ELEMENTARY CHEMICAL REACTOR ANALYSIS

by Rutherford Aris

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PRENTICE-HALL, INC.

Englewood Cliffs, N. J.

PRENTICE-HALL INTERNATIONAL, INC., *London*
PRENTICE-HALL OF AUSTRALIA, PTY. LTD., *Sydney*
PRENTICE-HALL OF CANADA, LTD., *Toronto*
PRENTICE-HALL OF INDIA PRIVATE LTD., *New Delhi*
PRENTICE-HALL OF JAPAN, INC., *Tokyo*

Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

Library of Congress Catalog Card Number 69-12840

Printed in the United States of America

Preface

This book is a more thorough rewriting of my *Introduction to the Analysis of Chemical Reactors* than might appear at first sight, for though I have retained the structure and most of the headings of the former volume there are few sections that have not been largely rewritten. I am still convinced of the soundness of the general plan and of the necessity of making the undergraduate grasp the fundamental ideas and become aware of the more advanced topics and difficult problems. What I have endeavored to do here is to soften the mathematical aspect which some found rather forbidding in the *Introduction* and to answer the criticism that too few practical examples were given. This has been done by introducing each topic with a fairly extensive discussion of the simplest example, by treating the mathematics descriptively as well as analytically, and by omitting certain topics. I hope that the result is not too much "like a missionary talking to cannibals"—as Littlewood said of a much better and more famous book—or that, if it is, then it at least escapes the venial sin of condescension, in the unpleasant sense which that word has lately acquired. I have added a great number of illustrative examples taken where possible from actual reactions. At the same time I feel that no apology is needed for using examples such as $A \longrightarrow B$, $A_1 - A_2 - A_3 = 0$, $A \longrightarrow B \longrightarrow C$, or $\sum \alpha_{ij} A_j = 0$; they are entirely suitable to the task of illustrating the principles of the subject, and what they lack in the charm of Titchmarshian "picturesqueness" they make up for by the virtues of Boudartian "asceticism."

A partial list of examples used in the text and in the exercises is given after the table of contents, for, though all these items could be found from the index, it is useful to know what there is to look for. The teacher's manual contains a discussion of some of the pedagogical problems of a course in reactor analysis, as well as a number of quiz questions and the solutions of the 200 problems of the text. A few of these problems have been taken from the Cambridge University Tripos and Qualifying Examinations and I am indebted to the Syndics of the Cambridge University Press for permission to use them. They are denoted by the initials C.U. A few of the figures are reproduced from papers in the journal literature and I am most grateful to the several editors and authors for allowing this. The specific acknowledgements are made in the legends to these figures.

In writing this book I have incurred even more numerous obligations than before and I must start by asking the pardon of any whom I inadvertently overlook. I owe to Michel Boudart the original suggestion that it would be possible, not to say desirable, to present the scheme of the *Introduction* in a more elementary form. Many correspondents took up points of difficulty, supplied corrigenda for the previous book, or commented on their use of it in the classroom. Among these my colleagues A. G. Fredrickson, R. W. Carr, and L. D. Schmidt should have first mention, but D. W. Condiff, J. M. Douglas, L. C. Eagleton, G. C. Frazier, G. R. Gavalas, J. M. Prausnitz, T. W. F. Russel, G. D. Shilling, J. C. R. Turner, and J. Wei have also made valuable contributions. Among the students who have assisted in the course, looked over manuscript or proof and have made useful comment K. J. Anselmo, I. Copelowitz, D. W. Drott, M. Gackstetter, A. P. Jackman, J. G. Jouven, R. H. Knapp, D. J. Kudish, R. D. Megee, R. Palas, T. M. Pell, S. Rester, P. A. Rouyer, D. V. Rudd, D. R. Schneider, J. M. Wheeler deserve mention. As usual my colleagues, notably N. R. Amundson, H. T. Davis, J. S. Dahler, K. H. Keller and L. E. Scriven, have helped to clarify various points. The business of deciphering my holograph and producing an excellent typescript was performed by Mrs. John Grose, Mrs. Jay Poissant, Miss Linda Anderson, and Miss Sharon Wellmann. As always Messrs John Davis and John McCanna of Prentice-Hall have been most helpful and considerate, and it has been a pleasure to work with the production editor Mr. John S. Covell on the book and Mr. Nicholas Romanelli on the teacher's manual.

