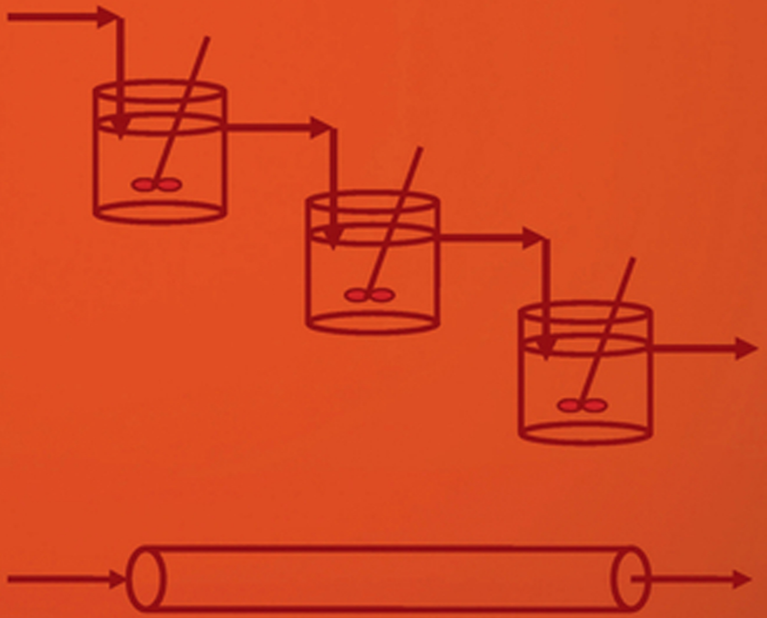
Introduction to Chemical Engineering Kinetics & Reactor Design

Second Edition

Charles G. Hill, Jr.   Thatcher W. Root



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Charles G. Hill, Jr.
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University of Wisconsin – Madison

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

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Library of Congress Cataloging-in-Publication Data:

Hill, Charles G., 1937–
Introduction to chemical engineering kinetics & reactor design / Charles G. Hill, Jr., Thatcher W. Root, professors of chemical and biological engineering, University of Wisconsin, Madison. – Second edition.
pages cm
Includes bibliographical references and index.
ISBN 978-1-118-36825-1 (cloth)
1. Chemical kinetics. 2. Chemical reactors–Design and construction. I. Root, Thatcher W. 1957- II. Title. III. Title: Introduction to chemical engineering kinetics and reactor design.
QD502.H54 2014
660′.2832–dc23
2013023526

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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Preface

More than three decades have elapsed since the publication of the first edition of this book in 1977. Although the basic principles on which the exposition in the body of the text is based remain unchanged, there have been noteworthy advances in the tools employed by practicing engineers in solving problems associated with the design of chemical reactors. Some of these tools need to be present in the knowledge base of chemical engineers engaged in studies of the principles of chemical kinetics and reactor design—the need for preparation of a second edition is thus evident. It has been primarily the pressure of other professional responsibilities, rather than a lack of interest on the part of the principal author, which has been responsible for the time elapsed between editions. Only since Professor Hill's retirement was precipitated by complications from surgery have sufficiently large blocks of time become available to permit a concerted effort to prepare the manuscript for the second edition.

Both the major thrust of the book as an introductory textbook focusing on chemical kinetics and reactor design, and the pedagogical approach involving applications of the laws of conservation of mass and energy to increasingly difficult situations remain at heart the same as the exposition in the first edition. The major changes in the second edition involve a multitude of new problems based on articles in the relevant literature that are designed to provide stimulating challenges to the development of a solid understanding of this material. Both students and instructors will benefit from scrutiny of the problems with a view to determining which problems are most germane to developing the problem-solving skills of the students in those areas that are most relevant to the particular topics emphasized by the instructor. Practicing engineers engaged in self study will also find the large array of problems useful in assessing their own command of the particular topic areas of immediate interest. We believe that it is only when one can apply to challenging new situations the basic principles in an area that he or she has been studying that one truly comprehends the subject matter. Hence one of the distinctive features of both the first and second editions is the inclusion of a large number of practical problems encompassing a wide range of situations featuring actual chemical compounds and interpretation of actual data from the literature, rather than problems involving nebulous species A, B, C, and so on, and hypothetical rate constants which are commonly found in most undergraduate textbooks. Roughly 75% of the problems are new, and these new problems were often designed to take advantage of advances in both the relevant computer software (i.e., spreadsheets, equation solvers, MathCad, Matlab, etc.) and the degree of computer literacy expected of students matriculating in chemical engineering programs. We believe that regardless of whether the reader is a student, a teaching assistant or instructor, or a practicing engineer, he or she will find many of the problems in the text to be both intellectually challenging and excellent vehicles for sharpening one's professional skills in the areas of chemical kinetics, catalysis, and chemical reactor design.

Even though the International System of units (SI) is used extensively in the text and the associated problems, we do not apologize for the fact that we do not employ this system of units to the exclusion of others. One powerful tool that chemical engineers have employed for more than a century is the use of empirical correlations of data obtained from equipment carrying out one or more traditional unit operation(s). Often these empirical correlations are based on dimensional analysis of the process and involve use of physical properties, thermochemical properties, transport properties, transfer coefficients, and so on, that may or may not be readily available from the literature in SI units. The ability of practicing chemical engineers to make the necessary conversion of units correctly has long been a hallmark of the profession. Especially in the area of chemical kinetics and heterogeneous catalytic reactor design, students must be able to convert units properly to be successful in their efforts to utilize these empirical correlations.

The senior author has always enjoyed teaching the undergraduate course in chemical kinetics and reactor design and has regarded the positive feedback he received from students during his 40+ years as a teacher of this subject as a generous return on investments of his time preparing new problems, giving and updating lectures, counseling individual students, and preparing the manuscripts for both the first and second editions of this book. It is always a pleasure to learn of the successes achieved by former students, both undergraduate and graduate. Although individual students are responsible for the efforts leading to their own success, I have been pleased to note that five students who were in my undergraduate course in kinetics have gone on to base their research careers in kinetics and catalysis at leading departments of chemical engineering and have served as chairs of said departments. At least I did nothing to turn off their interest in this aspect of chemical engineering.

This preface would be incomplete if I did not acknowledge the invaluable contributions of some 30 to 40 teaching assistants and undergraduate paper graders who worked with me in teaching this course. They often pointed out ambiguities in problem statements, missing data, or other difficulties associated with individual problem statements. I am grateful for their contributions but am reluctant to name them for fear of not properly acknowledging others whose contributions occurred decades ago.

We also need to acknowledge the invaluable assistance of several members of the department staff in providing assistance when problems with computers exceeded our abilities to diagnose and correct computer related difficulties. Todd Ninman and Mary Heimbecker were particularly helpful in this respect. Many undergraduates addressed Professor Hill's needs for help in generating accurate versions of the numerous equations in the book. They removed one of the major impediments to generating enthusiasm for the Sisyphean task of reducing ideas to a finished manuscript. At various points along the path to a finished manuscript we sought and received assistance from our colleagues on the UW faculty and staff, both inside and outside the department. The occasions were numerous and we much appreciate their cooperation. During the final stages of preparing the manuscript for the second edition, Jody Hoesly of the University of Wisconsin's Wendt Engineering Library was an wonderful resource in helping Professor Hill to locate and chase down the holders of the copyrights or viable alternatives for materials appearing in the first edition that were also needed in the second edition. She was an invaluable guide in helping us fulfill our responsibilities under copyright law.

Professor Hill also wishes to acknowledge the inspiration of the late Professor Robert C. Reid of MIT as a role model for how a faculty member should interact with students and research assistants. He is also grateful for the technique that Bob taught him of requiring participants in a course to read an article in the relevant literature and to prepare a problem (with the associated solution) based on an article that applies to material learned in this class. Typically, the assignment was made in the last week or two of the course. Professor Hill has used this assignment for decades as a vehicle for both demonstrating to students not only how much they have learned in the class as they prepare for the final exam, but also that they can read and comprehend much of the literature focusing on kinetics and reactor design. Often, the problems posed by students are trivial or impossibly difficult, but the benefit for the instructor is that the students identify for future generations of students not only interesting articles, but articles that are sufficiently relevant to the course that they may merit review with the idea that a senior instructor may use the article as the basis for challenging and stimulating problems at an appropriate pedagogical level. Such problems form the basis for many of the problems in the text that utilize techniques or data taken directly from the literature.

Professor Root is pleased to help rejuvenate this book for use by future classes of students seeking to improve their knowledge and understanding of this very important aspect of chemical engineering. Professor Hill hopes that readers enjoy the subject area as much as he has in more than four decades of studying and teaching this material.

Madison, Wisconsin CHARLES G. HILL, JR.
June 1, 2013 THATCHER W. ROOT

Preface to the First Edition

One feature that distinguishes the education of the chemical engineer from that of other engineers is an exposure to the basic concepts of chemical reaction kinetics and chemical reactor design. This textbook provides a judicious introductory level overview of these subjects. Emphasis is placed on the aspects of chemical kinetics and material and energy balances that form the foundation for the practice of reactor design.

The text is designed as a teaching instrument. It can be used to introduce the novice to chemical kinetics and reactor design and to guide him/her until he/she understands the fundamentals well enough to read both articles in the literature and more advanced texts with understanding. Because the chemical engineer who practices reactor design must have more than a nodding acquaintance with the chemical aspects of reaction kinetics, a significant portion of this textbook is devoted to this subject. The modern chemical process industry, which has played a significant role in the development of our technology-based society, has evolved because the engineer has been able to commercialize the laboratory discoveries of the scientist. To carry out the necessary scale-up procedures safely and economically, the reactor designer must have a sound knowledge of the chemistry involved. Modern introductory courses in physical chemistry usually do not provide the breadth or the in-depth treatment of reaction kinetics that is required by the chemical engineer who is faced with a reactor design problem. More advanced courses in kinetics that are taught by physical chemists naturally reflect the research interests of the individuals involved; they do not stress the transmittal of that information which is most useful to individuals engaged in the practice of reactor design. Seldom is significant attention paid to the subject of heterogeneous catalysis and to the key role that catalytic processes play in the industrial world.

