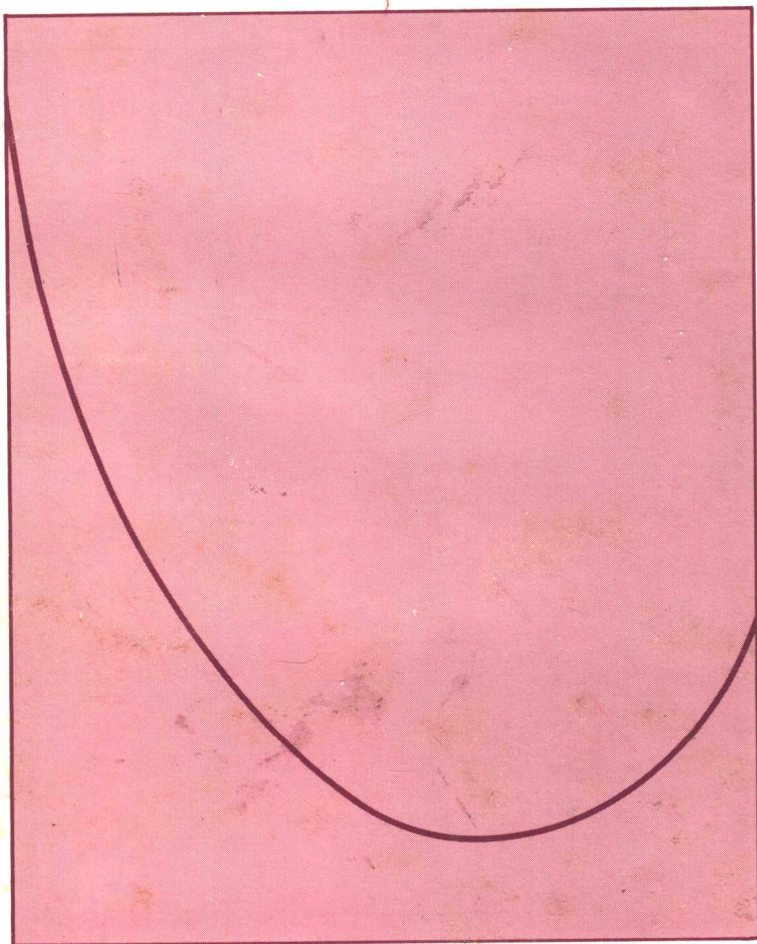


# *Chemical Reaction Equilibrium Analysis*

**theory and algorithms**



**William R. Smith  
Ronald W. Missen**

# Chemical Reaction Equilibrium Analysis: Theory and Algorithms

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A Wiley-Interscience Publication

**JOHN WILEY & SONS**

New York / Chichester / Brisbane / Toronto / Singapore

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***Library of Congress Cataloging in Publication Data:***

Smith, William R. (William Robert), 1943–

Chemical reaction equilibrium analysis.

“A Wiley-Interscience publication.”

Bibliography: p.

Includes indexes.

1. Chemical equilibrium. 2. Chemical equilibrium—  
Computer programs. I. Missen, Ronald W. (Ronald  
William), 1928– II. Title.

QD503.S58 541.3'92 82-6968

ISBN 0-471-09347-5 AACR2

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

# Preface

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We have written this book to describe and develop the fundamental basis for determining the composition at equilibrium of a chemical system and to provide computer algorithms for such a determination. Implicit in this purpose is the additional objective of exploring the usefulness of the equilibrium state as a model for predicting the behavior of chemically reacting systems, in full knowledge that the applicability of such a model is limited.

Our overall goal is thus to show both the usefulness and the limitations of chemical reaction equilibrium analysis and to provide for the requirements of those who wish to perform equilibrium computations for systems of any size or complexity. The first part of the goal recognizes that the model of the equilibrium state is not the appropriate model in many cases, and hence there is the need to discriminate between cases where it is useful and cases where it is not. The second part of the goal is not easily achieved, in view of the apparent abundance of approaches available and the present incomplete state of knowledge about nonideal systems. We attempt to provide a more unified approach to computing equilibrium compositions subject to these limitations.

The current state of affairs in this subject can be considered in terms of three aspects: the establishment of the physicochemical principles and structure underlying the problem; the accumulation and representation of requisite data; and the development of computational procedures for exploiting this structure in conjunction with appropriate numerical techniques. The first aspect was essentially completed by J. W. Gibbs just over a century ago, the second has been taking place since before that time and is still far from complete, and the third is a relatively recent occurrence that has been greatly facilitated by developments in high-speed digital computation over the past quarter century.

