CHEMICAL THERMODYNAMICS

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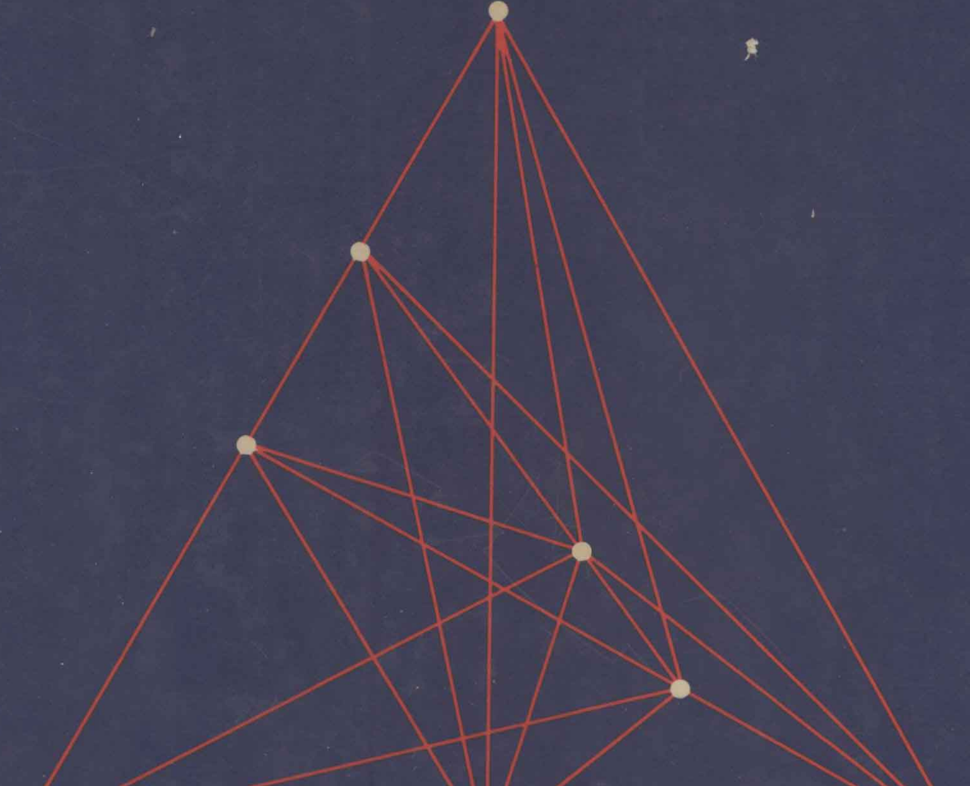

FOURTH EDITION

CHEMICAL THERMODYNAMICS

Basic Theory and Methods

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FOURTH EDITION

CHEMICAL THERMODYNAMICS

Basic Theories and Methods

Dedicated to the memory of
Thomas Fraser Young
September 28, 1897–April 1, 1977
Esteemed scientist, dedicated teacher

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"A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore, the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown."

Albert Einstein,
Autobiographical Notes, page 33 in
The Library of Living Philosophers, Vol. VII;
Albert Einstein: Philosopher-Scientist,
edited by P. A. Schilpp,
Open Court Publishing Company,
La Salle, Illinois, 1973.

Preface

This revision presents the fourth version of a textbook that appeared originally thirty-five years ago. The fundamental purpose of the book remains unchanged, to present to the student the logical foundations and interrelationships of the theory of thermodynamics and to teach the student the methods by which the theoretical methods may be applied to practical problems.

In the treatment of theoretical principles, we have adopted the classical, or phenomenological, approach to thermodynamics and have excluded entirely the statistical viewpoint. This attitude has several pedagogical advantages. First, it permits the maintenance of a logical unity throughout the book. In addition, it offers an opportunity to stress the "operational" approach to abstract concepts. Furthermore, it makes some contribution toward freeing the student from a perpetual yearning for a mechanical analogue for every new concept that is introduced. Finally, and perhaps most important, it avoids the promulgation of an all-too-common point of view toward statistical thermodynamics as an appendage which can be conveniently grafted on to the body of thermodynamics. A logical development of the statistical approach should probably be based on a previous introduction to the fundamental quantum-mechanical concept of energy level and should emphasize the much broader scope of the phenomena that it can treat. An effective presentation of statistical theory should be, therefore, an independent and complementary one to phenomenological thermodynamics.

A great deal of attention is paid in this text to training the student in the application of the theory of thermodynamics to problems that are commonly encountered by the chemist, the biologist, and the geologist. The mathematical tools that are necessary for this purpose are considered in more detail than is usual. In addition, computational techniques, graphical, numerical, and analytical, are described fully and are used frequently, both in illustrative and in assigned problems. Furthermore, exercises have been designed to simulate more than in most texts the type of problem that may be encountered by the practicing scientist. Short, unrelated exercises are thus kept to a minimum, whereas series of computations or derivations, illustrating a technique or principle of general applicability, are emphasized.

We have also made a definite effort to keep this volume within limits that can be covered in a course of lectures extending over a period of twelve to fifteen weeks. Too often, a textbook that attempts to be exhaustive in its coverage merely serves to overwhelm the student. On the other hand, if a student can be guided to a sound grasp of the fundamental principles and shown how these can be applied to a few typical problems, that student will be capable of examining other special topics independently or with the aid of one of the excellent comprehensive treatises that are available.

