

# **AN INTRODUCTION TO CHEMICAL ENGINEERING KINETICS & REACTOR DESIGN**

CHARLES G. HILL, JR.

The University of Wisconsin

JOHN WILEY & SONS

New York Chichester

Brisbane Toronto

Singapore

To my family:  
Parents, Wife, and Daughters

Copyright © 1977, by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Sections 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc.

*Library of Congress Cataloging in Publication Data:*

Hill, Charles G. 1937-

An introduction to chemical engineering kinetics and reactor design.

Bibliography: p.

Includes indexes.

1. Chemical reaction, Rate of. 2. Chemical reactors—Design and construction. I. Title.

QD502.H54 660.2'83 77-8280

ISBN 0-471-39609-5

Printed in the United States of America

20 19 18

# Board of Advisors, Engineering

|  |   |
|--|---|
| A. H-S, Ang<br>University of Illinois                                      | Civil Engineering—Systems and Probability |
| Donald S. Berry<br>Northwestern University                                 | Transportation Engineering                |
| James Gere<br>Stanford University  | Civil Engineering and Applied Mechanics   |
| J. Stuart Hunter<br>Princeton University                                   | Engineering Statistics                    |
| T. William Lambe<br>R. V. Whitman<br>Massachusetts Institute of Technology | Civil Engineering—Soil Mechanics          |
| Perry L. McCarty<br>Stanford University                                    | Environmental Engineering                 |
| Don T. Phillips<br>Texas A & M   | Industrial Engineering                    |
| Dale Rudd<br>University of Wisconsin                                       | Chemical Engineering                      |
| Robert F. Steidel, Jr,<br>University of California—Berkeley                | Mechanical Engineering                    |
| R. N. White<br>Cornell University  | Civil Engineering—Structures              |

# Preface

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 until he 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 13 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 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. The illustrative problems in Chapter 13 indicate the facility with which the basic concepts may be rephrased or applied in computer language, but this material is presented only after the student has been thoroughly exposed to the concepts involved and has learned to use them in attacking reactor design problems. I believe that the subject of computer-aided design should be deferred to graduate courses in reactor design and to more advanced texts.

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 design framework developed in the text.

The material on catalysis and heterogeneous reactions in Chapters 6, 12, and 13 is a useful framework for an intermediate level graduate course in catalysis and chemical reactor design. In the latter course emphasis is placed on developing the student's ability to analyze critically actual kinetic data obtained from the literature in order to acquaint him with many of the traps into which the unwary may fall. Some of the problems in Chapter 12 and the illustrative case studies in Chapter 13 have evolved from this course.

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 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 wife and children have at times been neglected during the preparation of this textbook; for their cooperation and inspiration I am particularly grateful.

Madison, Wisconsin

CHARLES G. HILL, Jr.

# Supplementary References

Since this is an introductory text, all topics of potential interest cannot be treated to the depth that the reader may require. Consequently, a number of useful supplementary references are listed below.

## A. References Pertinent to the Chemical Aspects of Kinetics

1. I. Amdur and G. G. Hammes, *Chemical Kinetics: Principles and Selected Topics*, McGraw-Hill, New York, 1966.
2. S. W. Benson, *The Foundations of Chemical Kinetics*, McGraw-Hill, New York, 1960.
3. M. Boudart, *Kinetics of Chemical Processes*, Prentice-Hall, Englewood Cliffs, N.J., 1968.
4. A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, Wiley, New York, 1961.
5. W. C. Gardiner, Jr., *Rates and Mechanisms of Chemical Reactions*, Benjamin, New York, 1969.
6. K. J. Laidler, *Chemical Kinetics*, McGraw-Hill, New York, 1965.

