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MOLECULAR THERMODYNAMICS OF FLUID-PHASE EQUILIBRIA

Second Edition

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Second Edition

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Preface to the First Edition

Since the generality of thermodynamics makes it independent of molecular considerations, the expression "molecular thermodynamics" requires explanation.

Classical thermodynamics presents broad relationships between macroscopic properties, but it is not concerned with quantitative prediction of these properties. Statistical thermodynamics, on the other hand, seeks to establish relationships between macroscopic properties and intermolecular forces through partition functions; it is very much concerned with quantitative prediction of bulk properties. However, useful configurational partition functions have been constructed only for nearly ideal situations and, therefore, statistical thermodynamics is at present insufficient for many practical purposes.

Molecular thermodynamics seeks to overcome some of the limitations of both classical and statistical thermodynamics. Molecular phase-equilibrium thermodynamics is concerned with application of molecular physics and chemistry to the interpretation, correlation, and prediction of the thermodynamic properties used in phase-equilibrium calculations. It is an engineering science, based on classical thermodynamics but relying on molecular physics and statistical thermodynamics to supply insight into the behavior of matter. In application, therefore, molecular thermodynamics is rarely exact; it must necessarily have an empirical flavor.

In the present work I have given primary attention to gaseous and liquid mixtures. I have been concerned with the fundamental problem of how best to calculate fugacities of components in such mixtures; the analysis should therefore be useful to engineers engaged in design of equipment for separation operations. Chapters 1, 2, and 3 deal with basic thermodynamics and, to facilitate molecular interpretation of thermodynamic properties, Chapter 4 presents a brief discussion of intermolecular forces. Chapter 5 is devoted to calculation of fugacities in gaseous mixtures and Chapter 6 is concerned with excess functions of liquid mixtures. Chapter 7 serves as an introduction to the theory of liquid solutions with attention to both "physical" and "chemical" theories. Fugacities of gases dissolved in liquids are discussed in Chapter 8 and those of solids dissolved in liquids in Chapter 9. Finally, Chapter 10 considers fluid-phase equilibria at high pressures.

While it is intended mainly for chemical engineers, others interested in fluid-phase equilibria may also find the book useful. It should be of value to university seniors or first-year graduate students in chemistry or chemical engineering who have completed a standard one-year course in physical chemistry and who have had some previous experience with classical thermodynamics.

The subjects discussed follow quite naturally from my own professional activities. Phase-equilibrium thermodynamics is a vast subject, and no attempt has been made to be exhaustive. I have arbitrarily selected those topics with which I am familiar and have omitted others which I am not qualified to discuss; for example, I do not consider solutions of metals or electrolytes. In essence, I have written about those topics which interest me, which I have taught in the classroom, and which have comprised much of my research. As a result, emphasis is given to results from my own research publications, not because they are in any sense superior, but because they encompass material with which I am most closely acquainted.

In the preparation of this book I have been ably assisted by many friends and former students; I am deeply grateful to all. Helpful comments were given by J. C. Berg, R. F. Blanks, P. L. Chueh, C. A. Eckert, M. L. McGlashan, A. L. Myers, J. P. O'Connell, Otto Redlich, Henri Renon, F. B. Sprow, and H. C. Van Ness. Generous assistance towards improvement of the manuscript was given by R. W. Missen and by C Tsonopoulos who also prepared the index. Many drafts of the manuscript were cheerfully typed by Mrs. Irene Blowers and Miss Mary Ann Williams and especially by my faithful assistant for over twelve years, Mrs. Edith Tyalor, whose friendship and conscientious service deserve special thanks.

Much that is here presented is a reflection of what I have learned from my teachers of thermodynamics and phase equilibria: G. J. Su, R. K. Toner, R. L. Von Berg, and the late R. H. Wilhelm; and from my colleagues at Berkeley: B. J. Alder, Leo Brewer, K. S. Pitzer and especially J. H. Hildebrand, whose strong influence on my thought is evident on many pages.