This book is intended to be used by students, teachers, and practitioners in fields in which chemical equilibrium is important—that is, in such fields as chemistry, chemical engineering, metallurgy, geochemistry, and physics. It is addressed to those who need to know the basis for equilibrium calculations and to have available computer algorithms, whether they are engaged in

research and development work, engineering design and field work, or teaching. We have thus attempted to provide a book that can be used widely and flexibly—for formal senior undergraduate and graduate courses, for continuing education and professional development courses, and for self-study. It is assumed that the reader has some prior knowledge of chemical thermodynamics and associated physicochemical data. Some knowledge of such mathematical topics as multivariable calculus and linear algebra is also required, and an elementary understanding of computer programming is desirable.

The scope of the book is reflected in some of its main features. The treatment embraces both reaction and phase equilibrium—that is, physicochemical equilibrium in general. It also deals with both ideal and nonideal chemical systems. Types of systems addressed include those involving solutions of nonelectrolytes and electrolytes in addition to gases, and gases together with many single-species phases. Included in the appendixes are computer program listings for implementing algorithms discussed in the text. The problems at the ends of the chapters are an important part of the book. They are intended both to illustrate the discussion in the text itself and to extend it. The problems are self-contained in the sense that sufficient information is given for their solution, and in most cases references are given to literature sources for comparison of approaches and results. The answers to selected problems are given at the back of the book.

The book is divided into nine chapters. Chapter 1 provides an introduction to the general nature of the chemical equilibrium problem and its potentially useful applications; included is a brief historical sketch of the concept of chemical equilibrium and of attendant computational methods. Chapters 2 and 3 describe the two main criteria. The first is the closed-system constraint, which implies a careful examination of chemical stoichiometry. The second is the equilibrium condition, which involves criteria provided by chemical thermodynamics. Two computational methods are illustrated in Chapter 4 for relatively simple systems so that the basic approaches can be seen. In Chapter 5 we present a brief survey of numerical methods for solving optimization problems and sets of nonlinear equations. Then in Chapter 6 we present and analyze algorithms for solving chemical equilibrium problems for ideal systems. In Chapter 7 we show how the methods of Chapter 6 can be extended to treat nonideal systems. We discuss the dependence of equilibrium composition on the data used in such computations in Chapter 8. In Chapter 9 we discuss some important practical matters concerning equilibrium computations, including special situations, and emphasizing potential difficulties.

The book can be used effectively in various ways. For example, those interested in the fundamental basis will follow the text and study the worked

examples; those interested in solving equilibrium problems arising in their own work will concentrate on the examples and the problems provided. An undergraduate course can be based on the first four chapters and the use of the programs as “black boxes”; a graduate course could use the first four chapters for review and begin at Chapter 5.

We acknowledge our indebtedness to those who have contributed to this subject and on whose work we have drawn. Mr. J.-P. Schoch developed the BASIC computer programs and assisted in solving problems and examples. Dr. Henry Tan developed the HP-41C programs. Dr. T. W. Melnyk and Dr. O. H. Scalise assisted in developing the BNR and VCS FORTRAN programs. Mrs. Debora Foster was a research assistant in the development of much of the manuscript. Miss Claudette Gariépy did all the typing of a rather difficult final manuscript. Miss Diana Cowan, Miss Louisa Franceschi, Mrs. Donna Mokren, and Mrs. Jeanne O’Sullivan assisted in typing parts of drafts of the manuscript and in preparing copy for the appendixes and illustrations. Financial assistance for research in this field over the years has been received from the Natural Sciences and Engineering Research Council of Canada.

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*May 1982*

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## CHAPTER ONE

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# Introduction

Chemical reaction equilibrium analysis has two principal concerns: to establish whether the equilibrium state of a chemical system is a useful model for a particular purpose; and to determine the equilibrium composition of the system under specified conditions, such as stipulated temperature and pressure. A related concern is the effect of changing conditions on this composition.

There are thus three questions regarding this type of analysis:

- 1 Is an equilibrium model appropriate?
- 2 What is the composition of the equilibrium state at specified conditions?
- 3 What is the effect of changing conditions?

The basis for obtaining answers to these questions is the subject of this book. We begin in this first chapter by considering chemical equilibrium in its various aspects, such as its nature, importance, relation to kinetics, scope in terms of constraints and applications, and historical development in outline.

### 1.1 THE NATURE OF CHEMICAL EQUILIBRIUM

We use the phrase “equilibrium state of a closed system” (i.e., a *locally stable* equilibrium state), and by this, as a preliminary statement, we mean a state that is

- 1 Independent of time.
- 2 Independent of the previous history of the system.
- 3 Resistant to fluctuations (within limits of magnitude but not of direction) of composition; that is, any such fluctuations are damped out.
- 4 Independent of position within the system; this excludes, for example, a system subject to a potential gradient resulting in a flux of mass or energy within it.