## B. References Pertinent to the Engineering or Reactor Design Aspects of Kinetics

1. R. Aris, *Introduction to the Analysis of Chemical Reactors*, Prentice-Hall, Englewood Cliffs, N.J., 1965.
2. J. J. Carberry, *Chemical and Catalytic Reaction Engineering*, McGraw-Hill, New York, 1976.
3. A. R. Cooper and G. V. Jeffreys, *Chemical Kinetics and Reactor Design*, Oliver and Boyd, Edinburgh, 1971.
4. H. W. Cremer (Editor), *Chemical Engineering Practice*, Volume 8, *Chemical Kinetics*, Butterworths, London, 1965.
5. K. G. Denbigh and J. C. R. Turner, *Chemical Reactor Theory*, Second Edition, Cambridge University Press, London, 1971.
6. H. S. Fogler, *The Elements of Chemical Kinetics and Reactor Calculations*, Prentice-Hall, Englewood Cliffs, N.J., 1974.
7. H. Kramers and K. R. Westerterp, *Elements of Chemical Reactor Design and Operation*, Academic Press, New York, 1963.
8. O. Levenspiel, *Chemical Reaction Engineering*, Second Edition, Wiley, New York, 1972.
9. E. E. Petersen, *Chemical Reaction Analysis*, Prentice-Hall, Englewood Cliffs, N.J., 1965.
10. C. N. Satterfield, *Mass Transfer in Heterogeneous Catalysis*, MIT Press, Cambridge, Mass., 1970.
11. J. M. Smith, *Chemical Engineering Kinetics*, Second Edition, McGraw-Hill, New York, 1970.

# Contents

|  |     |
|--|-----|
| Preface  | vii |
| 1 Stoichiometric Coefficients and Reaction Progress Variables                        | 1   |
| 2 Thermodynamics of Chemical Reactions   | 5   |
| 3 Basic Concepts in Chemical Kinetics—Determination of the Reaction Rate Expression  | 24  |
| 4 Basic Concepts in Chemical Kinetics—Molecular Interpretations of Kinetic Phenomena | 76  |
| 5 Chemical Systems Involving Multiple Reactions                                      | 127 |
| 6 Elements of Heterogeneous Catalysis  | 167 |
| 7 Liquid Phase Reactions   | 215 |
| 8 Basic Concepts in Reactor Design and Ideal Reactor Models                          | 245 |
| 9 Selectivity and Optimization Considerations in the Design of Isothermal Reactors   | 317 |
| 10 Temperature and Energy Effects in Chemical Reactors                               | 349 |
| 11 Deviations from Ideal Flow Conditions   | 388 |
| 12 Reactor Design for Heterogeneous Catalytic Reactions                              | 425 |
| 13 Illustrative Problems in Reactor Design   | 540 |
| Appendix A Thermochemical Data   | 570 |
| Appendix B Fugacity Coefficient Chart  | 574 |
| Appendix C Nomenclature  | 575 |
| Name Index   | 581 |
| Subject Index  | 584 |

# 1 Stoichiometric Coefficients and Reaction Progress Variables

## 1.0 INTRODUCTION

Without chemical reaction our world would be a barren planet. No life of any sort would exist. Even if we 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 clothing, and no engines to power our vehicles.

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 analysis in a manner that benefits society. Consequently, chemical engineers must be well acquainted with the fundamentals of chemical kinetics and the manner in which they are applied in chemical reactor design. This textbook provides a systematic introduction to these subjects.

Chemical kinetics 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 primarily interested in chemical kinetics 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 resultant 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 a point that far surpasses the development of theoretical work in chemical kinetics.

The dynamic viewpoint of chemical kinetics may be contrasted with the essentially static viewpoint of thermodynamics. A kinetic system is a system in unidirectional movement toward a condition of thermodynamic equilibrium. The chemical composition of the system changes continuously with time. 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 case where 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 given reactant feed stock should be the 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 a maximum limit on the product yield that may be obtained. Chemical engineers must also use thermodynamics to determine heat transfer requirements for proposed reactor configurations.

## 1.1 BASIC STOICHIOMETRIC CONCEPTS

### 1.1.1 Stoichiometric Coefficients

Consider the following general reaction.



where  $b$ ,  $c$ ,  $s$ , and  $t$  are the stoichiometric coefficients of the species  $B$ ,  $C$ ,  $S$ , and  $T$ , respectively. We define generalized stoichiometric coefficients  $v_i$  for the above reaction by rewriting it in the following manner.

$$0 = v_B B + v_C C + \cdots + v_S S + v_T T + \cdots \quad (1.1.2)$$

where

$$\begin{aligned} v_B &= -b & v_S &= s \\ v_C &= -c & v_T &= t \end{aligned}$$

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 inverted form with the zero first to emphasize the use of this sign convention, even though this inversion is rarely used in practice.