I hope that I have been able to communicate to the reader some of the fascination I have experienced in working on and writing about phase-equilibrium thermodynamics. To think about and to describe natural phenomena, to work in science and engineering—all these are not only useful but they are enjoyable to do. In writing this book I have become aware that for me phase-equilibrium thermodynamics is a pleasure as well as a profession; I shall consider it a success if a similar awareness can be awakened in those students and colleagues for whom this book is intended.

Felix qui potuit rerum cognoscere causas.

Finally, I must recognize what is all too often forgotten—that no man lives or works alone, but that he is molded by those who share his life, who make him what he truly is. Therefore I dedicate this book to Susie, who made is possible, and to Susi and Toni, who prepared the way.

J. M. Prausnitz
Berkeley, California

Preface to the Second Edition

Molecular thermodynamics is an engineering science in the sense that its goal is to provide quantitative estimates of equilibrium properties for mixtures as required for chemical process design. To provide these estimates, molecular thermodynamics uses not only classical thermodynamics but also concepts from statistical thermodynamics and chemical physics; the operational procedure can be summarized by these steps:

1. Use statistical thermodynamics whenever possible, at least as a point of departure.
2. Apply appropriate concepts from molecular science.
3. Construct physically grounded models for expressing (abstract) thermodynamic functions in terms of (real) measurable properties.
4. Obtain model parameters from a few, but representative, experimental measurements.
5. Reduce the model to practice through a computer program that efficiently interfaces with engineering-design calculations.

The second edition, like the first, attempts to provide some guidance toward establishing the principles of molecular thermodynamics. This guidance is intended primarily for seniors or first-year graduate students in chemical engineering, but practicing engineers also may find it useful.

In preparing the second edition, I have taken a position of compromise between on the one hand, a "scientific" book that stresses molecular theory and on the other, an "engineering" book that gives practical advice toward specific design procedures. As in the first edition, emphasis is placed on fundamental concepts and how they can be reduced to practice to yield useful results.

Like the earlier edition, the second edition contains ten chapters and several appendices. All chapters have been partially revised and updated. Major changes are in Chapters 4, 6, 7, and 8, and much of Chapter 10 is totally new. Some earlier appendices have been removed and others have been added: Appendix II gives a brief introduction to statistical thermodynamics, while Appendices VIII and IX present summaries of some special aspects of the theory of solutions as addenda to Chapter 7.

Many new problems have been added. Solving problems is essential for serious students. Numerical answers to numerous problems are given in the final Appendix.

Since work for the first edition ceased in 1968, there have been formidable developments in a variety of areas that bear on molecular thermodynamics. It is not possible, in a reasonable number of pages, to do justice to all or even a major part of these developments. I have had to omit much that might have been included, lest this book become even larger; I can only ask my colleagues to forgive me if some of their contributions are not here mentioned for reasons of economy.

Perhaps the most promising development in the last fifteen years is in the statistical thermodynamics of fluids and fluid mixtures, especially through perturbation theory and computer simulation. There is little doubt that these developments will continue toward eventual direct application in engineering design. However, it is also likely that such direct application is not in the immediate future and that therefore, the semi-empirical methods discussed in this book will be utilized for many more years. Nevertheless, chemical-engineering students should now receive at least some introduction to the statistical thermodynamics of fluids, not only because of utility in the future, but also because idealized results from contemporary statistical thermodynamics are already now of much use in guiding development of semitheoretical models toward thermodynamic-property correlations. Therefore, some limited discussion of applied statistical thermodynamics is now included in Chapters 4, 7, and 10.

I am deeply grateful to many colleagues who have contributed to my understanding of molecular thermodynamics and its applications, and thereby to this book; perhaps the most helpful of these has been B. J. Adler. In addition to those mentioned in the Preface to the First Edition, I want to record here my thanks to R. A. Heidemann, E. U. Franck, K. E. Gubbins, R. C. Reid, the late T. K. Sherwood, H. Knapp, F. Kohler, C. Tsonopoulos, L. C. Claitor, H. C. van Ness, F. Selleck, and C. J. King. Further, I owe much to my numerous co-workers (graduate students and post-doctoral visitors) who have provided me with new information, stimulating questions and good fellowship.