A stable equilibrium state is distinguished from an unsteady (kinetic) state by point 1, from a nearby, path-dependent (kinetic) state by point 2, from an

unstable or a metastable equilibrium state by point 3, and from what is sometimes referred to as a *steady state* for such a system by point 4.

The chemical system of interest is by definition undergoing change in chemical composition in approaching an equilibrium state from some initial nonequilibrium state. This takes place by reaction or by mass transfer or by a combination of the two. The possibility of mass transfer implies that the system may consist of more than one phase. We thus include both reaction equilibrium and phase equilibrium in our use of the term "chemical equilibrium."

## 1.2 THE IMPORTANCE OF CHEMICAL REACTION EQUILIBRIUM ANALYSIS

The importance of chemical reaction equilibrium analysis derives from the circumstances in which the equilibrium state is a useful model for describing the state of an actual system. The following circumstances include the usual ones for which this is the case:

- 1 The equilibrium model may be useful when rates of change (reaction and mass transfer) are relatively rapid. This tends to be the case when temperature is relatively high, as in a rocket engine, or when catalytic activity is relatively high, as in the case of a sulfur dioxide converter. The inferences of analytical chemistry involving ionic species are also normally based on this model.
- 2 The equilibrium model may be useful in a positive sense as a reference state to which rate considerations are applied, as in the cases of maximum conversion in a chemical reactor, electromotive force (emf) of a chemical cell, and stagewise operations in separation processes.
- 3 The equilibrium model may be useful in a negative sense, such as in predicting too low a conversion or yield or in avoiding equilibrium with respect to certain undesired species.
- 4 The equilibrium model may be useful as a guide in choosing process conditions, including the evaluation of a catalyst, particularly in conjunction with the effects of changing conditions.

The usefulness of the equilibrium model will normally diminish in favor of a kinetic model whenever rates of change are relatively slow. We may thus be led astray by a particular equilibrium model, if this is the case in the actual system.

## 1.3 THE PROBLEM OF COMPUTATION

Once we have decided that the equilibrium model is worth investigating, we must determine the equilibrium state (its composition) under particular condi-

tions and perhaps also its dependence on these conditions. This involves an application of the second law of thermodynamics since this law provides the requisite criteria. To exploit these criteria, we must construct appropriate forms of the potential functions involved and must have appropriate information (equations of state or their equivalent and energy and "free"-energy data), to specify the parameters of the problem.

The problem then becomes essentially a mathematical one. As such, it can be viewed either as one of optimization (e.g., the minimization of the Gibbs function subject to certain constraints, including the mass-balance constraints) or as one involving the solution of a set of simultaneous nonlinear algebraic equations (which arise from the necessary mathematical conditions for this minimization). These viewpoints are essentially equivalent, and we stress this in later chapters. A great deal of misconception and fruitless argument has resulted in the literature from overly enthusiastic proponents of one viewpoint to the exclusion of the other.

Since the mass-balance constraints are linear in the mole numbers of the species present and the potential function is nonlinear in these variables, any general method of solution is necessarily an iterative one. For small systems, solutions may be effected by means of *hand calculation methods* or programmable hand calculators. For large systems, however (e.g., 100 species involving 10 elements), we must of necessity resort to the use of numerical methods in conjunction with digital computers. Throughout most of this book we are interested mainly in general computational algorithms that can handle large systems, but we also consider algorithms that can be used for smaller systems. The latter approach can exploit the growing use of small computers in addition to programmable hand calculators.

To understand the many computation methods that have appeared in the literature, some mathematics results must be used. Our point of view in this matter is that of an investigator using mathematical sophistication where necessary, rather than that of a mathematician exploring the use of mathematics in a chemical setting. We mention briefly here some of the concepts used in later chapters.

We need to use ideas from the fields of optimization and numerical analysis. For example, among other approaches, we consider the method of Lagrange multipliers for constrained optimization and the Newton-Raphson method for solving nonlinear algebraic equations. Since the molecular formulas of chemical species can be associated with vectors and the mass-balance constraints are linear in the mole numbers, we also need to use some concepts from linear algebra. Among the most important notions are vector-matrix manipulation (e.g., vector-matrix multiplication), the solution of systems of linear equations, the concept of linear dependence and independence of vectors, and the concept of the rank of a matrix.

An understanding of the mathematics underlying the computational techniques is necessary for appreciation of the differences among them. It is also necessary for those who wish to formulate their own computation algorithms.