To all these I am most grateful for their several favors and most particularly to my wife for her patience with my preoccupation and perverseness—even if at times it has driven her to the philosophy of Charlie Brown, who learned to "dread only one day at a time"!

RUTHERFORD ARIS

Contents

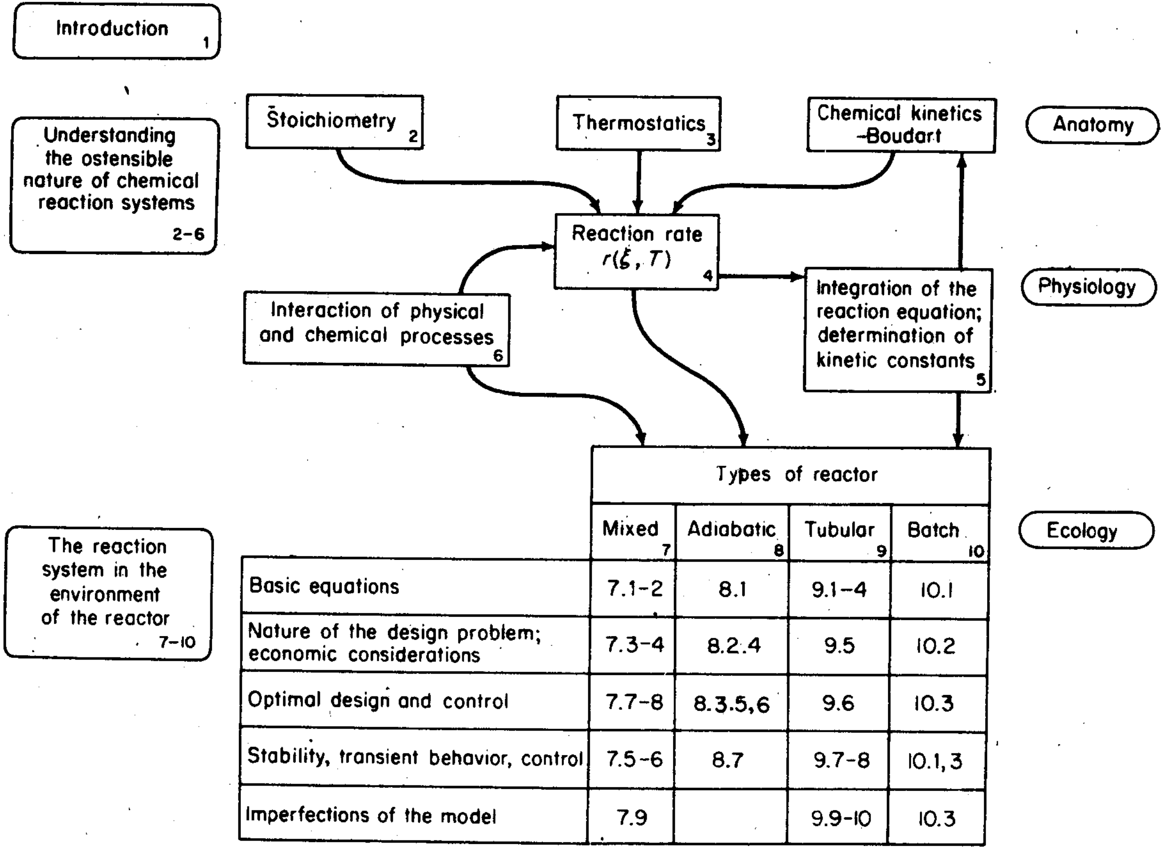
What is Chemical Reactor Analysis?

1

1.1 A General Look at the Subject

The analysis and synthesis of chemical reactors is par excellence the domain of the chemical engineer. For, while other engineers share his interest in fluid mechanics and transport phenomena and the chemist his concern with the kinetics and mechanisms of reactions, it is his business to combine a knowledge of these subjects for the better understanding, design, and control of the reactor. This book discusses the basic principles of reactor design and if the word "analysis" figures in the title it is not there to exclude synthesis, but to emphasize that the parts can only be put together when the functioning of each one and its relation to others have first been understood. Thus in the first half of the book we shall be examining the parts severally, with our principal concern the chemical reaction; in the second half, our attention will center on the reactor (see Fig. 1.1).