Chapters 3 to 7 treat the aspects of chemical kinetics that are important to the education of a well-read chemical engineer. To stress further the chemical problems involved and to provide links to the real world, I have attempted where possible to use actual chemical reactions and kinetic parameters in the many illustrative examples and problems. However, to retain as much generality as possible, the presentations of basic concepts and the derivations of fundamental equations are couched in terms of the anonymous chemical species A, B, C, U, V, etc. Where it is appropriate, the specific chemical reactions used in the illustrations are reformulated in these terms to indicate the manner in which the generalized relations are employed.

Chapters 8 to 12 provide an introduction to chemical reactor design. We start with the concept of idealized reactors with specified mixing characteristics operating isothermally and then introduce complications such as the use of combinations of reactors, implications of multiple reactions, temperature and energy effects, residence time effects, and heat and mass transfer limitations that are often involved when heterogeneous catalysts are employed. Emphasis is placed on the fact that chemical reactor design represents a straightforward application of the bread and butter tools of the chemical engineer - the material balance and the energy balance. The fundamental design equations in the second half of the text are algebraic descendents of the generalized material balance equation

$$\text{rate of input} = \text{rate of output} + \text{rate of accumulation} \\ + \text{rate of disappearance by reaction} \quad (\text{P.1})$$

In the case of nonisothermal systems one must write equations of this form for both for energy and for the chemical species of interest, and then solve the resultant equations simultaneously to characterize the effluent composition and the thermal effects associated with operation of the reactor. Although the material and energy balance equations are not coupled when no temperature changes occur in the reactor, the design engineer still must solve the energy balance equation to ensure that sufficient capacity for energy transfer is provided so that the reactor will indeed operate isothermally. The text stresses that the design process merely involves an extension of concepts learned previously. The application of these concepts in the design process involves equations that differ somewhat in mathematical form from the algebraic equations normally encountered in the introductory material and energy balance course, but the underlying principles are unchanged. The illustrations involved in the reactor design portion of the text are again based where possible on real chemical examples and actual kinetic data. I believe that the basic concepts underlying the subject of chemical kinetics and reactor design as developed in this text may readily be rephrased or applied in computer language. However, my pedagogical preference is to present material relevant to computer-aided reactor design only after the students have been thoroughly exposed to the fundamental concepts of this subject and mastered their use in attacking simple reactor design problems. I believe that full exposure to the subject of computer-aided reactor design should be deferred to intermediate courses in reactor design (and to more advanced texts), but this text focuses on providing a rational foundation for such courses while deliberately avoiding any discussion of the (forever-evolving) details of the software currently used to solve problems of interest in computer-aided design.

The notes that form the basis for the bulk of this textbook have been used for several years in the undergraduate course in chemical kinetics and reactor design at the University of Wisconsin. In this course, emphasis is placed on Chapters 3 to 6 and 8 to 12, omitting detailed class discussions of many of the mathematical derivations. My colleagues and I stress the necessity for developing a "seat of the pants" feeling for the phenomena involved as well as an ability to analyze quantitative problems in terms of the design framework developed in the text.

The material on catalysis and heterogeneous reactions in Chapters 6 and 12 is a useful framework for an intermediate level course in catalysis and chemical reactor design. In such a course emphasis is placed on developing the student's ability to critically analyze actual kinetic data obtained from the literature in order to acquaint him/her with many of the traps into which the unwary may fall. Some of the problems in Chapter 12 have evolved from a course of this type.

Most of the illustrative examples and problems in the text are based on actual data from the kinetics literature. However, in many cases, rate constants, heats of reaction, activation energies, and other parameters have been converted to SI units from various other systems. To be able to utilize the vast literature of kinetics for reactor design purposes, one must develop a facility for making appropriate transformations of parameters from one system of units to another. Consequently, I have chosen not to employ SI units exclusively in this text.

Like other authors of textbooks for undergraduates, I owe major debts to the instructors who first introduced me to this subject matter and to the authors and researchers whose publications have contributed to my understanding of the subject. As a student, I benefited from instruction by R. C. Reid, C. N. Satterfield, and I. Amdur and from exposure to the texts of Walas, Frost and Pearson, and Benson. Some of the material in Chapter 6 has been adapted with permission from the course notes of Professor C. N. Satterfield of MIT, whose direct and indirect influence on my thinking is further evident in some of the data interpretation problems in Chapters 6 and 12. As an instructor I have found the texts by Levenspiel and Smith to be particularly useful at the undergraduate level; the books by Denbigh, Laidler, Hinshelwood, Aris, and Kramers and Westerterp have also helped to shape my views of chemical kinetics and reactor design. I have tried to use the best ideas of these individuals and the approaches that I have found particularly useful in the classroom in the synthesis of this textbook. A major attraction of this subject is that there are many alternative ways of viewing the subject. Without an exposure to several viewpoints, one cannot begin to grasp the subject in its entirety. Only after such exposure, bombardment by the probing questions of one's students, and much contemplation can one begin to synthesize an individual philosophy of kinetics. To the humanist it may seem a misnomer to talk in terms of a philosophical approach to kinetics, but to the individuals who have taken kinetics courses at different schools or even in different departments and to the individuals who have read widely in the kinetics literature, it is evident that several such approaches do exist and that specialists in the area do have individual philosophies that characterize their approach to the subject.

The stimulating environment provided by the students and staff of the Chemical Engineering Department at the University of Wisconsin has provided much of the necessary encouragement and motivation for writing this textbook. The Department has long been a fertile environment for research and textbook writing in the area of chemical kinetics and reactor design. The text by O. A. Hougen and K. M. Watson represents a classic pioneering effort to establish a rational approach to the subject from the viewpoint of the chemical engineer. Through the years these individuals and several members of our current staff have contributed significantly to the evolution of the subject. I am indebted to my colleagues, W. E. Stewart, S. H. Langer, C. C. Watson, R. A. Grieger, S. L. Cooper, and T. W. Chapman, who have used earlier versions of this textbook as class notes or commented thereon, to my benefit. All errors are, of course, my own responsibility.

I am grateful to the graduate students who have served as my teaching assistants and who have brought to my attention various ambiguities in the text or problem statements.

These include J. F. Welch, A. Yu, R. Krug, E. Guertin, A. Kozinski, G. Estes, J. Coca, R. Safford, R. Harrison, J. Yurchak, G. Schrader, A. Parker, T. Kumar, and A. Spence. I also thank the students on whom I have tried out my ideas. Their response to the subject matter has provided much of the motivation for this textbook.

Since drafts of this text were used as course notes, the secretarial staff of the department, which includes D. Peterson, C. Sherven, M. Sullivan, and M. Carr, deserves my warmest thanks for typing this material. I am also very appreciative of my (former) wife's efforts in typing the final draft of this manuscript and in correcting the galley proofs. Vivian Kehane, Jacqueline Lachmann, and Peter Klein of Wiley were particularly helpful in transforming my manuscript into this text.

My (former) wife and my children were at times neglected during the preparation of this book; for their cooperation and inspiration I am particularly grateful.

Madison, Wisconsin CHARLES G. HILL, JR.

Chapter 1

Stoichiometric Coefficients and Reaction Progress Variables

1.0 INTRODUCTION

In the absence of chemical reactions, Earth would be a barren planet. No life of any sort would exist. Even if we were to exempt the fundamental reactions involved in life processes from our proscription on chemical reactions, our lives would be extremely different from what they are today. There would be no fire for warmth and cooking, no iron and steel with which to fashion even the crudest implements, no synthetic fibers for making clothing or bedding, no combustion engines to power our vehicles, and no pharmaceutical products to treat our health problems.

One feature that distinguishes the chemical engineer from other types of engineers is the ability to analyze systems in which chemical reactions are occurring and to apply the results of his or her analysis in a manner that benefits society. Consequently, chemical engineers must be well acquainted with the fundamentals of chemical reaction kinetics and the manner in which they are applied in reactor design. In this book we provide a systematic introduction to these subjects. Three fundamental types of equations are employed in the development of the subject: material balances, energy balances, and rate expressions.

Chemical kinetics is the branch of physical chemistry that deals with quantitative studies of the rates at which chemical processes occur, the factors on which these rates depend, and the molecular acts involved in reaction processes. A description of a reaction in terms of its constituent molecular acts is known as the *mechanism* of the reaction. Physical and organic chemists are interested in chemical kinetics primarily for the light that it sheds on molecular properties. From interpretations of macroscopic kinetic data in terms of molecular mechanisms, they can gain insight into the nature of reacting systems, the processes by which chemical bonds are made and broken, and the structure of the resulting product. Although chemical engineers find the concept of a reaction mechanism useful in the correlation, interpolation, and extrapolation of rate data, they are more concerned with applications of chemical kinetics in the development of profitable manufacturing processes.

Chemical engineers have traditionally approached kinetics studies with the goal of describing the behavior of reacting systems in terms of macroscopically observable quantities such as temperature, pressure, composition, and Reynolds number. This empirical approach has been very fruitful in that it has permitted chemical reactor technology to develop to the point that it can be employed in the manufacture of an amazing array of products that enhance our quality of life.