I am, however, especially grateful to my two co-authors, R. N. Lichtenthaler and E. G. Azevedo, who ably assisted me in making revisions and additions to the original manuscript. Their contributions to the second edition are considerable and they deserve much credit for whatever success the second edition may achieve. All three authors are particularly indebted to P. Rasmussen for his critical review, to S. F. Barreiros for preparing the index and to R. Spontak for assistance in proof-reading.

Almost all of the new and revised sections of the second edition were prepared in the period 1978–80. It is unfortunate that, for a variety of reasons, publication was so long delayed. The final manuscript was sent to the publisher in February 1983.

The second edition maintains the pragmatic (engineering-science) philosophy that characterized the first edition: it is useful and ultimately economic to utilize whatever theoretical concepts may be suitable, but it is also important consistently to bear in mind the ultimate applied objective. To attain that objective, theory is rarely sufficient and inevitably at least some experimental data are required. The goal must always be to attain a healthy balance between theory and experiment, to avoid extreme emphasis in either direction.

This need for balance was recognized many years ago by a pioneer in applied science, Sir Francis Bacon, who used an analogy between scientific enterprise and the world of insects. In "Novum Organum" (1620), Bacon wrote about ants, spiders, and bees:

> Those who have handled sciences, have been either men of experiment or men of dogmas. The men of experiment are like the ant; they only collect and use. The reasoners resemble spiders who make cobwebs out of their own substance. But the bee takes a middle course: it gathers its material from the flowers of the garden and of the field, and transforms and digests it by a power of its own. Therefore, from a closer and purer league between these two faculities, the experimental and the rational, much may be hoped.

Finally, as in the Preface faculties, the First Edition, I want to stress once again that studying, practicing and extending molecular thermodynamics is not only a useful activity but also one that provides a sense of joy and satisfaction. I shall be glad if some of that sense is infectious so that the reader may attain from molecular thermodynamics the same generous rewards that it has given to me.

J. M. Prausnitz
Berkeley, California

About 14 years ago I met J. M. Prausnitz for the first time. He immediately stimulated my interest in the exciting science of phase-equilibrium thermodynamics and ever since he has strongly sustained my work in this field. Throughout the years, we usually agreed quickly on how to approach and to solve problems but when we did not, open, honest and sometimes tough discussions always brought us to mutual agreement. To be one of the co-authors of this book is the culminating point so far in our joint effort to establish molecular thermodynamics as a useful engineering science for practical application. Thank you, John!

A scientist demands a lot of sacrifice from those who share his life. Therefore I owe many, many thanks to my wife Brigitte, and to my children, Ulrike, Heike, Felix and Philipp who give me enduringly all the support I need to pursue my scientific work in the way I do it.

R. N. Lichtenthaler
Heidelberg, Federal Republic of Germany

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The Phase-Equilibrium Problem 1

We live in a world of mixtures—the air we breathe, the food we eat, the gasoline in our automobiles. Wherever we turn, we find that our lives are linked with materials which consist of a variety of chemical substances. Many of the things we do are concerned with the transfer of substances from one mixture to another; for example, in our lungs, we take oxygen from the air and dissolve it in our blood, while carbon dioxide leaves the blood and enters the air; in our coffee maker, water-soluble ingredients are leached from the coffee grains into the water; and when someone stains his tie with gravy, he relies on cleaning fluid to dissolve and thereby remove the greasy spot. In each of these common daily experiences, as well as in many others in physiology, home life, industry, and so on, there is a transfer of a substance from one phase to another. This occurs because when two phases are brought into contact, they tend to exchange their constituents until the composition of each phase attains a constant value; when that state is reached, we say that the phases are in equilibrium. The equilibrium compositions of two phases are often very different from one another, and it is precisely this difference which enables us to separate mixtures by distillation, extraction, and other phase-contacting operations.

The final, or equilibrium, phase compositions depend on several variables, such as the temperature and pressure, and on the chemical nature and concentrations of the substances in the mixture. Phase-equilibrium thermodynamics seeks to establish the relations among the various properties (in particular,