One may further generalize equation 1.1.2 by rewriting it as

$$0 = \sum_i v_i A_i \quad (1.1.3)$$

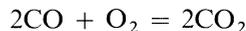
where the sum is taken over all components  $A_i$  present in the system.

There are, of course, many equivalent ways of writing the stoichiometric equation for a reaction. For example, one could write the carbon

monoxide oxidation reaction in our notation as



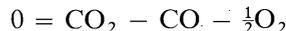
instead of in the more conventional form, which has the reactants on the left side and the products on the right side.



This second form is preferred, provided that one keeps the proper sign convention for the stoichiometric coefficients in mind.

$$v_{\text{CO}} = -2 \quad v_{\text{O}_2} = -1 \quad v_{\text{CO}_2} = 2$$

Alternatively, the reaction could be written as



with

$$v_{\text{CO}} = -1 \quad v_{\text{O}_2} = -\frac{1}{2} \quad v_{\text{CO}_2} = 1$$

The choice is a matter of personal convenience. The essential point is that the ratios of the stoichiometric coefficients are unique for a given reaction {i.e.,  $v_{\text{CO}}/v_{\text{O}_2} = (-2/-1) = [-1/(-1/2)] = 2$ }. Since 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

In order to measure the progress of a reaction it is necessary to define a parameter, which is a measure of the degree of conversion of the reactants. We will find it convenient to use the concept of the *extent* or degree of *advancement* of reaction. This concept has its origins in the thermodynamic literature, dating back to the work of de Donder (1).

Consider a closed system (i.e., 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 is defined as

$$\xi = \frac{n_i - n_{i0}}{\nu_i} \quad (1.1.4)$$

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  $\xi$  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  $j$  and  $k$  can be related to one another by eliminating  $\xi$  between two expressions that may be derived from equation 1.1.4.

$$n_k = n_{k0} + \left(\frac{\nu_k}{\nu_j}\right)(n_j - n_{j0}) \quad (1.1.5)$$

If more than one chemical reaction is possible, an extent may be defined for each reaction. If  $\xi_k$  is the extent of the  $k$ th reaction, and  $\nu_{ki}$  the stoichiometric coefficient of species  $i$  in reaction  $k$ , the total change in the number of moles of species  $A_i$  because of  $R$  reactions is given by

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

Another advantage of using the concept of extent is that it permits one to specify uniquely the rate of a given reaction. This point is discussed in Section 3.0. The major drawback of the concept is that the extent is an extensive variable and consequently is proportional to the mass of the system being investigated.

The fraction conversion  $f$  is an intensive measure of the progress of a reaction, and 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

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

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 ( $\xi_{\max}$ ). 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.

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  $n_{\text{lim}}$  and equating the resultant expressions.

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

or

$$\xi = -\frac{fn_{\text{lim},0}}{\nu_{\text{lim}}} \quad \text{and} \quad \xi_{\max} = -\frac{n_{\text{lim},0}}{\nu_{\text{lim}}} \quad (1.1.9)$$

In some cases the extent of reaction is limited by the position of chemical equilibrium, and this extent ( $\xi_e$ ) will be less than  $\xi_{\max}$ . However, in many cases  $\xi_e$  is approximately equal to  $\xi_{\max}$ . 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 will classify these reactions as *irreversible*. When the extent of reaction at

equilibrium differs measurably from  $\xi_{\max}$ , we will classify the reaction involved as *reversible*. From a thermodynamic point of view, all reactions are reversible. However, when one is analyzing a reacting system, it is often convenient to neglect the reverse reaction in order to simplify the analysis. For “irreversible” reac-

tions, one then arrives at a result that is an extremely good approximation to the correct answer.

#### LITERATURE CITATION

1. De Donder, Th., *Leçons de Thermodynamique et de Chimie-Physique*, Paris, Gauthier-Villus, 1920.

# 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 concerned with equilibrium systems . . . systems that are undergoing *no net change* with time. This chapter will remind the student of the key thermodynamic principles with which he 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 is 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 given reactant system is 75%, and the observed yield from a given reactor is only 30%, it is obviously possible to obtain major improvements in the process yield. On the other hand, if the process yield were close to 75%, the potential improvement in the yield is minimal and additional efforts aimed at improving the yield may not be warranted. 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.

