative relations concerning composition and its change are usually rather complicated. There is a special role of traditions and conventions established during the development of this science to describe the “chemical” aspects. This book – after a concise introduction to the principles of thermodynamics – concentrates on the thermodynamic description depending on the composition of equilibrium states and a detailed discussion of the underlying conventions. To establish the general principles is unavoidable before actual applications to chemically interesting systems, thus the first part of the book describes the very foundations of thermodynamics.

As mentioned before, the science of thermodynamics was developed by the interpretation of how steam engines, or in a wider sense and after later inventions, heat engines in general operate. This is the reason why its traditional treatment is based on conclusions drawn from the operation of those engines. This treatment is quite complicated and is not best suited to develop the principles underlying chemical applications. There is another possibility to set the foundations of a science, as it is common practice, e.g., in geometry, number theory, probability theory, or in physical sciences like mechanics, electrodynamics, and quantum mechanics. This is the *postulatory* foundation when a few *postulates* (or *axioms*) are formulated, from which all theorems can be proved or all important relations derived. Already at the end of the nineteenth century, the American physicist Josiah Willard Gibbs proposed mathematically sound foundations of thermodynamics, but a genuine system of postulates has only been formulated in the middle of the twentieth century, mainly due to László Tisza, an American physicist of Hungarian origin. The treatment of this book concerning the foundations of thermodynamics is closely related to the frequently referred textbook by Herbert B. Callen (a former student of Tisza) published 1960 with the title “Thermodynamics,” as well as its second edition published 1985. In addition to this – concerning especially statistical thermodynamics and chemical applications – a number of other textbooks have been used as resources, which are listed at the end of the chapters.

## Further Reading

Callen HB (1985) Thermodynamics and an introduction to thermostatistics, 2nd edn. Wiley, New York