The dynamic viewpoint of chemical kinetics focuses on variations in chemical composition with either time in a batch reactor or position in a continuous flow reactor. This situation may be contrasted with the essentially static perspective of thermodynamics. A *kinetic system* is a system in which there is unidirectional movement toward thermodynamic equilibrium. The chemical composition of a closed system in which a reaction is occurring evolves as time elapses. A system that is in thermodynamic equilibrium, on the other hand, undergoes no net change with time. The thermodynamicist is interested only in the initial and final states of the system and is not concerned with the time required for the transition or the molecular processes involved therein; the chemical kineticist is concerned primarily with these issues.

In principle, one can treat the thermodynamics of chemical reactions on a kinetic basis by recognizing that the equilibrium condition corresponds to the situation in which the rates of the forward and reverse reactions are identical. In this sense kinetics is the more fundamental science. Nonetheless, thermodynamics provides much vital information to the kineticist and to the reactor designer. In particular, the first step in determining the economic feasibility of producing a given material from a specified

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feedstock should be a determination of the product yield at equilibrium at the conditions of the reactor outlet. Since this composition represents the goal toward which the kinetic process is moving, it places an upper limit on the product yield that may be obtained. Chemical engineers must also employ thermodynamics to determine heat transfer requirements for proposed reactor configurations.

1.1 BASIC STOICHIOMETRIC CONCEPTS

1.1.1 Stoichiometric Coefficients

An arbitrary chemical reaction may be written as

$$bB + cC + \cdots = sS + tT + \cdots \tag{1.1.1}$$

where b, c, s, and t are the stoichiometric coefficients of the species B, C, S, and T, respectively. We define generalized stoichiometric coefficients (ν_i) for reaction (1.1.1) by rewriting it in the following manner:

$$0 = \nu_B B + \nu_C C + \nu_S S + \nu_T T + \cdots \tag{1.1.2}$$

where $\nu_B = -b$, $\nu_C = -c$, $\nu_S = s$, and $\nu_T = t$. The generalized stoichiometric coefficients are defined as positive quantities for the products of the reaction and as negative quantities for the reactants. The coefficients of species that are neither produced nor consumed by the indicated reaction are taken to be zero. Equation (1.1.2) has been written in transposed form with the zero first to emphasize the use of this sign convention, even though this transposition is rarely used in practice. One may further generalize equation (1.1.2) by rewriting it as

$$0 = \sum_i \nu_i A_i \tag{1.1.3}$$

where the sum is taken over all components A_i present in the system.

There are many equivalent ways of writing the stoichiometric equation for a reaction. For example, one could write the oxidation of carbon monoxide in our notation as

$$0 = 2CO_2 - 2CO - O_2$$

instead of the more conventional form, which has the reactants on the left side and the products on the right side:

$$2CO + O_2 = 2CO_2$$

This second form is preferred, provided that one keeps in mind the proper sign convention for the stoichiometric coefficients. For the example above, $\nu_{CO} = -2$, $\nu_{O_2} = -1$, and $\nu_{CO_2} = 2$.

Alternatively, this reaction may be written as

$$0 = CO_2 - CO - \tfrac{1}{2}O_2$$

The choice is a matter of personal convenience. The essential point is that the ratios of the stoichiometric coefficients are unique for a specific reaction. In terms of the two forms of the chemical equation above,

$$\frac{\nu_{CO}}{\nu_{O_2}} = \frac{-2}{-1} = \frac{-1}{-1/2} = 2$$

Because the reaction stoichiometry can be expressed in various ways, one must always write down a stoichiometric equation for the reaction under study during the initial stages of the analysis and base subsequent calculations on this reference equation. If a consistent set of stoichiometric coefficients is used throughout the calculations, the results can be readily understood and utilized by other workers in the field.

1.1.2 Reaction Progress Variables

To measure the progress of a reaction along a particular pathway, it is necessary to define a parameter that provides a measure of the degree of conversion of the reactants. For this purpose it is convenient to use the concept of the *extent* or degree of *advancement* of a reaction. This concept has its origins in the thermodynamic literature, dating back to the work of de Donder (1). Consider a *closed system*, one in which there is no exchange of matter between the system and its surroundings, where a single chemical reaction may occur according to equation (1.1.3). Initially, there are n_{i0} moles of constituent A_i present in the system. At some later time there are n_i moles of species A_i present. At this time the molar extent of reaction (ξ) is defined as

$$\xi = \frac{n_i - n_{i0}}{\nu_i} \tag{1.1.4}$$

This equation is valid for all species A_i, a fact that is a consequence of the law of definite proportions. The molar extent of reaction ξ is a time-dependent extensive variable that is measured in moles. It is a useful measure of the progress of the reaction because it is not tied to any particular species A_i. Changes in the mole numbers of two species i and j can be related to one another by eliminating ξ between two expressions that may be derived using equation (1.1.4):

$$n_j = n_{j0} + \frac{\nu_j}{\nu_i}(n_i - n_{i0}) \tag{1.1.5}$$

If more than one chemical reaction is possible, an extent may be defined for each reaction. If ξ_k is the extent of the kth reaction, and ν_{ki} is the stoichiometric coefficient of species i in reaction k, the total change in the number of moles of species A_i as a consequence of r reactions is

$$n_i - n_{i0} = \sum_{k=1}^{k=r} \nu_{ki}\xi_k \qquad (1.1.6)$$

Another advantage of using the concept of extent is that it permits a unique specification of the rate of a given reaction. This point is discussed in Section 3.0. The major drawbacks of the concept are that the extent is defined for a closed system and that it is an extensive variable. Consequently, the extent is proportional to the mass of the system being investigated.

The fraction conversion f is an intensive measure of the progress of a reaction. It is a variable that is simply related to the extent of reaction. The fraction conversion of a reactant A_i in a closed system in which only a single reaction is occurring is given by

$$f = \frac{n_{i0} - n_i}{n_{i0}} = 1 - \frac{n_i}{n_{i0}} \qquad (1.1.7)$$

The variable f depends on the particular species chosen as a reference substance. In general, the initial mole numbers of the reactants do not constitute simple stoichiometric ratios, and the number of moles of product that may be formed is limited by the amount of one of the reactants present in the system. If the extent of reaction is not limited by thermodynamic equilibrium constraints, this limiting reagent is the one that determines the maximum possible value of the extent of reaction (ξ_{max}). We should refer our fractional conversions to this stoichiometrically limiting reactant if f is to lie between zero and unity. Consequently, the treatment used in subsequent chapters will *define fractional conversions in terms of the limiting reactant*. In analyzing conventional batch reactors in which only a single reaction is occurring, one may employ either the concept of fraction conversion or the concept of extent of reaction. A batch reactor is a closed system, a system for which there is no transport of matter across the boundaries between the system and its surroundings. When multiple reactions take place in a batch reactor, it is more convenient to employ the extent concept. However, for open systems such as continuous flow reactors, the fraction conversion of the limiting reagent is more useful in conducting the analysis, sometimes in conjunction with the concept of reaction yield, as described in Chapter 9. An *open system* is one whose analysis requires consideration of the transport of matter across the boundaries between the system and its surroundings.

One can relate the extent of reaction to the fraction conversion by solving equations (1.1.4) and (1.1.7) for the number of moles of the limiting reagent n_{lim} and equating the resulting expressions:

$$n_{\text{lim}} = n_{\text{lim},0} + \nu_{\text{lim}}\xi = n_{\text{lim},0}(1 - f) \qquad (1.1.8)$$

or

$$\xi = -\frac{f n_{\text{lim},0}}{\nu_{\text{lim}}} \qquad (1.1.9)$$

The maximum extent of an irreversible reaction ($\xi_{\text{max,irr}}$) can be obtained by setting f in equation (1.1.9) equal to 1. However, for reversible reactions, the maximum extent of reaction is limited by the position of chemical equilibrium. For these situations, equation (1.1.9) becomes

$$\xi_e = -\frac{f_e n_{\text{lim},0}}{\nu_{\text{lim}}} \qquad (1.1.10)$$

where f_e and ξ_e are the conversion and extent of reaction at equilibrium, respectively. ξ_e will always be less than $\xi_{\text{max,irr}}$. However, in many cases ξ_e is approximately equal to $\xi_{\text{max,irr}}$. In these cases the equilibrium for the reaction highly favors formation of the products, and only an *extremely small* quantity of the limiting reagent remains in the system at equilibrium. We classify these reactions as *irreversible*. When the extent of reaction at equilibrium differs measurably from ξ_{max}, we classify the reaction involved as *reversible*. From a thermodynamic point of view, all reactions are reversible. However, to simplify the analysis, when one is analyzing a reacting system, it is often convenient to neglect the reverse reaction. For "irreversible" reactions, one then arrives at a result that is an extremely good approximation to the correct answer.

LITERATURE CITATION

1. De Donder, T., *Leçons de thermodynamique et de chemie-physique*, Gauthier-Villars, Paris 1920.

Chapter 2

Thermodynamics of Chemical Reactions

2.0 INTRODUCTION

The science of chemical kinetics is concerned primarily with chemical changes and the energy and mass fluxes associated therewith. Thermodynamics, on the other hand, is focused on equilibrium systems—systems that are undergoing *no net change* with time. In this chapter we remind the reader of the key thermodynamic principles with which he or she should be familiar. Emphasis is placed on calculations of equilibrium extents of reaction and enthalpy changes accompanying chemical reactions.

Of primary consideration in any discussion of chemical reaction equilibria are the constraints on the system in question. If calculations of equilibrium compositions are to be in accord with experimental observations, one must include in his or her analysis all reactions that occur at appreciable rates relative to the time frame involved. Such calculations are useful in that the equilibrium conversion provides a standard against which the actual performance of a reactor may be compared. For example, if the equilibrium yield of a particular reaction under specified conditions is 75% and the yield observed from a reactor operating under these conditions is only 30%, one can presumably obtain major improvements in the process yield by appropriate manipulation of the reaction conditions. On the other hand, if the process yield is close to 75%, potential improvements in yield would be minimal unless there are opportunities for making major changes in process conditions that have significant effects on the equilibrium yield. Additional efforts aimed at improving the process yield may not be fruitful if such changes cannot be made. Without a knowledge of the equilibrium yield, one might be tempted to look for catalysts giving higher yields when, in fact, the present catalyst provides a sufficiently rapid approach to equilibrium for the temperature, pressure, and feed composition specified.