The basic criterion for the establishment of chemical reaction equilibrium is that

$$\sum_i v_i \mu_i = 0 \quad (2.0.1)$$

where the  $\mu_i$  are the chemical potentials of the

various species in the reaction mixture. If  $r$  reactions may occur in the system and equilibrium is established with respect to each of these reactions, it is required that

$$\sum_i v_{ki} \mu_i = 0 \quad k = 1, 2, \dots, r \quad (2.0.2)$$

These equations are equivalent to a requirement that the Gibbs free energy change for each reaction ( $\Delta G$ ) be zero at equilibrium.

$$\Delta G = \sum_i v_i \mu_i = 0 \text{ at equilibrium} \quad (2.0.3)$$

## 2.1 CHEMICAL POTENTIALS AND STANDARD STATES

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

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

where

$R$  is the gas constant

$T$  is the absolute temperature

$\mu_i^0$  is 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 to calculations giving reproducible results. Although different standard states may be chosen for various species, *throughout any set of calculations it is important that the standard state of a component be kept the same so as to minimize possibilities for error.*

Certain choices of standard states have found such widespread use that they have achieved

the status of recognized conventions. In particular, those listed 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.

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 1 atm pressure; this is a valid approximation for most real gases). |
| Liquid               | Pure liquid in the most stable form at 1 atm   |
| Solid                | Pure solid in the most stable form at 1 atm.   |

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 Gibbs free energy change for this process is

$$\Delta G^0 = \sum v_i \mu_i^0 \quad (2.1.2)$$

where the superscript zero on  $\Delta G$  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 ( $\Delta H^0$ ) and standard entropy changes ( $\Delta S^0$ ) for this process.

## 2.2 ENERGY EFFECTS ASSOCIATED WITH CHEMICAL REACTIONS

Since 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. It is also useful in determining the effect of temperature on the equilibrium constant of the reaction and thus on the reaction yield. The Gibbs free energy is 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 calculates changes in these energy functions.

1. A chemical process whereby reactants, each in its standard state, are converted into 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.

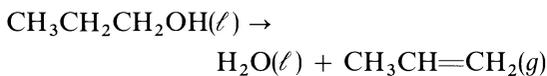
One must be very careful not to confuse actual energy effects with those that are associated with the process whose initial and final states are the standard states of the reactants and products respectively.

In order 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  $T$ ).

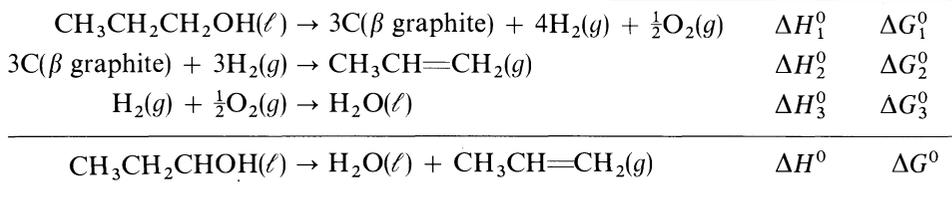
The enthalpy and Gibbs free energy changes for a standard reaction are denoted by the

symbols  $\Delta H^0$  and  $\Delta G^0$ , 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 mole for the reaction as written. 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 this data in the calculation of  $\Delta G^0$  and  $\Delta H^0$  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 one compound. The dehydration of n-propanol



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



For the overall reaction,

$$\Delta H^0 = \Delta H_1^0 + \Delta H_2^0 + \Delta H_3^0 \quad (2.2.1)$$

$$\Delta G^0 = \Delta G_1^0 + \Delta G_2^0 + \Delta G_3^0 \quad (2.2.2)$$

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

called the enthalpy (or heat) of formation of the compound and is denoted by the symbol  $\Delta H_f^0$ .

Thus,

$$\Delta H_{\text{overall}}^0 = \Delta H_{f, \text{water}(\ell)}^0 + \Delta H_{f, \text{propylene}}^0 - \Delta H_{f, \text{propanol}(\ell)}^0 \quad (2.2.3)$$

and

$$\Delta G_{\text{overall}}^0 = \Delta G_{f, \text{water}(\ell)}^0 + \Delta G_{f, \text{propylene}}^0 - \Delta G_{f, \text{propanol}(\ell)}^0 \quad (2.2.4)$$

where  $\Delta G_f^0$  refers to the standard Gibbs free energy of formation.

