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Thermodynamics

For Physicists, Chemists and Materials
Scientists

 Springer

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Preface

Many of us associate thermodynamics with blotchy photographs of men in old-fashioned garments posing in front of ponderous steam engines. In fact thermodynamics was developed mainly as a framework for understanding the relation between heat and work and how to convert heat into mechanical work efficiently. Nevertheless, the premises or laws from which thermodynamics is developed are so general that they provide insight far beyond steam engine engineering. Today new sources of useful energy, energy storage, transport, and conversion, requiring development of novel technology, are of increasing importance. This development strongly affects many key industries. Thus, it seems that thermodynamics will have to be given more prominence particularly in the physics curriculum—something that is attempted in this book.

Pure thermodynamics is developed, without special reference to the atomic or molecular structure of matter, on the basis of bulk quantities like internal energy, heat, and different types of work, temperature, and entropy. The understanding of the latter two is directly rooted in the laws of thermodynamics—in particular the second law. They relate the above quantities and others derived from them. New quantities are defined in terms of differential relations describing material properties like heat capacity, thermal expansion, compressibility, or different types of conductance. The final result is a consistent set of equations and inequalities. Progress beyond this point requires additional information. This information usually consists in empirical findings like the ideal gas law or its improvements, most notably the van der Waals theory, the laws of Henry, Raoult, and others. Its ultimate power, power in the sense that it explains macroscopic phenomena through microscopic theory, thermodynamics attains as part of Statistical Mechanics or more generally Many-body Theory.

The structure of this text is kept simple in order to make the succession of steps as transparent as possible. The first chapter (*Two Fundamental Laws of Nature*) explains how the first and the second law of thermodynamics can be cast into a useful mathematical form. It also explains different types of work as well as concepts like temperature and entropy. The final result is the differential entropy change expressed through differential changes in internal energy and the various types of work. This is a fundamental relation throughout equilibrium as well as non-equilibrium thermodynamics. The second chapter (*Thermodynamic Functions*),

aside from introducing most of the functions used in thermodynamics, in particular internal energy, enthalpy, Helmholtz, and Gibbs free energy, contains examples allowing to practice the development and application of numerous differential relations between thermodynamic functions. The discussion includes important concepts like the relation of the aforementioned free energies to the second law, extensiveness, and intensiveness as well as homogeneity. In the third chapter (*Equilibrium and Stability*) the maximum entropy principle is explored systematically. The phase concept is developed together with a framework for the description of stability of phases and phase transitions. The chemical potential is highlighted as a central quantity and its usefulness is demonstrated with a number of applications. The fourth chapter (*Simple Phase Diagrams*) focuses on the calculation of simple phase diagrams based on the concept of interacting molecules. Here the description is still phenomenological. Equations, rules, and principles developed thus far are combined with van der Waals' picture of molecular interaction. As a result a qualitative theory for simple gases and liquids emerges. This is extended to gas and liquid mixtures as well as to macromolecular solutions, melts, and mixtures based on ideas due to Flory and others. The subsequent chapter (*Microscopic Interactions*) explains how the exact theory of microscopic interactions can be combined with thermodynamics. The development is based on Gibbs' ensemble picture. Different ensembles are introduced and their specific uses are discussed. However, it also becomes clear that exactness usually is not a realistic goal due to the enormous complexity. In the sixth chapter (*Thermodynamics and Molecular Simulation*) it is shown how necessary and crude approximations sometimes can be avoided with the help of computers. Computer algorithms may even allow tackling problems eluding analytical approaches. This chapter therefore is devoted to an introduction of the Metropolis Monte Carlo method and its application in different ensembles. Thus far the focus has been equilibrium thermodynamics. The last chapter (*Non-equilibrium Thermodynamics*) introduces concepts in non-equilibrium thermodynamics. The starting point is linear irreversible transport described in terms of small fluctuations close to the equilibrium state. Onsager's reciprocity relations are obtained and their significance is illustrated in various examples. Entropy production far from equilibrium is discussed based on the balance equation approach and the concept of local equilibrium. The formation of dissipative structures is discussed focusing on chemical reactions. This chapter also includes a brief discussion of evolution in relation to non-equilibrium thermodynamics. There are several appendices. Appendix A: Thermodynamics does not require much math. Most of the necessary machinery is compiled in this short appendix. The reason that thermodynamics is often perceived difficult is not because of its difficult mathematics. It is because of the physical understanding and meticulous care required when mathematical operations are carried out under constraints imposed by process conditions. Appendix B: The appendix contains a listing of a Grand-Canonical Monte Carlo algorithm in Mathematica. The interested reader may use this program to recreate results presented in the text in the context of equilibrium adsorption. Appendix C: This appendix compiles constants, units, and references to useful tables. Appendix D: References are included in the text and as a

separate list in this appendix. Of course, there are other texts on Thermodynamics or Statistical Thermodynamics, which are nice and valuable sources of information—even if or because some of them have been around for a long time. A selected list is contained in a footnote on page 16. Another listing can be found in the preface to Hill (1986).

Wuppertal, Germany

Reinhard Hentschke

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