The basic criterion for the establishment of equilibrium with respect to reaction k is that

$$\Delta G_k = \sum_i \nu_{ki}\mu_i = 0 \qquad (2.0.1)$$

where ΔG_k is the change in the Gibbs free energy associated with reaction k, μ_i the chemical potential of species i in the reaction mixture, and ν_{ki} the stoichiometric coefficient of species i in the kth reaction. If r reactions may occur in the system and equilibrium is established with respect to each of these reactions, thermodynamics requires that

$$\sum_i \nu_{ki}\mu_i = 0 \qquad \text{for} \quad k = 1, 2, \ldots, r \qquad (2.0.2)$$

These equations are equivalent to a requirement that at equilibrium the Gibbs free-energy change (ΔG) be zero for every reaction.

2.1 CHEMICAL POTENTIALS AND STANDARD STATES

The activity a_i of species i is related to its chemical potential by

$$\mu_i = \mu_i^0 + RT \ln a_i \qquad (2.1.1)$$

where R is the gas constant, T the absolute temperature, and μ_i^0 the standard chemical potential of species i in a reference state where its activity is taken as unity.

The choice of the standard state is largely arbitrary and is based primarily on experimental convenience and reproducibility. The temperature of the standard state is the same as that of the system under investigation. In some cases, the standard state may represent a hypothetical condition that cannot be achieved experimentally, but that is susceptible

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Introduction to Chemical Engineering Kinetics and Reactor Design, Second Edition. Charles G. Hill, Jr. and Thatcher W. Root.
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Table 2.1 Standard States for Chemical Potential Calculations (for use in studies of chemical reaction equilibria)

State of aggregation	Standard state
Gas	Pure gas at unit fugacity (for an ideal gas the fugacity is unity at a pressure of 1 bar; this approximation is valid for most real gases)
Liquid	Pure liquid in the most stable form at 1 bar
Solid	Pure solid in the most stable form at 1 bar

to calculations giving reproducible results. Although different standard states may be chosen for various species, *throughout any set of calculations, to minimize possibilities for error it is important that the standard state of a particular component be kept the same*. Certain choices of standard states have found such widespread use that they have achieved the status of recognized conventions. In particular, those included in Table 2.1 are used in calculations dealing with chemical reaction equilibria. In all cases the temperature is the same as that of the reaction mixture.

Once the standard states for the various species have been established, one can proceed to calculate a number of standard energy changes for processes involving a change from reactants, all in their respective standard states, to products, all in their respective standard states. For example, the standard Gibbs free energy change (ΔG^0) for a single reaction is

$$\Delta G^0 = \sum_i \nu_i \mu_i^0 \tag{2.1.2}$$

where the superscript zero emphasizes the fact that this is a process involving standard states for both the final and initial conditions of the system. In a similar manner, one can determine standard enthalpy (ΔH^0) and standard entropy changes (ΔS^0) for this process.

2.2 ENERGY EFFECTS ASSOCIATED WITH CHEMICAL REACTIONS

Because chemical reactions involve the formation, destruction, or rearrangement of chemical bonds, they are invariably accompanied by changes in the enthalpy and Gibbs free energy of the system. The enthalpy change on reaction provides information that is necessary for any engineering analysis of the system in terms of the first law of thermodynamics. Standard enthalpy changes are also useful in determining the effect of temperature on the equilibrium constant for the reaction and thus on the reaction yield. Gibbs free energy changes are useful in determining whether or not chemical equilibrium exists in the system being studied and in determining how changes in process variables can influence the yield of the reaction.

In chemical kinetics there are two types of processes for which one is typically interested in changes in these energy functions:

1. A chemical process whereby stoichiometric quantities of reactants, each in its standard state, are completely converted to stoichiometric amounts of products, each in its standard state, under conditions such that the initial temperature of the reactants is equal to the final temperature of the products.
2. An actual chemical process as it might occur under either equilibrium or nonequilibrium conditions in a chemical reactor.

One must be very careful not to confuse actual energy effects with those that are associated with the process whose initial and final states are the standard states of the reactants and products, respectively.

To have a consistent basis for comparing different reactions and to permit the tabulation of thermochemical data for various reaction systems, it is convenient to define enthalpy and Gibbs free energy changes for standard reaction conditions. These conditions involve the use of stoichiometric amounts of the various reactants (each in its standard state at some temperature T). The reaction proceeds by some unspecified path to end up with complete conversion of reactants to the various products (each in its standard state at the same temperature T).

The enthalpy and Gibbs free energy changes for a standard reaction are denoted by the symbols ΔH^0 and ΔG^0, where the superscript zero is used to signify that a "standard" reaction is involved. Use of these symbols is restricted to the case where the extent of reaction is 1 mol for the reaction as written with a specific set of stoichiometric coefficients. The remaining discussion in this chapter refers to this basis.

Because G and H are state functions, changes in these quantities are independent of whether the reaction takes place in one or in several steps. Consequently, it is possible to tabulate data for relatively few reactions and use these data in the calculation of ΔG^0 and ΔH^0 for other reactions. In particular, one tabulates data for the standard reactions that involve the formation of a compound from its elements. One may then consider a reaction involving several compounds as being an appropriate algebraic sum of a number of elementary reactions, each of which involves the formation of a single compound. The dehydration of *n*-propanol,

$$\mathrm{CH_3CH_2CH_2OH(l) \rightarrow H_2O(l) + CH_3CH{=}CH_2(g)}$$

may be considered as the algebraic sum of the following series of reactions:

$$
\begin{array}{lll}
CH_3CH_2CH_2OH(l) \rightarrow 3C\,(\beta\,\text{graphite}) + 4H_2(g) + \frac{1}{2}O_2(g) & \Delta H_1^0 & \Delta G_1^0 \\
3C\,(\beta\,\text{graphite}) + 3H_2\,(g) \rightarrow CH_3CH{=}CH_2(g) & \Delta H_2^0 & \Delta G_2^0 \\
H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) & \Delta H_3^0 & \Delta G_3^0 \\
\hline
CH_3CH_2CHOH\,(l) \rightarrow H_2O(l) + CH_3CH{=}CH_2(g) & \Delta H^0 & \Delta G^0
\end{array}
$$

For the overall reaction,

$$\Delta H^0 = \Delta H_1^0 + \Delta H_2^0 + \Delta H_3^0 \tag{2.2.1}$$

$$\Delta G^0 = \Delta G_1^0 + \Delta G_2^0 + \Delta G_3^0 \tag{2.2.2}$$

However, each of the individual reactions involves the formation of a compound from its elements or the decomposition of a compound into those elements. The standard enthalpy change of a reaction that involves the formation of a compound from its elements is referred to as the *enthalpy* (or heat) of formation of that compound and is denoted by the symbol ΔH_f^0. Thus, for the dehydration of *n*-propanol,

$$\Delta H^0_{\text{overall}} = -\Delta H^0_{f\,\text{propanol}} + \Delta H^0_{f\,\text{water}} + \Delta H^0_{f\,\text{propylene}} \tag{2.2.3}$$

and

$$\Delta G^0_{\text{overall}} = -\Delta G^0_{f\,\text{propanol}} + \Delta G^0_{f\,\text{water}} + \Delta G^0_{f\,\text{propylene}} \tag{2.2.4}$$

where $\Delta G^0_{f\,i}$ refers to the standard Gibbs free energy of formation of the indicated compound *i*.

This example illustrates the principle that values of ΔG^0 and ΔH^0 may be calculated from values of the enthalpies and Gibbs free energies of formation of the products and reactants. In more general form,

$$\Delta H^0 = \sum_i \nu_i \, \Delta H^0_{f,i} \tag{2.2.5}$$

$$\Delta G^0 = \sum_i \nu_i \, \Delta G^0_{f,i} \tag{2.2.6}$$

When an element enters into a reaction, its standard Gibbs free energy and standard enthalpy of formation are taken as zero if its state of aggregation is identical to that selected as the basis for the determination of the standard Gibbs free energy and enthalpy of formation of its compounds. If ΔH^0 is negative, the reaction is said to be *exothermic;* if ΔH^0 is positive, the reaction is said to be *endothermic*.

It is not necessary to tabulate values of ΔG^0 or ΔH^0 for all conceivable reactions. It is sufficient to tabulate values of these parameters only for the reactions that involve the formation of a compound from its elements. The problem of data compilation is further simplified by the fact that it is unnecessary to record ΔG_f^0 and ΔH_f^0 at all temperatures, because of the relations that exist between these quantities and other thermodynamic properties of the reactants and products. The convention that is most commonly accepted in engineering practice today is to report values of standard enthalpies of formation and Gibbs free energies of formation at 25°C (298.16 K), although 0 K is sometimes used as the reference state. The problem of calculating a value for ΔG^0 or ΔH^0 at temperature T thus reduces to one of determining values of ΔG^0 and ΔH^0 at 25°C or 0 K and then adjusting the value obtained to take into account the effects of temperature on the property in question. The appropriate techniques for carrying out these adjustments are indicated below.

For temperatures in K, the effect of temperature on ΔH^0 is given by

$$\Delta H_T^0 = \Delta H^0_{298.16} + \int_{298.16\,\text{K}}^{T} \left(\sum_i \upsilon_i C^0_{p,i} \right) dT \tag{2.2.7}$$

where $C^0_{p,i}$ is the constant pressure heat capacity of species *i* in its standard state.