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

$$\Delta H^0 = \sum_i \nu_i \Delta H_{f,i}^0 \quad (2.2.5)$$

$$\Delta G^0 = \sum_i \nu_i \Delta G_{f,i}^0 \quad (2.2.6)$$

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 that selected as the basis for

the determination of the standard Gibbs free energy and enthalpy of formation of its compounds. If  $\Delta H^0$  is negative, the reaction is said to be *exothermic*; if  $\Delta H^0$  is positive, the reaction is said to be *endothermic*.

It is not necessary to tabulate values of  $\Delta G^0$  or  $\Delta H^0$  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  $\Delta G_f^0$  and  $\Delta H_f^0$  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 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) or at 0 °K. The problem of calculating a value for  $\Delta G^0$  or  $\Delta H^0$  at temperature  $T$  thus reduces to one of determining values of  $\Delta G_f^0$  and  $\Delta H_f^0$  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.

The effect of temperature on  $\Delta H^0$  is given by

$$\Delta H_T^0 = \Delta H_{298.16}^0 + \int_{298.16 \text{ °K}}^T \left( \sum_i \nu_i C_{p,i}^0 \right) dT \quad (2.2.7)$$

where  $C_{p,i}^0$  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  $\Delta H_{298.16}^0$ . However, if one is to be able to evaluate properly the standard heat of reaction 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 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 temperature is:

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

In Section 2.5 we will 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 this parameter varies with temperature. If one desires to obtain an expression for  $\Delta G^0$  itself as a function of temperature, equation 2.2.7 may be integrated to give  $\Delta H^0$  as a function of temperature. This relation may then be used with equation 2.2.8 to arrive at the desired relation.

The effect of pressure on  $\Delta G^0$  and  $\Delta H^0$  depends on the choice of standard states employed. When the standard state of each component of the reaction system is taken at 1 atm pressure, whether the species in question is a gas, liquid, or solid, the values of  $\Delta G^0$  and  $\Delta H^0$  refer to a process that starts and ends at 1 atm. For this choice of standard states, the *values of  $\Delta G^0$  and  $\Delta H^0$  are independent of the system 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 actual process as it occurs in nature. This choice of standard states at 1 atm pressure 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  $\Delta G^0$  and  $\Delta H^0$ . In such cases thermodynamic analysis indicates that

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

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. 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 conventionally used in the analysis of chemically reacting systems. Furthermore,

in the vast majority of cases the summation term on the right side of the equation is very small compared to the magnitude of  $\Delta H_{1\text{atm}}^0$  and, indeed, is usually considerably smaller than the uncertainty in this term.

The Gibbs free energy analog of equation 2.2.9 is

$$\Delta G_P^0 = \Delta G_{1\text{atm}}^0 + \sum_i v_i \int_1^P V_i dP \quad (2.2.10)$$

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

Thermochemical data for several common species are contained in Appendix A. Other useful standard references are listed below.

1. F. D. Rossini, et al., *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh, 1953; also loose-leaf supplements. Data compiled by Research Project 44 of the American Petroleum Institute.
2. F. D. Rossini, et al., "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circular 500 and Supplements, 1952.
3. E. W. Washburn (Editor), *International Critical Tables*, McGraw-Hill, New York, 1926.
4. T. Hilsenrath, et al., "Thermal Properties of Gases," National Bureau of Standards Circular 564, 1955.
5. D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," *Adv. Chem. Ser.*, 18, 1956.
6. *Landolt-Börnstein Tabellen*, Sechste Auflage, Band II, Teil 4, Springer-Verlag, Berlin, 1961.
7. *Janaf Thermochemical Tables*, D. R. Stull, Project Director, PB 168370, Clearinghouse for Federal Scientific and Technical Information, 1965.

The following references contain techniques for estimating thermochemical data.

1. R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, Second Edition, McGraw-Hill, New York, 1966.
2. S. W. Benson, *Thermochemical Kinetics*, Wiley, New York, 1968.
3. G. J. Janz, *Estimation of Thermodynamic Properties of Organic Compounds*, Academic Press, New York, 1958.