However, for those whose primary goal is to use a working computer program for performing equilibrium calculations, we give in the appendixes program listings and user's instructions for algorithms discussed in the text.

## 1.4 THE CONSTRAINTS

We consider constraints in three categories:

- 1 Overriding constraints that exclude certain types of problem for the purpose of this book.
- 2 Mandatory constraints that are independent of the nature of a particular problem.
- 3 Specific constraints that serve to define the parameters of a particular problem; these parameters are normally taken to be temperature, pressure, elemental abundances, molecular formulas, and standard chemical potentials.

Category 1 includes the following: (a) no surface or tensile effects (we are dealing with bulk systems in which the only external mechanical stress is that of a uniform fluid pressure); (b) no field effects (gravitational, electrical, etc.); (c) no macroscopic kinetic energy effects; and (d) no nuclear effects. Category 2 includes the following: (a) the closed-system or mass-balance constraint, which in this context means the conservation of elemental species; this includes the charge-balance constraint for ionic systems; and (b) the nonnegativity constraint—the number of moles of species  $i$ ,  $n_i$ , is either positive or zero for all  $i$ ; that is,

$$n_i \geq 0. \quad (1.4-1)$$

In category 3 there are various possibilities, but they would typically arise from the following: (a) specification of temperature  $T$  and pressure  $P$  by means of thermodynamic conditions or constraints; and (b) specification of the remaining parameters; normally these are given numerically at the outset, but there are situations in which they may also be specified by means of auxiliary conditions or constraints.

At this point we elaborate on category 3a but defer further consideration of category 3b to Chapter 8. Because of the importance of  $T$  and  $P$  as independent variables, which implies the Gibbs function  $G$  as the proper potential, we work entirely in terms of this set of variables—recasting, if necessary, other problems in terms of this standard  $(T, P)$  problem. Some of the important types of problem are:

- 1 Parameters  $(T, P)$  specified;  $T$  and  $P$  are fixed at given values.



- 2 Parameters  $(T, V)$  specified;  $T$  is fixed at a given value, and  $P$  is specified indirectly by an equation of state that links volume  $V$  to  $T$ ,  $P$ , and the equilibrium composition. This specification is appropriate for a chemical system in a rigid container; the procedure involves the simultaneous solution of the equilibrium condition in terms of  $T$ ,  $P$ , and the equation of state. The approach described is alternative to the use of  $T$  and  $V$  as independent variables, which implies the Helmholtz function  $A$  as the proper potential.
- 3 Parameters  $(\Delta H, P)$  specified;  $P$  is fixed, and  $T$  is specified indirectly by an energy balance that links enthalpy change  $(\Delta H)$  to  $T$ ,  $P$ , and the equilibrium composition. This specification is appropriate, for example, when the inlet  $T$  to a reactor is specified and the energy balance is determined by heat transfer considerations between the inlet and the point at which equilibrium is postulated; a special case is that for adiabatic change ( $\Delta H = 0$  under certain circumstances); the procedure involves the simultaneous solution of the equilibrium condition and the energy balance.
- 4 Parameters  $(T, \Delta P)$  specified;  $T$  is fixed, and  $P$  is specified indirectly by a momentum balance that links pressure drop  $\Delta P$  to  $T$ ,  $P$ , and the equilibrium composition; this specification is appropriate, for example, when the inlet  $P$  to a reactor is specified, and the momentum balance is determined by pressure-drop considerations between the inlet and the point at which equilibrium is postulated. The procedure involves simultaneous solution of the equilibrium condition and the momentum balance.
- 5 Parameters  $(\Delta H, \Delta P)$  specified; neither  $T$  nor  $P$  is fixed; both are specified indirectly by an energy balance and a momentum balance. This specification is appropriate when both inlet  $T$  and  $P$  are specified; that is, this situation is a combination of cases 3 and 4, and the procedure involves simultaneous solution of the equilibrium condition, the energy balance, and the momentum balance.
- 6 Parameters  $(S, P)$  specified;  $P$  is fixed, and  $T$  is specified indirectly by an equation that links entropy  $S$  to  $T$ ,  $P$ , and the equilibrium composition; this specification is appropriate, for example, when a process can be considered adiabatic and reversible (i.e., isentropic), as in flow through a perfect nozzle.

These examples of the specification of thermodynamic constraints are summarized in Table 1.1.

## 1.5 APPLICATIONS OF CHEMICAL EQUILIBRIUM ANALYSIS

The following examples illustrate situations in which consideration of equilibrium is an important part of the overall analysis. Other situations are