In many cases the magnitude of the last term on the right side of equation (2.2.7) is very small compared to $\Delta H^0_{298.16}$. However, if one is to be able to evaluate the standard heat of reaction properly at some temperature other than 298.16 K, one must know the constant pressure heat capacities of the reactants and the products as functions of temperature as well as the standard heat of reaction at 298.16 K. Data of this type and techniques for estimating these properties are contained in the references in Section 2.3.

The most useful expression for describing the variation of standard Gibbs free energy changes with the *absolute* temperature is

$$\left[\frac{\partial \left(\Delta G^0 / T \right)}{\partial T} \right]_P = -\frac{\Delta H^0}{T^2} \tag{2.2.8}$$

In Section 2.5 we shall see that the equilibrium constant for a chemical reaction is simply related to $\Delta G^0/T$ and that equation (2.2.8) is useful in determining how equilibrium constants vary with temperature. If one desires to obtain an expression for ΔG^0 itself as a function of temperature, equation (2.2.7) may be integrated to give ΔH^0 as a function of temperature. This relation may then be used with equation (2.2.8) to arrive at the desired relation.

The effects of pressure on ΔG^0 and ΔH^0 depend on the choice of standard states employed. When the standard state of each component of the reaction system is taken at 1 bar whether the species in question is a gas, liquid, or solid, the values of ΔG^0 and ΔH^0 refer to a process that starts and ends at 1 bar. For this choice of standard states, the *values of ΔG^0 and ΔH^0 are independent of the pressure at which the reaction is actually carried out*. It is important to note in this connection that we are calculating the enthalpy change for a hypothetical process, not for the process as it actually occurs in nature. The choice of standard states at a pressure (or fugacity) of 1 bar is the convention that is customarily adopted in the analysis of chemical reaction equilibria.

For cases where the standard-state pressure for the various species is chosen as that of the system under investigation, changes in this variable will alter the values of ΔG^0 and ΔH^0. In such cases a thermodynamic analysis indicates that

$$\Delta H_P^0 = \Delta H_{1\text{bar}}^0 + \sum_i \nu_i \int_1^P \left[V_i - T\left(\frac{\partial V_i}{\partial T}\right)_P \right] dP \qquad (2.2.9)$$

where V_i is the molal volume of component i in its standard state and where each integral is evaluated for the species in question along an isothermal path between 1 bar and the final pressure P. The term in brackets represents the variation of the enthalpy of a component with pressure at constant temperature $(\partial H/\partial P)_T$.

It should be emphasized that the choice of standard states implied by equation (2.2.9) is *not* that which is used conventionally in the analysis of chemically reacting systems. Furthermore, *in the vast majority of cases the summation term on the right side of this equation is very small compared to the magnitude of $\Delta H_{1\text{bar}}^0$ and, indeed, is usually considerably smaller than the uncertainty in this term*.

The Gibbs free energy analog of equation (2.2.9) is

$$\Delta G_P^0 = \Delta G_{1\text{bar}}^0 + \sum_i \nu_i \int_1^P V_i \, dP \qquad (2.2.10)$$

where the integral is again evaluated along an isothermal path. For cases where the species involved is a condensed phase, V_i will be a very small quantity and the contribution of this species to the summation will be quite small unless the system pressure is extremely high. For ideal gases, the integral may be evaluated directly as $RT \ln P$. For nonideal gases the integral is equal to $RT \ln f_i^0$, where f_i^0 is the fugacity of pure species i at pressure P.

2.3 SOURCES OF THERMOCHEMICAL DATA

There are a large number of scientific handbooks and textbooks that contain thermochemical data. In addition, many websites serve as sources of such data. Some useful supplementary references are listed below.

1. NIST (National Institutes of Standards and Technology) Scientific and Technical Databases (http://www.nist.gov/srd/thermo.htm), most notably the NIST Chemistry WebBook (2005), which contains an extensive collection of thermochemical data for over 7000 organic and small inorganic compounds.
2. D. R. Lide and H. V. Kehiaian (Eds.), *CRC Handbook of Thermophysical and Thermochemical Data*, CRC Press, Boca Raton, FL, 1994.
3. M. Binnewies and E. Milke (Eds.), *Thermochemical Data of Elements and Compounds*, 2nd rev. ed., Wiley-VCH, Weinheim, Germany, 2002.
4. W. M. Haynes (Ed.), *CRC Handbook of Chemistry and Physics*, 92nd ed., CRC Press, Boca Raton, FL, 2011.
5. J. B. Pedley, R. D. Naylor, and S. P. Kirby, *Thermochemical Data of Organic Compounds*, 2nd ed., Chapman & Hall, New York, 1986.
6. J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York, 1970.
7. D. R. Stull, E. F. Westrum, and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1969.
8. D. W. Green and R. H. Perry (Eds.), *Perry's Chemical Engineers' Handbook*, 8th ed., McGraw-Hill, New York, 2008.

If thermochemical data are not available, the following references are useful to describe techniques for estimating thermochemical properties from a knowledge of the molecular structures of the compounds of interest.

1. B. E. Poling, J. M. Prausnitz, and J. O'Connell, *The Properties of Gases and Liquids*, 5th rev. ed., McGraw-Hill, New York, 2000.
2. N. Cohen and S. W. Benson, Estimation of Heats of Formation of Organic Compounds by Additivity Methods, *Chem. Rev.*, **93**, 2419–2438 (1993).

2.4 THE EQUILIBRIUM CONSTANT AND ITS RELATION TO ΔG^0

The basic criterion for equilibrium with respect to a given chemical reaction is that the Gibbs free energy change associated with the progress of the reaction be zero:

$$\Delta G = \sum_i \nu_i \mu_i = 0 \qquad (2.4.1)$$

where the μ_i are the chemical potentials of the various species in the equilibrium mixture. The *standard* Gibbs free energy change for a reaction refers to the process wherein stoichiometric quantities of reactants, each in its standard state of unit activity, at some arbitrary temperature T are completely converted to products, each in its standard state of unit activity at this same temperature. In general, the standard Gibbs free energy change, ΔG^0, is nonzero and is given by

$$\Delta G^0 = \sum_i \nu_i {\mu_i}^0 \qquad (2.4.2)$$

where the ${\mu_i}^0$ are the chemical potentials of the various species in their standard states at the temperature of the reaction mixture.

Subtraction of equation (2.4.2) from (2.4.1) gives

$$\Delta G - \Delta G^0 = \sum_i \nu_i(\mu_i - \mu_i^0) \tag{2.4.3}$$

This equation may be rewritten in terms of the activities of the various species by making use of equation (2.1.1):

$$\Delta G - \Delta G^0 = RT \sum_i [\nu_i \ln a_i] = RT \ln \left(\prod_i a_i^{\nu_i} \right) \tag{2.4.4}$$

where $\prod_i$ denotes a product over i species of the term that follows.

For a general reaction of the form

$$b\text{B} + c\text{C} + \cdots \leftrightarrow s\text{S} + t\text{T} + \cdots \tag{2.4.5}$$

the equations above lead to

$$\Delta G - \Delta G^0 = RT \ln \left(\frac{a_\text{S}^s a_\text{T}^t \cdots}{a_\text{B}^b a_\text{C}^c \cdots} \right) \tag{2.4.6}$$

For a system at equilibrium, $\Delta G = 0$, so

$$\Delta G^0 = -RT \ln \left(\frac{a_\text{S}^s a_\text{T}^t \cdots}{a_\text{B}^b a_\text{C}^c \cdots} \right) = -RT \ln K_a \tag{2.4.7}$$

where the equilibrium constant for the reaction (K_a) at temperature T is defined as the ln term. The subscript a in the symbol K_a has been used to emphasize that an equilibrium constant is written properly as a product of the activities raised to appropriate powers. Thus, in general,

$$K_a = \prod_i a_i^{\nu_i} = e^{-\Delta G^0/RT} \tag{2.4.8}$$

Inspection of equation (2.4.8) indicates that the equilibrium constant for a reaction is determined by the absolute temperature and the standard Gibbs free energy change (ΔG^0) for the process. The latter quantity depends, in turn, on temperature, the definitions of the standard states of the various components, and the stoichiometric coefficients of these species. Consequently, in assigning a numerical value to an equilibrium constant, one must be careful to specify all three of these quantities to give meaning to this value. Once one has thus specified the point of reference, this value may be used to calculate the equilibrium composition of the mixture in the manner described in Sections 2.6 to 2.9.

2.5 EFFECTS OF TEMPERATURE AND PRESSURE CHANGES ON THE EQUILIBRIUM CONSTANT

Equilibrium constants are very sensitive to temperature changes. A quantitative description of the influence of temperature changes is readily obtained by combining equations (2.2.8) and (2.4.7):

$$\left[\frac{\partial \left(-\Delta G^0/T\right)}{\partial T} \right]_P = \left(\frac{R\, \partial \ln K_a}{\partial T} \right)_P = \frac{\Delta H^0}{T^2} \tag{2.5.1}$$

or

$$\left(\frac{\partial \ln K_a}{\partial T} \right)_P = \frac{\Delta H^0}{RT^2} \tag{2.5.2}$$

and

$$\left[\frac{\partial \ln K_a}{\partial (1/T)} \right]_P = -\frac{\Delta H^0}{R} \tag{2.5.3}$$

For cases where ΔH^0 is essentially independent of temperature, plots of data in the form $\ln K_a$ versus $1/T$ are linear with a slope equal to $-\Delta H^0/R$. Such plots are often referred to as *van't Hoff plots*. For cases where the heat capacity term in equation (2.2.7) is appreciable, this equation must be substituted into either equation (2.5.2) or (2.5.3) to determine the temperature dependence of the equilibrium constant. For exothermic reactions (ΔH^0 is negative), the equilibrium constant decreases with increasing temperature, whereas for endothermic reactions the equilibrium constant increases with increasing temperature.