### 2.4 THE EQUILIBRIUM CONSTANT AND ITS RELATION TO $\Delta G^0$

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.

$$\Delta G = \sum_i v_i \mu_i = 0 \quad (2.4.1)$$

The standard Gibbs free energy change for a reaction refers to the process wherein the reaction proceeds isothermally, starting with stoichiometric quantities of reactants each in its standard state of unit activity and ending with products each at unit activity. In general it is nonzero and given by

$$\Delta G^0 = \sum_i v_i \mu_i^0 \quad (2.4.2)$$

Subtraction of equation 2.4.2 from equation 2.4.1 gives

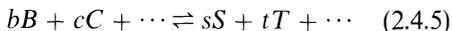
$$\Delta G - \Delta G^0 = \sum_i v_i (\mu_i - \mu_i^0) \quad (2.4.3)$$

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

$$\Delta G - \Delta G^0 = RT \sum_i v_i \ln a_i = RT \ln \left( \prod_i a_i^{v_i} \right) \quad (2.4.4)$$

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

For a general reaction of the form



the above equations become:

$$\Delta G - \Delta G^0 = RT \ln \left( \frac{a_S^s a_T^t \cdots}{a_B^b a_C^c \cdots} \right) \quad (2.4.6)$$

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

$$\Delta G^0 = -RT \ln \left[ \frac{a_S^s a_T^t \cdots}{a_B^b a_C^c \cdots} \right] = -RT \ln K_a \quad (2.4.7)$$

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

$$K_a = \prod_i a_i^{v_i} = e^{-\Delta G^0/RT} \quad (2.4.8)$$

As equation 2.4.8 indicates, the equilibrium constant for a reaction is determined by the temperature and the standard Gibbs free energy change ( $\Delta G^0$ ) for the process. The latter quantity in turn depends 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 the three parameters mentioned above in order 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 FOR A REACTION

Equilibrium constants are quite 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.

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

or

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

and

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

For cases where  $\Delta H^0$  is essentially independent of temperature, plots of  $\ln K_a$  versus  $1/T$  are linear with slope  $-(\Delta H^0/R)$ . For cases where the heat capacity term in equation 2.2.7 is appreciable, this equation must be substituted in either equation 2.5.2 or equation 2.5.3 in order to determine the temperature dependence of the equilibrium constant. For exothermic reactions ( $\Delta H^0$  negative) the equilibrium constant decreases with increasing temperature, while for endothermic reactions the equilibrium constant increases with increasing temperature.

For cases where the standard states of the reactants and products are chosen as 1 atm, the value of  $\Delta G^0$  is pressure independent. Consequently, equation 2.4.7 indicates that  $K_a$  is also pressure independent for this choice of standard states. For the unconventional choice of standard states discussed in Section 2.2, equations 2.4.7 and 2.2.10 may be combined to give the effect of pressure on  $K_a$ .

$$\left( \frac{\partial \ln K_a}{\partial P} \right)_T = -\frac{\sum_i v_i V_i}{RT} \quad (2.5.4)$$

where the  $V_i$  are the standard state molal

volumes of the reactants and products. However, 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.

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

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

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

where  $\hat{f}_B$  is the fugacity of species  $B$  as it exists in the 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

$$\hat{f}_B = y_B f_B^0 \quad (2.6.3)$$

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,

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

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 are gases, combination of equations 2.6.1, 2.6.2, and 2.6.4 gives

$$K_a = \left( \frac{y_S^s y_T^t}{y_B^b y_C^c} \right) \left[ \frac{\left( \frac{f}{P} \right)_S^s \left( \frac{f}{P} \right)_T^t}{\left( \frac{f}{P} \right)_B^b \left( \frac{f}{P} \right)_C^c} \right] P^{s+t-b-c} \quad (2.6.5)$$

The first term in parentheses is assigned the symbol  $K_y$ , while the term in brackets 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  $K_p$ .

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

since each term in parentheses is a component partial pressure. Thus

$$K_a = K_{f/P} K_p \quad (2.6.7)$$

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 B may be used to calculate  $K_{f/P}$ .

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

$$y_B = \frac{n_B}{n_B + n_C + \cdots + n_S + n_T + \cdots + n_I} \quad (2.6.8)$$

Combination of equations 2.6.5 to 2.6.7 and defining equations similar to equation 2.6.8 for