In practice the chemical engineer will meet a situation much less clearly defined than that studied in the classroom. Information about reaction kinetics will always be incomplete and usually inaccurate, and he must hazard a design on such a basis. Moreover, there are economic considerations in



	Types of reactor			
	Mixed 7	Adiabatic 8	Tubular 9	Batch 10
Basic equations	7.1–2	8.1	9.1–4	10.1
Nature of the design problem; economic considerations	7.3–4	8.2.4	9.5	10.2
Optimal design and control	7.7–8	8.3.5,6	9.6	10.3
Stability, transient behavior, control	7.5–6	8.7	9.7–8	10.1,3
Imperfections of the model	7.9		9.9–10	10.3

Fig. 1.1 The structure of the book (numbers refer to chapters).

design which fall quite outside the scope of this book. If then the art of the engineer lies in making intelligent guesses in the presence of uncertainty we may wonder if general analytical considerations are not rather beside the point. On the contrary, a general "feel" for the form of the subject becomes all the more important for this will help to fill out, as well as bound, his partial knowledge. For example, it is shown in Chap. 7 that if the maximum reaction rate of an exothermic reaction rate is known for several conversions, then an optimal design of several stirred tanks in series can be calculated. Although this result is established from equations that contain a precise reaction rate expression for all temperatures and pressures, its final form shows that much less complete information would be usable. Such considerations may allow the engineer to design with greater confidence from available data or may show him in what direction further data are needed. Provided that no essential feature is ignored, the quantitative study of a simplified model may give qualitatively valid results in the sense that it reveals trends that would otherwise be difficult to perceive and shows their directions even when it cannot accurately predict their magnitudes.

With the assurance that analysis and synthesis, like theory and experiment, are complementary rather than competitive, let us take a general look at the territory we wish to explore. The subject is also referred to as "chemical reaction engineering" or "applied chemical kinetics," and the latter suggests that we should first make the distinction between "pure" and "applied" kinetics. Pure chemical kinetics is concerned with elucidating the chemical features of the reaction and is interested in the reaction rate as one of the clues in this search. The notion of the reaction rate is also central to applied kinetics but in the sense that it bears on the behavior of the reactor rather than on the mechanism of the reaction. Thus the applied chemical kineticist can be content with a comparatively gross description of the reaction provided that it yields a usable expression for the reaction rate. In keeping with this, we shall be quite content to draw on the results of chemical kinetics, recognizing its importance but not having occasion here to delve into it. Fortunately, an excellent introduction is to be found in Boudart's text in this series.

The three principal ingredients of the reaction rate expression are shown in the top boxes of Fig. 1.1. Stoichiometry deals with the changes of composition that may take place by reaction. From thermostatics we can learn much about the heat effects of reactions and the nature of equilibrium, and from chemical kinetics we shall take any result that is available and useful. These three factors form the anatomy of our subject, whose physiology emerges when we ask just what they mean in terms of the behavior of the reaction rate expression. In Chap. 4 we will examine the reaction rate expression and in Chap. 5 we will see what this implies for the course of the reaction in time. But we must also look at the interaction of physical and chemical processes for it may be that the step that controls the rate of the process is one of mass transfer rather than of reaction.

The ecological aspect of the subject comes into prominence when we study the reaction in its habitat, the reactor. The final chapters are therefore devoted to four types of reactor: the perfectly mixed reactor, the adiabatic, the tubular, and the batch reactor. The simplest model of the steady state of the tubular reactor is described by the same equations as for the batch reactor. The term *adiabatic* really refers to the mode of operation of the reactor rather than to its construction. We therefore really have two main types of reactor, the tubular (in which it is generally desirable to have as little mixing as possible as the reactants flow through it) and the stirred tank (in which good mixing is deliberately cultivated). For each type we first set up the basic equations and from these we see what elements enter into the design problem. This brings up the question of how good the design is and what methods are available for finding an optimal design. The full analysis of the control of a reactor is generally very difficult, but a surprising amount of information can be obtained from a careful examination of the basic equations. The same remark applies to questions of stability and sensitivity which, though very deep, can be usefully elucidated in quite simple terms. Finally, we turn and look again at the basic model to see how it can be made more realistic.