Figure 2.1 contains van't Hoff plots for three industrially significant reactions. The mathematical models used to correlate the data incorporate the dependence of ΔH^0 on the absolute temperature. The quasi-linearity of the two plots for exothermic reactions (those with positive slopes) attests to the fact that the dominant term in equation (2.2.7) is the standard enthalpy change at temperature T and that the heat capacity term may frequently be neglected over fairly wide temperature ranges. In terms of this simplifying assumption, one in essence regards the standard enthalpy change as a constant that can be determined from the slope of a best-fit line through experimental data plotted in the form of equation (2.2.8). The fact that $\Delta G^0 = \Delta H^0 - T\,\Delta S^0$ implies that the intercept corresponding to a reciprocal absolute temperature of zero for such lines is equal to $\Delta S^0/R$. The plot in Figure 2.1 that has a negative slope is characteristic of many dehydrogenation reactions. Such slopes identify the reaction as endothermic. In this case the stoichiometry of the reaction is

$$C_6H_5C_2H_5 \leftrightarrow H_2 + C_6H_5CH{=}CH_2$$

For cases in which the standard states of the reactants and products are chosen as 1 bar, the value of ΔG^0 is independent of pressure. Consequently, equation (2.4.7) indicates that K_a *is also pressure independent for this choice of standard states*. This convention is the one normally encountered in engineering practice. For the *unconventional* choice of standard states discussed in Section 2.2,

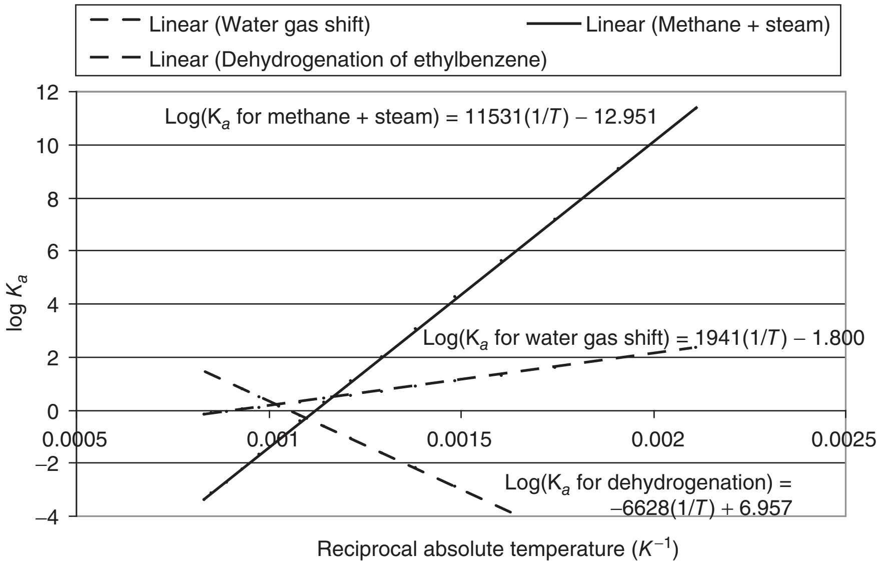

Figure 2.1 Dependence of equilibrium constants on absolute temperature plotted using coordinates suggested by the van't Hoff relation. The plots for exothermic reactions (water gas shift and methane + steam) have positive slopes. The reaction of methane with steam is $CH_4 + H_2O \leftrightarrow CO + 3H_2$, and the stoichiometry of the water gas shift is $CO + H_2O \leftrightarrow CO_2 + H_2$. The plot with a negative slope corresponds to the endothermic dehydrogenation of ethylbenzene to form styrene (1). Because we have plotted the logarithms of the equilibrium constants rather than using natural logarithms, the slopes of these plots correspond to $-\Delta H^0/2.303R$ and the intercepts to $\Delta S^0/2.303R$. [These plots are based on correlating equations contained in Appendixes 6 and 7 of M. V. Twigg (Ed.), *Catalyst Handbook*, 2nd ed., Wolfe Publishing, London, 1989.]

equations (2.4.7) and (2.2.10) may be combined to give the effect of pressure on K_a:

$$\left(\frac{\partial \ln K_a}{\partial P}\right)_T = -\frac{\sum_i \nu_i V_i^0}{RT} \tag{2.5.4}$$

where the V_i^0 are the standard-state molar volumes of the reactants and products. However, use of this choice of standard states is extremely rare in engineering practice.

2.6 DETERMINATION OF EQUILIBRIUM COMPOSITIONS

The basic equation from which one calculates the composition of an equilibrium mixture is equation (2.4.7). Application of this relation to the chemical reaction defined by equation (2.4.5) gives

$$\Delta G^0 = -RT \ \ln \ K_a = -RT \ \ln \left(\frac{a_S^s a_T^t}{a_B^b a_C^c}\right) \tag{2.6.1}$$

In a system that involves gaseous components, one normally chooses as the standard state the pure component gases, each at unit fugacity (essentially, 1 bar). The activity of a gaseous species B is then given by

$$a_B = \frac{\hat{f}_B}{f_{B,SS}} = \frac{\hat{f}_B}{1} = \hat{f}_B \tag{2.6.2}$$

where $\hat{f}_B$ is the fugacity of species B as it exists in the equilibrium reaction mixture and $f_{B,SS}$ is the fugacity of species B in its standard state.

The fugacity of species B in an ideal solution of gases is given by the *Lewis and Randall rule*,

$$\hat{f}_B = y_B f_B^0 \tag{2.6.3}$$

where y_B is the mole fraction B in the gaseous phase and f_B^0 is the fugacity of pure component B evaluated at the temperature and total pressure (P) of the reaction mixture. Alternatively,

$$\hat{f}_B = y_B \left(\frac{f}{P}\right)_B P \tag{2.6.4}$$

where $(f/P)_B$ is the fugacity coefficient for pure component B at the temperature and total pressure of the system.

If all of the species involved in the reaction are gases, combining equations (2.6.1), (2.6.2), and (2.6.4) gives

$$K_a = \frac{y_S^s y_T^t}{y_B^b y_C^c} \frac{(f/P)_S^s (f/P)_T^t}{(f/P)_B^b (f/P)_C^c} P^{s+t-b-c} \tag{2.6.5}$$

The first term on the right is assigned the symbol K_y, while the second term is assigned the symbol $K_{f/P}$. The quantity $K_{f/P}$ is constant for a given temperature and pressure. However, unlike the equilibrium constant K_a, the term $K_{f/P}$ is affected by changes in the system pressure as well as by changes in temperature. The product of K_y and $P^{s+t-b-c}$ is assigned the symbol K_P:

$$K_P \equiv K_y P^{s+t-b-c} = \frac{(y_S P)^s (y_T P)^t}{(y_B P)^b (y_C P)^c} = \frac{P_S^s P_T^t}{P_B^b P_C^c} \tag{2.6.6}$$

because each term in parentheses is a component partial pressure. Thus,

$$K_a = K_{f/P} K_P \tag{2.6.7}$$

For cases where the gases behave ideally, the fugacity coefficients may be taken as unity and the term K_P equated to K_a. At higher pressures, where the gases are no longer ideal, the $K_{f/P}$ term may differ appreciably from unity and have a significant effect on the equilibrium composition. The corresponding states plot of fugacity coefficients contained in Appendix A may be used to estimate $K_{f/P}$.

In a system containing an inert gas I in the amount of n_I moles, the mole fraction of reactant gas B is given by

$$y_B = \frac{n_B}{n_B + n_C + \cdots + n_S + n_T + \cdots + n_I} \tag{2.6.8}$$

where the n_i refer to the mole numbers of reactant and product species. Combination of equations (2.6.5) to (2.6.7) and defining equations similar to equation (2.6.8) for the various mole fractions gives

$$K_a = K_{f/P} \left(\frac{n_S^s n_T^t}{n_B^b n_C^c} \right) \times \left(\frac{P}{n_B + n_C + \cdots + n_S + n_T + \cdots + n_I} \right)^{s+t-b-c} \tag{2.6.9}$$

This equation is extremely useful for calculating the equilibrium composition of the reaction mixture. The mole numbers of the various species at equilibrium may be related to their values at time zero using the extent of reaction. When these relations are substituted into equation (2.6.9), one obtains a single equation in a single unknown, the equilibrium extent of reaction. This technique is utilized in Illustration 2.1. If more than one independent reaction is occurring in a given system, one requires as many equations of the form of equation (2.6.9) as there are independent reactions. These equations are then written in terms of the various extents of reaction to obtain a set of independent equations equal to the number of unknowns. Such a system is considered in Illustration 2.2.

ILLUSTRATION 2.1 Calculation of Equilibrium Yield for a Chemical Reaction

Problem

Calculate the equilibrium composition of a mixture of the following species:

N_2	15.0 mol%
H_2O	60.0 mol%
C_2H_4	25.0 mol%

The mixture is maintained at a constant temperature of 527 K and a constant pressure of 264.2 bar. Assume that the only significant chemical reaction is

$$H_2O(g) + C_2H_4(g) \leftrightarrow C_2H_5OH(g)$$

The standard state of each species is taken as the pure material at unit fugacity. Use only the following critical properties, thermochemical data, and a fugacity coefficient chart.

