THE COMPUTATION OF CHEMICAL EQUILIBRIA

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FOREWORD

This book represents a major contribution to the literature of the thermodynamics of complex chemical equilibria. It should be welcomed by workers already in the field because it provides a critical survey of the analytical techniques developed in many different countries and laboratories over the last quarter century. For those unfamiliar with these developments this book provides an excellent introduction to methods of great generality and power, which should find ever increasing application in the next few years. There is every reason to hope that the successes already achieved in high temperature reactions, explosive design and chemical processing can be extended and enlarged, even to such complex fields as biology and geology.

From the academic standpoint this book should also be well received. Thus for some years the graduate thermodynamics course for chemical and mechanical engineers at Washington University has included a discussion of complex chemical equilibrium problems. The presentation has been handicapped by the fact that the methods described in this book were not generally available in textbook form. While many fine texts, such as Denbigh's *Principles of Chemical Equilibrium* do discuss the problem of free energy minimization, to the student it always appears that the method, though general in principle, is confined in practice to systems in which the stoichiometric equations can be written and where each derived constituent is represented in the final set of equations by a chemical equilibrium or mass action equation. While this method is certainly valid the problem is more instructively considered and conceptually easier to approach by disregarding the details of the processes. The total free energy of the system can be considered in terms of the chemical potentials of the reactants and a set of possible products and finding the composition at the minimum of the multidimensional free energy-composition surface. The method is limited only by the size of the computational facilities available and by the number of chemical compounds and temperature ranges for which standard

chemical potentials are tabulated. It is useful for the student to learn that thermodynamic data are now tabulated (albeit in sometimes obscure locations) for many compounds even to temperatures in the 20,000 °K range. Discussion of the origin of the numbers in these tables is in itself a most instructive pastime but for the student it becomes a matter of considerable interest to compute equilibrium compositions in such exotic reactions as those between diborane and oxygen-bifluoride, at say, 6,000 °K. The ease with which temperature, pressure and starting compositions can be varied can almost be said to add a new dimension to the instruction of students in the thermodynamics of chemical equilibrium.

Although this book could thus serve as a supplementary text for advanced thermodynamics courses it is primarily designed for those actively working in the field. If a complaint could be made about this book it is a complaint that can be levelled against much of the published literature—there are too few papers in which the theoretical calculations are compared with experimental results. Perhaps this book will inspire the publication of observations which can be checked against the associated computations. This becomes particularly important when questions of chemical kinetics may be significant, as for example in shock tube studies. This raises speculations beyond the scope of this work but which may well be of major concern in certain particular cases; the equilibrium compositions will, however, always be needed. In any event, there is reason to believe that this book in its own way will help to make the next twenty-five years of study of complex reactions as productive and interesting as the last.

E. B. BAGLEY

St Louis, Missouri
November 1968

PREFACE

It is difficult to overestimate the effect of the increased availability of electronic digital computers on the field of chemical equilibrium computation over the last fifteen to twenty years. The last and only comprehensive monograph in this field was the publication by Kobe and Leland, in 1954. Since that time, computers have assumed more and more the often prodigious numerical tedium involved in equilibrium calculations. Also, with the increasing importance of the problem in high temperature, high pressure processing, in rocketry, and in explosives technology, a revival of interest in the equilibrium problem has led to the accumulation of a considerable body of additional technical literature. The work of S. R. Brinkley and his collaborators, in the late 1940s, laid the groundwork for systematic treatments of the problem. These have replaced the older semi-intuitive manual methods. The range of applications is amply demonstrated by the number of different journals in which descriptions of novel techniques have appeared. In fact, owing to the lack of a recent comprehensive treatment of the various techniques now available, and to the wide spread in the literature, some duplication has already occurred.

It is hoped that this book will be of use in three areas. First, since there is now a sufficient variety of methods available to allow one to be chosen to fit a given problem, the book provides a guide to the methods available and their properties, for those who have specific problems to solve. Secondly, the fundamental chemical thermodynamic and numerical analytic material has been selected so as to make the book suitable as a graduate level text, in particular for students in Chemical Engineering faculties. Finally, this book should represent, for a short while, a summary of the current position for workers in the field. It is with all three aims in mind that the notation has been made as consistent as possible throughout the book, and an attempt has been made to indicate under which problem conditions some of the published methods are less unsatisfactory than others.

The authors would like to express their thanks to Canadian Industries Limited and to the University of Liverpool, for permission to write the book, and for allowing the use of computational, library and office facilities during its preparation. Particular thanks are due to Professor A. Young and to his successor, Professor M. R. Sampford, of the Department of Computational and Statistical Science of the University of Liverpool, for their encouragement and for their interest in this work. The authors are much indebted to Professor E. B. Bagley, of the Department of Chemical Engineering of Washington University, St Louis, Mo., who read the book in draft and made many useful comments, and for writing a foreword to this book. Many others have been connected with the work at various times; numerous computations have been carried out over the past six years by Mrs M. L. Taylor, Mrs N. Brownlie and Mrs A. D. Lovie, Mr H. R. Hughes has given valuable clerical assistance. Mrs F. Mang, Mrs J. F. O'Connor and Miss N. Prout have performed excellently the very considerable task of converting the authors' handwriting into the final typescript. To all of these the authors would like to extend their grateful thanks.

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