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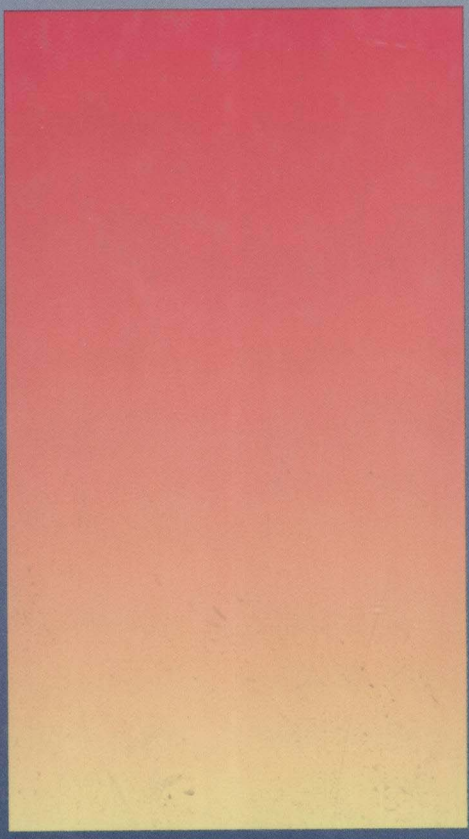

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Molecular Engineering

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To Dr. Waldemar T. Ziegler ("Wal"), Regents Professor of Chemical Engineering (retired), Georgia Institute of Technology, who introduced the author and so many more of his students to the power and beauty of the molecular perspective in engineering

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Preface

Scientific understanding and engineering design have increasingly become parallel rather than sequential activities. Applied science seems inevitably multidisciplinary, and practitioners of each discipline must enjoy real scientific communication if we are to ensure optimum progress. Engineers typically have well-developed continuum points of view, but their molecular perspective is usually weak.

The language of all of the physical sciences is the language of molecules, and if the applied scientist or engineer is to communicate with physicists or with chemists, the engineer must speak the language of molecular orbitals, energy states, vibrational modes, and all the rest. Molecular theory forms the common language of both pure and applied science. Even modern techniques of analysis such as infrared, nuclear magnetic resonance (NMR), x-ray diffraction, or coherent anti-Stokes Raman spectroscopy (CARS) can be understood as analytical schemes only in terms of the molecular behavior of matter. The engineer then is unable to judge the suitability of some instrumental scheme without such insights.

The structural and dynamic properties of a molecule are described by quantum mechanics. But the behavior of 10^{23} of these molecules is described by statistical mechanics, which is itself divided into two parts—equilibrium statistical mechanics or statistical thermodynamics and nonequilibrium statistical mechanics or kinetic theory. The macroscopic world presents a complex array of phenomena and processes. All of these may be divided into either equilibrium processes or rate processes, that is, into either thermodynamic or transport-kinetic processes and properties. Macroscopic descriptions of thermodynamic and transport-kinetic processes inevitably involve phenomenological coefficients such as heat capacity, viscosity, or specific rate coefficient. Statistical thermodynamics is the bridge from the properties of one molecule to the value of these phenomenological coefficients, that is, the thermodynamic properties of 10^{23} of those molecules. Similarly, kinetic theory is the bridge from the description of individual molecular collisions to the transport and kinetic coefficients of 10^{23} molecules.

We understand complex macroscopic pheonomena as mere artifacts

of innumerable molecular events. If we can understand the energetics, the structures, and the interactions of molecules, we will be able to understand the bulk behavior of matter. More important from an engineering perspective, this understanding allows the engineer to manipulate molecular behavior to yield some desired macroscopic property or process. This is the definition of molecular engineering.

This book is concerned with statistical thermodynamics and kinetic theory with an assumed starting point of basic chemistry, physics, and mathematics through some aspects of ordinary and partial differential equations. This book explores in detail the molecular understanding and the computation of phenomenological coefficients, and each idea and technique is illustrated with many examples. The goal is to build a sufficient scaffold to see over into more esoteric areas and to develop a manipulative competency with useful calculational schemes. The goal is to be able to converse with intelligence and understanding with the chemical physicists or the physical chemists about new developments in their more esoteric areas and to then be able to make an independent judgment as to the value of the new insight or the new theory in one's own particular applied problem area. With each topic, the reader is taken to the point of greatly diminishing returns regarding applicability to real problems. As quickly as possible after presenting some inevitably abstract idea, I have tried to present applications of physical meaning or intuitive feel. All of this is designed to help make the abstract idea real.

Molecular partition functions are used throughout for ease of comprehension rather than the more general, but conceptually troublesome, ensemble approach. Molecular theory is here demystified.

The following pages contain most of what the applications-oriented person needs to know about statistical thermodynamics, kinetic theory, and chemical reaction dynamics. There is nothing herein that must be unlearned or modified if one should later elect to become expert in this subject matter. The reader is, however, completely dependent on my judgment as to the position of many dividing lines that are drawn between the "useful" and the "esoteric." Here one must make the leap of faith and then see if, in one's subsequent practice, he or she will have found my judgments to be accurate or wanting. The theoretical arguments in this book are terribly impressive, and they are extraordinarily valuable to the applied scientist, but they are also frequently incomplete and inexact. If it were not so, there would be computer codes that would calculate any property of any substance under any experimental condition. This happy state of affairs does not yet exist. We must learn herein the boundaries of what existence there is.