Compound	T_C (K)	P_C(bar)
$H_2O(g)$	647.3	218.2
$C_2H_4(g)$	283.1	50.5
$C_2H_5OH(g)$	516.3	63.0

Compound	$\Delta G^0_{f298.16}$ (kJ/mol)	$\Delta H^0_{f298.16}$ (kJ/mol)
$H_2O(g)$	−228.705	−241.942
$C_2H_4(g)$	68.156	52.308
$C_2H_5OH(g)$	−168.696	−235.421

Solution

The basis is 100 mol of initial gas. To calculate the equilibrium composition, one must know the equilibrium constant for the reaction at 527 K. From the values of $\Delta G^0_{f,i}$ and $\Delta H^0_{f,i}$ at 298.16 K and equations (2.2.5) and (2.2.6):

$$\Delta G^0_{298} = (1)(-168.696) + (-1)(68.156) + (-1)(-228.705) = -8.147 \text{ kJ/mol}$$

$$\Delta H^0_{298} = (1)(-235.421) + (-1)(52.308) + (-1)(-241.942) = -45.787 \text{ kJ/mol}$$

The equilibrium constant at 298.16 K may be determined from equation (2.4.7):

$$\Delta G^0 = -RT \ln K_a$$

or

$$\ln K_a = -\frac{-8147}{8.31(298.16)} = 3.29$$

The equilibrium constant at 527 K may be determined using equation (2.5.3):

$$\left[\frac{\partial \ln K_a}{\partial (1/T)} \right]_P = -\frac{\Delta H^0}{R}$$

If one assumes that ΔH^0 is independent of temperature, this equation may be integrated to obtain

$$\ln K_{a,2} - \ln K_{a,1} = \frac{\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

For our case,

$$\ln K_{a,2} - 3.29 = \frac{-45{,}787}{8.31}\left(\frac{1}{298.16} - \frac{1}{527}\right) = -8.02$$

or

$$K_{a,2} = 8.83 \times 10^{-3} \text{ at } 527 \text{ K}$$

Because the standard states are the pure materials at unit fugacity, equation (2.6.5) may be rewritten as

$$K_a = \frac{y_{C_2H_5OH}}{y_{H_2O}y_{C_2H_4}} \frac{(f/P)_{C_2H_5OH}}{(f/P)_{H_2O}(f/P)_{C_2H_4}} \frac{1}{P} \tag{A}$$

The fugacity coefficients (f/P) for the various species may be determined from a corresponding states chart if one knows the reduced temperature and pressure corresponding to the species in question. Therefore:

Species	Reduced temperature, 527 K	Reduced pressure, 264.2 atm	f/P
H_2O(g)	527/647.3 = 0.814	264.2/218.2 = 1.211	0.190
C_2H_4(g)	527/283.1 = 1.862	264.2/50.5 = 5.232	0.885
C_2H_5OH(g)	527/516.3 = 1.021	264.2/63.0 = 4.194	0.280

From the stoichiometry of the reaction it is possible to determine the mole numbers of the various species in terms of the extent of reaction and their initial mole numbers:

$$n_i = n_{i,0} + \nu_i \xi$$

Species	Initial moles	Moles at extent ξ
N_2	15.0	15.0
H_2O	60.0	$60.0 - \xi$
C_2H_4	25.0	$25.0 - \xi$
C_2H_5OH	0.0	$0.0 + \xi$
Total	100.0	$100.0 - \xi$

The various mole fractions are readily determined from this table. Note that the upper limit on ξ is 25.0. Substitution of numerical values and expressions for the various mole fractions into equation (A) gives

$$8.83 \times 10^{-3} = \left[\frac{\dfrac{\xi}{100.0 - \xi}}{\left(\dfrac{60.0 - \xi}{100.0 - \xi}\right)\left(\dfrac{25.0 - \xi}{100.0 - \xi}\right)}\right] \times \left\{\left[\frac{0.280}{0.190\,(0.885)}\right]\frac{1}{264.2}\right\}$$

or

$$\frac{\xi(100.0 - \xi)}{(60.0 - \xi)(25.0 - \xi)} = 8.83 \times 10^{-3}(264.2)\left[\frac{0.190\,(0.885)}{0.280}\right] = 1.404$$

This equation is quadratic in ξ. The solution is $\xi = 10.9$. On the basis of 100 mol of starting material, the equilibrium composition is then as follows:

Species	Mole numbers	Mole percentages
N_2	15.0	16.83
H_2O	49.1	55.11
C_2H_4	14.1	15.82
C_2H_5OH	10.9	12.23
Total	89.1	99.99

2.7 EFFECTS OF REACTION CONDITIONS ON EQUILIBRIUM YIELDS

Equation (2.6.9) is an extremely useful relation for determining the effects of changes in process parameters on the equilibrium yield of a specific product in a system in which only a single gas-phase reaction is important. Rearrangement of this equation gives

$$\frac{n_S^s n_T^t}{n_B^b n_C^c} = \frac{K_a}{K_{f/P}}\left(\frac{n_B + n_C + \cdots + n_S + n_T + \cdots + n_I}{P}\right)^{s+t-b-c} \tag{2.7.1}$$

Any change that increases the right side of equation (2.7.1) will increase the ratio of products to reactants in the equilibrium mixture and thus correspond to increased conversions.

2.7.1 Effects of Temperature Changes

The temperature affects the equilibrium yield primarily through its influence on the equilibrium constant K_a. From equation (2.5.2) it follows that for exothermic reactions the equilibrium conversion decreases as the temperature increases. The equilibrium yield increases with increasing temperature for endothermic reactions. Temperature changes also affect the value of $K_{f/P}$. The changes in this term, however, are generally very small compared to those in K_a.

2.7.2 Effects of Total Pressure

The equilibrium constant K_a is independent of pressure for those cases where the standard states are taken as the pure components at 1 bar. This situation was used as the basis for deriving equation (2.6.9). The effects of pressure changes then appear in the terms $K_{f/P}$ and $P^{s+t-b-c}$. For reactions that produce a change in the total number of gaseous species in the system, the term that has the largest effect on the equilibrium yield of products is $P^{s+t-b-c}$. Thus, if a reaction produces a decrease in the total number of gaseous components, the equilibrium yield is increased by an increase in pressure. If an increase in the total number of gaseous moles accompanies the reaction, the equilibrium yield decreases as the pressure increases.

The influence of moderate changes in pressure on $K_{f/P}$ is normally negligible. However, for situations in which there is no change in the total number of gaseous moles during the reaction, this term is the only one by which pressure changes can affect the equilibrium yield. To determine the effect of major changes in pressure on the equilibrium yield, one should calculate the value of $K_{f/P}$ using generalized fugacity coefficient charts for the system and conditions of interest.

2.7.3 Effect of Addition of Inert Gases

The only term in equation (2.7.1) that is influenced by the addition of inert gases is n_{I}. Thus, for reactions in which there is no change in the total number of gaseous moles, addition of inerts has no effect on the equilibrium yield. For cases where there is a change, the effect produced by addition of inert gases is in the same direction as that which would be produced by a pressure decrease.

2.7.4 Effect of Addition of Catalysts

The equilibrium constant and equilibrium yield are independent of whether or not a catalyst is present. If the catalyst does not remove any of the passive restraints that have been placed on the system by opening up the possibility of additional reactions, the equilibrium yield will not be affected by the presence of this material.

2.7.5 Effect of Excess Reactants

If nonstoichiometric amounts of reactants are present in the initial system, the presence of excess reactants tends to increase the equilibrium fractional conversion of the limiting reagent above that which would be obtained with stoichiometric ratios of the reactants.

2.8 HETEROGENEOUS REACTIONS

The fundamental fact on which the analysis of heterogeneous reactions is based is that when a component is present as a pure liquid or as a pure solid, its activity may be taken as unity, provided that the pressure on the system is not extremely high. For very high pressures, the effects of pressure on the activities of pure solids or liquids may be determined using the *Poynting correction factor*:

$$\ln\left(\frac{a_{P=P}}{a_{P=1\mathrm{bar}}}\right) = \frac{\int_1^P V\,dP}{RT} \tag{2.8.1}$$

where V is the molar volume of the condensed phase. The activity ratio is essentially unity at moderate pressures.

If we now return to our generalized reaction (2.4.5) and add to our gaseous components B, C, S, and T a pure liquid or solid reactant D and a pure liquid or solid product U with stoichiometric coefficients d and u, respectively, the reaction may be written as

$$\begin{aligned} b\mathrm{B(g)} + c\mathrm{C(g)} + d\mathrm{D(l\ or\ s)} + \cdots &\leftrightarrow \\ s\mathrm{S(g)} + t\mathrm{T(g)} + u\mathrm{U(l\ or\ s)} + \cdots & \end{aligned} \tag{2.8.2}$$

The equilibrium constant for this reaction is

$$K_a = \frac{a_{\mathrm{S}}^s a_{\mathrm{T}}^t a_{\mathrm{U}}^u \cdots}{a_{\mathrm{B}}^b a_{\mathrm{C}}^c a_{\mathrm{D}}^d \cdots} \tag{2.8.3}$$

When the standard states for the solid and liquid species correspond to the pure species at a pressure of 1 bar or at a low equilibrium vapor pressure of the condensed phase, the activities of the pure species at equilibrium are taken as unity at all moderate pressures. Consequently, the gas-phase composition at equilibrium will not be affected by the amount of solid or liquid present. At very high pressures, equation (2.8.1) must be used to calculate these activities. When solid or liquid solutions are present, the activities of the components of these solutions are no longer unity even at moderate pressures. In this case, to determine the equilibrium composition of the system, one needs data on the activity coefficients of the various species and the solution composition.

2.9 EQUILIBRIUM TREATMENT OF SIMULTANEOUS REACTIONS

The treatment of chemical reaction equilibria outlined above can be generalized to cover the situation where multiple reactions occur simultaneously. In principle one can take all conceivable reactions into account in computing the composition of a gas mixture at equilibrium. However, because of kinetic limitations on the rate of approach of certain reactions to equilibrium, one can treat many systems as if equilibrium is achieved in some reactions but not in others. In many cases, reactions that are thermodynamically possible do not, in fact, occur at appreciable rates.