Another feature of this book is the extensive use of subheadings in outline form to indicate the position of a given topic in the general sequence of presentation. In using this method of presentation, we have been influenced strongly by the viewpoint expressed so aptly by Poincaré: "The order in which these elements are placed is much more important than the elements themselves. If I have the feeling... of this order, so as to perceive at a glance the reasoning as a whole, I need no longer fear lest I forget one of the elements, for each of them will take its allotted place in the array, and that without any effort of memory on my part."[1] It is a universal experience of teachers, that students are able to retain a body of information much more effectively if they are aware of the place of the parts in the whole.

Although thermodynamics has not changed fundamentally since the first edition was published, conventions and pedagogical approaches have changed, and new applications continue to appear. The application of thermodynamics to biological and geological problems has been particularly fruitful. We have taken the opportunity, therefore, to revise our approach to some topics, to use SI units, to use the new standard state of 0.1 MPa (1 bar), and to add problems that reflect new applications. In addition, we have added a new chapter on equilibrium in gravitational and ultracentrifugal fields, a subject of both geological and biological interest.

We acknowledge helpful comments on the manuscript from Henry Bent, David Volman, O. D. Bonner, Claude Meares, John E. Bauman, and Laurence Strong. We also thank Edgar Westrum for making it clear that the title of Chapter 18 needed revision. We thank Carol Techlin for careful typing of a difficult manuscript, Cheryl Chisnell for recording index entries into the computer, and E. Virginia Hobbs of McGaffey Associates for producing the index. We are grateful to Dr. E. Richard Cohen for the tentative values of the fundamental constants in Table 2-3. A solutions manual that contains solutions to most of the problems in the text is available from the publisher.

Evanston, Illinois
I.M.K.
Appleton, Wisconsin
R.M.R.

[1]H. Poincaré, *The Foundations of Science*, translated by G. B. Halsted, Science Press, 1913.

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CHAPTER 1

Introduction

1-1 ORIGINS OF CHEMICAL THERMODYNAMICS

An alert young scientist with only an elementary background in his or her field might be surprised to learn that a subject called "thermodynamics" has any relevance to chemical change or to biological and geological systems. The term *thermodynamics*, taken literally, implies a field concerned with the mechanical action produced by heat. Lord Kelvin invented the name to direct attention to the *dynamic* nature of *heat* and to contrast this perspective with previous conceptions of heat as a type of fluid.

In contrast to mechanics, electromagnetic field theory, or relativity, where the names of Newton, Maxwell, and Einstein stand out uniquely, the foundations of thermodynamics arose from the thinking of over half a dozen individuals: Carnot, Mayer, Joule, Helmholtz, Rankine, Kelvin, Clausius [1]. Each provided crucial steps leading to the grand synthesis of the two classical laws of thermodynamics.

The conceptual bottle into which was packaged eighteenth-century and early nineteenth-century views of the nature of heat was the principle of conservation of caloric. This principle is an eminently attractive basis for rationalizing simple observations such as temperature changes that occur when a cold body is placed in contact with a hot one. The cold body appears to have extracted something from the hot one. Furthermore, if both bodies are constituted of the same material, and the cold object has twice the mass of the hot one, then we observe that the increase in temperature of the former is only half the decrease in temperature of the latter. A conservation principle arises naturally. From this, the notion of the flow of a substance from the hot to the cold body appears almost intuitively, together with the concept that the total quantity of the caloric can be represented by the product of the mass multiplied by the temperature change. With these ideas in mind, Black was led to the discovery of specific heat, heat of fusion, and heat of vaporization. Such successes established the concept of caloric so solidly and persuasively that it blinded even the greatest scientists of the early nineteenth century. Thus, they missed seeing well-known facts that were common knowledge even in primitive cultures—for example, that heat can be produced by friction.

It seems clear that the earliest of the founders of thermodynamics, Carnot, accepted conservation of caloric as a basic axiom in his analysis [2] of the heat engine (although a few individuals [3] claim to see an important distinction in the contexts of Carnot's uses of "calorique" versus "chaleur").

Although Carnot's primary objective was to evaluate the mechanical efficiency of a steam engine, his analysis introduced certain broad concepts whose significance goes far beyond engineering problems. One of these concepts is the reversible process, which provides for thermodynamics the corresponding idealization that "frictionless motion" contributes to mechanics. The idea of "reversibility" has applicability much beyond ideal heat engines. Furthermore, it introduces continuity into the visualization of the process being considered; hence, it invites the introduction of the differential calculus. It was Clapeyron [4] who actually expounded Carnot's ideas in the notation of calculus and who thereby derived the vapor pressure equation associated with his name, as well as the performance characteristics of ideal engines.

Carnot also leaned strongly on the analogy between a heat engine and a hydrodynamic one (the water wheel) for, as he said,

> we can reasonably compare the motive power of heat
> with that of a head of water.

For the heat engine, one needs two temperature levels (a boiler and a condenser) that correspond to the two levels in height of a waterfall. For a waterfall, the quantity of water discharged by the wheel at the bottom level is the same as the quantity that entered originally at the top level, work being generated by the drop in gravitational level. Therefore, Carnot postulated that a corresponding thermal quantity, "calorique," was carried by the heat engine from a high temperature to a low one; the heat that entered at the upper temperature level was conserved and exited in exactly the same quantity at the lower temperature, work having been produced during the drop in temperature level. Using this postulate, he was able to answer in a general way the long-standing question of whether steam was suited uniquely for a heat engine; he did this by showing that in the ideal engine any other substance would be just as efficient. It was also from this construct that Kelvin subsequently realized that one could establish an absolute temperature scale independent of the properties of any substance.

When faced in the late 1840s with the idea of conservation of (heat plus work) proposed by Joule, Helmholtz, and Mayer, Kelvin at first rejected it (as did the Proceedings of the Royal Society when presented with one of Joule's manuscripts) because conservation of energy (work plus heat) was inconsistent

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