We here seek the development of attitudes and perspectives in ther-

modynamics, transport, and rate phenomena that would be essential to persons concerned with the invention and design of perhaps a laser-based process for isotope separation. Or one might be concerned with fundamental problems in combustion leading to greater fuel efficiencies and less pollution. Or one might be concerned with ion implantation for the development of new alloys or new and unusually doped materials of interest in electronics. Or one's application may require some property of matter that may be unknown. The applied scientist must work with too many substances, both pure and in an infinite array of mixtures, for experimental measurement to always be a viable route to a needed property. So theories and predictive correlations are needed, and the best of them are based on molecular arguments. From whatever the perspective, a molecular view is essential and a purely traditional or classical perspective unacceptably slows invention, hinders creativity, and frustrates original design.

This book will have served its purpose if its attitudes can be internalized. That is, long after we have forgotten just exactly how this or that particular argument or calculation goes, we will nonetheless instinctively think about any applied problem that we face in terms of what the molecules must be doing. That is the real, bottom-line goal.

Henry A. McGee, Jr.

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Chapter

1

Introduction

The goals of this discussion are to develop all of the current molecular theory that is applicable to the calculation of values for each of the thermodynamic, transport, and kinetic properties. We wish to understand these theoretical notions, but to limit our scope to only those ideas of practical utility. We will herein take our discussion of principles to some point that we will arbitrarily define as no longer practical in order that we may provide a vantage point to gaze over the ridge into those more uncertain or tentative areas that may yet someday become a part of our practical vocabulary. The applied scientist who understands the following arguments can well converse with the theorist and thereby reach a wise decision as to the value or relevance of any new idea to the real-world problems with which the applied scientist must deal. From a utilitarian perspective, the following discussion is a comprehensive one.

All of the relationships of classical thermodynamics are absolutely true whether molecules exist or not. But molecules do exist, and intuitively we believe that if we could but understand molecular structure, molecular energetics, and intermolecular interactions, we should somehow be able to calculate numerical values for thermodynamic properties. Statistical thermodynamics is the science that addresses this problem, and some strikingly successful theory has been developed. Our goal then is the calculation of numerical values of heat capacity, entropy, enthalpy, etc. at all temperatures and pressures for all substances. The input data will be bond angles, bond distances, intramolecular vibration frequencies, atomic masses, and the like. Many of these molecular parameters can be measured with very high accuracy.

Extensive compilations of the thermodynamic properties of matter have been developed by using statistical thermodynamical formalism,

and once we understand this formalism, we can then use existing and tabulated data with confidence, as well as calculate the properties of heretofore unstudied species in which we might have a particular interest.

There will be an additional more philosophical or attitudinal result from our study of molecular engineering that may be more valuable than the computational skill itself. Classical thermodynamics offers no explanation of why matter has the properties that it does, but we will now see that the macroscopic properties of matter have an underlying form and structure that are based on the molecular properties of matter. We will see that the various macroscopic properties are really just artifacts of the molecular character of the species. For example, we can use data on thermal conductivity to deduce the character of the intermolecular interaction from which we can then deduce the equation of state. Or vice versa. Thus the transport properties and the thermodynamic properties are linked through the molecular properties. Or we can make optical measurements of vibration frequencies and from those frequencies calculate the calorimetric quantities of heat capacity or entropy. Thus optical and calorimetric properties are linked through the molecular properties. Or we can measure the velocity of sound in a solid and from that calculate the heat capacity of that solid. Thus acoustical and calorimetric properties are linked through the molecular properties. And so on. These are powerful insights, and they are essential if one would hope to comprehend the physical world.

Our development will be divided into two parts. The introductory arguments of Chap. 2 are easy to follow, and they result in the introduction of the Boltzmann distribution function,

$$n_i = \frac{ne^{-\epsilon_i/kT}}{\sum_i e^{-\epsilon_i/kT}} \tag{1.1}$$

and the association (note, not derivation) of the macroscopic concept of entropy with microscopic statistics,

$$S = k \ln W \tag{1.2}$$

The meaning of the terms in these relationships will be made abundantly clear subsequently.

We will see too that molecules will distribute themselves among a set of energy levels in this exponential manner through the action of no force other than that of pure chance. In systems at thermodynamic equilibrium, the odds are overwhelming that the distribution will be exponential. But other unnatural distributions can be produced for short times, and indeed, the very important laser and maser phenom-

ena depend totally on the production of a so-called population inversion, that is, nonexponential distributions.

Although these arguments are all simple, one may also with impunity accept the two relationships of Eqs. (1.1) and (1.2) as valid, omit Chap. 2 altogether, and move immediately to the following chapters where these two results are utilized in the calculation of the thermodynamic, transport, and kinetic behavior of matter.

The second part of this book is concerned with nonequilibrium properties and behavior. Much of engineering concern with nonequilibrium behavior relates to the translational motions of molecules. Translation is classical rather than quantum in nature, so the Maxwell-Boltzmann distribution, Eq. (1.1), is recast in classical form and then used to develop what is called the kinetic theory of gases. These ideas allow a good conceptual understanding of the transport properties in all situations as well as useful schemes for calculating actual values of the transport coefficients for gases at up to modest pressures.

Kinetic theory also allows insight into chemical reaction kinetics. Chemical reaction does not occur in one step as we typically write an overall stoichiometric change. Rather, reaction occurs by a complex array of usually bimolecular encounters which together constitute the reaction mechanism. The rate of each of these steps of the mechanism depends on its particular reactant collision frequency, the relative energy involved in the collision, the energy states of each colliding species, and the relative geometry of the colliding species at the moment of impact. Reaction occurs only in collisions that occur with above some minimum threshold energy and even then only in collisions that occur with certain geometric orientations. Finally, the macroscopic or observed rate of the overall stoichiometric change is some sort of a complex average of these many different microscopic events.

Whether concern is with physical or chemical rate processes, we imagine all macroscopic or empirical behavior to be artifacts of innumerable microscopic events. We must understand these individual molecular events, and then we must properly average these events to deduce the macroscopic behavior that is always sought in engineering practice.

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