In practice, additional simplifications occur because at equilibrium many of the possible reactions either occur to a negligible extent, or else proceed substantially to completion. One criterion for determining if either of these conditions prevails is to examine the magnitude of the equilibrium constant in question. If it is many orders of magnitude greater than unity, the reaction may be said to go to completion. If it is orders of magnitude less than unity, the reaction may be assumed to occur to a negligible extent. In either event, the number of chemical species that must be considered is reduced and the analysis is thereby simplified. After the simplifications are made, there may remain a group of reactions whose equilibrium constants are neither extremely small nor very large, indicating that appreciable amounts of both products and reactants are present at equilibrium. All of these reactions must be considered in calculating the equilibrium composition.

To arrive at a consistent set of relationships from which complex reaction equilibria may be determined, one must develop the same number of independent equations as there are unknowns. The following treatment indicates the Gauss–Jordan method of arriving at a set of chemical reactions that are independent (2).

If R reactions occur simultaneously within a system composed of S species, one has R stoichiometric equations of the form

$$\sum_{i=1}^{S} \nu_{ki} A_i = 0 \qquad k = 1, 2, \ldots, R \tag{2.9.1}$$

where ν_{ki} is the stoichiometric coefficient of species i in reaction k.

Because the same reaction may be written with different stoichiometric coefficients, the importance of the coefficients lies in the fact that the ratios of the coefficients of two species must be identical, no matter how the reaction is written. Thus, the stoichiometric coefficients of a reaction are given only up to a constant multiplier λ. The equation

$$\sum_{i=1}^{S} \lambda \nu_{ki} A_i = 0 \qquad k = 1, 2, \ldots, R \tag{2.9.2}$$

has the same meaning as equation (2.9.1), provided that λ is nonzero.

If three or more reactions can be written for a given system, one must test to see if any is a multiple of one of the others and if any is a linear combination of two or more others. We will use a set of elementary reactions representing a mechanism for the reaction between H_2 and Br_2 as a vehicle for indicating how one may determine which of a set of reactions are independent.

$$\begin{gathered} Br_2 \rightarrow 2Br \\ Br + H_2 \rightarrow HBr + H \\ H + Br_2 \rightarrow HBr + Br \\ H + HBr \rightarrow H_2 + Br \\ 2Br \rightarrow Br_2 \end{gathered} \tag{2.9.3}$$

If we define

$$A_1 = Br_2 \quad A_2 = Br \quad A_3 = H_2 \quad A_4 = H \quad A_5 = HBr \tag{2.9.4}$$

the reactions in (2.9.3) may be rewritten as

$$\begin{array}{rrrrrl} -A_1 & +2A_2 & & & & = 0 \\ & -A_2 & -A_3 & +A_4 & +A_5 & = 0 \\ -A_1 & +A_2 & & -A_4 & +A_5 & = 0 \\ & A_2 & +A_3 & -A_4 & -A_5 & = 0 \\ A_1 & -2A_2 & & & & = 0 \end{array} \tag{2.9.5}$$

To test for independence, form the matrix of the stoichiometric coefficients of the foregoing reactions with ν_{ki} in the kth row and the ith column.

$$\begin{array}{rrrrr} -1 & 2 & 0 & 0 & 0 \\ 0 & -1 & -1 & 1 & 1 \\ -1 & 1 & 0 & -1 & 1 \\ 0 & 1 & 1 & -1 & -1 \\ 1 & -2 & 0 & 0 & 0 \end{array} \tag{2.9.6}$$

Next, take the first row with a nonzero element in the first column and divide through by the leading element. If $\nu_{ki} \neq 0$, this will give a new first row of

$$1 \quad \frac{\nu_{12}}{\nu_{11}} \quad \frac{\nu_{13}}{\nu_{11}} \quad \cdots \quad \frac{\nu_{1S}}{\nu_{11}} \tag{2.9.7}$$

This new row may now be used to make all other elements of the first column zero by subtracting ν_{ki} times the new first row from the corresponding element in the kth row. The row that results is

$$0 \quad \left(\nu_{k2} - \nu_{k1}\frac{\nu_{12}}{\nu_{11}}\right) \quad \left(\nu_{k3} - \nu_{k1}\frac{\nu_{13}}{\nu_{11}}\right) \quad \cdots \quad \left(\nu_{kS} - \nu_{k1}\frac{\nu_{1S}}{\nu_{11}}\right) \tag{2.9.8}$$

In the present example the revised coefficient matrix becomes

$$\begin{array}{rrrrr} 1 & -2 & 0 & 0 & 0 \\ 0 & -1 & -1 & 1 & 1 \\ 0 & -1 & 0 & -1 & 1 \\ 0 & 1 & 1 & -1 & -1 \\ 0 & 0 & 0 & 0 & 0 \end{array} \tag{2.9.9}$$

The next step is to ignore the first row and the first column of this matrix and repeat the reduction above on the resulting reduced matrix containing $R - 1$ rows. Thus, matrix (2.9.9) becomes

$$\begin{array}{rrrrr} 1 & -2 & 0 & 0 & 0 \\ 0 & 1 & 1 & -1 & -1 \\ 0 & 0 & 1 & -2 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{array} \tag{2.9.10}$$

This procedure may be repeated as often as necessary until one has 1’s down the diagonal as far as possible and 0’s beneath them. In the present case we have reached this point. If this had not been the case, the next step would have been to ignore the first two rows and columns and to repeat the operations above on the resulting array. The number of independent reactions is then equal to the number of 1’s on the diagonal.

Once the number of independent reactions has been determined, an independent subset can be chosen for use in subsequent calculations.

ILLUSTRATION 2.2 Determination of Equilibrium Compositions in the Presence of Simultaneous Reactions

This material has been adapted from Strickland-Constable (3), with permission.

Consider a system that consists initially of 1 mol of CO and 3 mol of H_2 at 1000 K. The system pressure is 25 bar. The following reactions are to be considered:

$$2CO + 2H_2 \leftrightarrow CH_4 + CO_2 \qquad \text{(A)}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \text{(B)}$$

$$CO_2 + H_2 \leftrightarrow H_2O + CO \qquad \text{(C)}$$

When the equilibrium constants for reactions (A) and (B) are expressed in terms of the partial pressures of the various species (in bar), the equilibrium constants for these reactions have the following values:

$$K_{P,A} = 0.046 \qquad K_{P,B} = 0.034 \qquad K_{P,C} = ?$$

Determine the equilibrium composition of the mixture.

Solution

The first step in the analysis is to determine if the chemical equations (A) to (C) are independent by applying the test described above. When one does this, one finds that only two of the reactions are independent. We will choose the first two for use in subsequent calculations. Let the variables ξ_A and ξ_B represent the equilibrium extents of reactions A and B, respectively. A mole table indicating the mole numbers of the various species present at equilibrium may be prepared using the following form of equation (1.1.6):

$$n_1 = n_{i0} + \nu_{Ai}\xi_A + \nu_{Bi}\xi_B$$

Species	Initial mole number	Equilibrium mole number
CO	1	$1 - 2\xi_A - \xi_B$
H_2	3	$3 - 2\xi_A - 3\xi_B$
CH_4	0	$\xi_A + \xi_B$
CO_2	0	ξ_A
H_2O	0	ξ_B
Total	4	$4 - 2\xi_A - 2\xi_B$

The fact that none of the mole numbers can ever be negative places maximum values of $\frac{1}{2}$ on ξ_A and 1 on ξ_B.

The values of K_P for reactions A and B are given by

$$K_{P,A} = \frac{P_{CH_4}P_{CO_2}}{P_{CO}^2 P_{H_2}^2} = \frac{y_{CH_4}y_{CO_2}}{y_{CO}^2 y_{H_2}^2 P^2}$$

$$K_{P,B} = \frac{P_{CH_4}P_{H_2O}}{P_{CO}P_{H_2}^3} = \frac{y_{CH_4}y_{H_2O}}{y_{CO}y_{H_2}^3 P^2}$$

The mole fractions of the various species may be expressed in terms of ξ_A and ξ_B, so that the above relations for K_P become

$$K_{P,A} = \frac{\left(\dfrac{\xi_A + \xi_B}{4 - 2\xi_A - 2\xi_B}\right)\left(\dfrac{\xi_A}{4 - 2\xi_A - 2\xi_B}\right)}{\left(\dfrac{1 - 2\xi_A - \xi_B}{4 - 2\xi_A - 2\xi_B}\right)^2\left(\dfrac{3 - 2\xi_A - 3\xi_B}{4 - 2\xi_A - 2\xi_B}\right)^2 P^2}$$

$$= \frac{\left(\xi_A + \xi_B\right)\xi_A\left(4 - 2\xi_A - 2\xi_B\right)^2}{(1 - 2\xi_B - \xi_B)^2(3 - 2\xi_A - 3\xi_B)^2 P^2}$$

$$K_{P,B} = \frac{\left(\dfrac{\xi_A + \xi_B}{4 - 2\xi_A - 2\xi_B}\right)\left(\dfrac{\xi_B}{4 - 2\xi_A - 2\xi_B}\right)}{\dfrac{1 - 2\xi_A - \xi_B}{4 - 2\xi_A - 2\xi_B}\left(\dfrac{3 - 2\xi_A - 3\xi_B}{4 - 2\xi_A - 2\xi_B}\right)^3 P^2}$$

$$= \frac{(\xi_A + \xi_B)\xi_B(4 - 2\xi_A - 2\xi_B)^2}{(1 - 2\xi_A - \xi_B)(3 - 2\xi_A - 3\xi_B)^3 P^2}$$

Substitution of numerical values for P, $K_{P,A}$, and $K_{P,B}$ gives two equations in two unknowns.

The resulting equations can be solved only by numerical techniques. In this case, a simple graphical approach can be employed in which one plots ξ_A versus ξ_B for each equation and notes the point of intersection. Values of $\xi_A = 0.128$ and $\xi_B = 0.593$ are consistent with these equations. Thus, at equilibrium,