The process of mathematical modeling is an iterative one in which careful study of a simple model leads to a more realistic, but more complex, one, which is itself the precursor of a better model. What is needed is a good feel for the right kind of simplification to be made in building a model and the ability to see the shape of the results that come from analyzing it. The word "shape" is used deliberately for it is only safe to start detailed computations when the form of the solution is understood. To do otherwise is to invite an expensive output of meaningless numbers and to sacrifice one's birthright of rationality for a mess of digits.

Two further remarks may be made about the boundaries of the territory we wish to explore. No reference is made to fluidized beds or to noncatalytic reactions with solid particles, not because they are unimportant, but because a line had to be drawn somewhere. An excellent introduction to these topics will be found in Levenspiel's book. Neither is any real attention paid to the hardware and technology of reactors. Again this is not due to any lack of importance of these topics—they are simply inappropriate to our approach. It is a disputed question whether real technological know-how can properly be taught in a university. It is important that the student should not despise technology in any way, but experience suggests that technology is best learned in its own setting.

To sum up, the viewpoint is structural and the methods are analytic. But structure is to be understood in the broadest sense, not as a static concept, but as including both function and interaction. Analysis is not to be thought of as the antithesis of synthesis, but rather as the ground on which sound synthetic methods can be based.

1.2 A Note on Presentation, Problems, and Prerequisites

I have endeavored to introduce each topic by taking the simplest example that brings out the characteristic features. At times, the analysis may seem painfully long and heavy-handed and the student who is able to do so should jump ahead. I hope that this will temper the wind of generality for those who find an algebraic notation obscure. At the same time, I make no apology for using the reactions $\sum \alpha_{ij} A_j = 0$, nor even the time-honored $A \longrightarrow B$ and $A \longrightarrow B \longrightarrow C$. Often little is added to the understanding of principles by giving particular instances, but they do make for a useful familiarity and where possible I have introduced an example.

Some of the problems extend the text by opening up the way into more general cases. Most of them are rather easy, for it is hard to find a problem in this area which is difficult without being unusually lengthy. I have added some problems which involve estimation of the importance of different effects and some which contain reference to actual processes. One or two of the problems do not have very definite answers and these are the type that will be met most of the time in practice. No attempt has been made to separate the problems into classes of various degrees of difficulty—life isn't like that.

A working knowledge of elementary calculus is presumed as is some acquaintance with elementary differential equations. Section 5.1 is a thumbnail sketch of some particularly important equations. A thorough course in thermodynamics is one of the staples of a chemical engineer's diet and should precede a course on reactors. Chapter 3 is therefore a bare outline of familiar thermochemistry in a notation conformable to the rest of the book. It is impossible to avoid duplications in notation and a list has been provided at the end of each chapter.

REFERENCES

The literature of chemical reactor analysis is vast and awaits an industrious bibliographer. We give here a partially annotated list of texts and monographs of general use in the field of applied chemical kinetics. The undergraduate should familiarize himself with the chemical engineering journals; those of particular value are as follows.

Chemical Engineering Science
Industrial and Engineering Chemistry
  Fundamentals
  Process Design and Development
A. I. Ch. E. Journal
Chemie-Ingenieur-Technik
Canadian Journal of Chemical Engineering

Three particularly valuable supplements to *Chemical Engineering Science* have been issued. They are the papers given at the first three European Symposia on Chemical Reaction Engineering in 1957, 1960, and 1964. The first was issued as a monograph and as Vol. 8; the second as Vol. 14. The third symposium is issued as a supplement by Pergamon Press. A fourth symposium took place in 1968.

One of the first texts in the field was:

O. A. Hougen and K. M. Watson, *Chemical Process Principles*, Vol. III. New York: John Wiley & Sons, Inc., 1947.

(The earlier volumes of this work, to which reference is made later, have been revised with the collaboration of R. A. Ragatz.)

See also:

J. M. Smith, *Chemical Engineering Kinetics*. New York: McGraw-Hill Book Co., 1956.

S. M. Walas, *Reaction Kinetics for Chemical Engineers*. New York: McGraw-Hill Book Co., 1959.

W. Brötz, *Grundriss der Chemischen Reaktionstechnik*. Weinheim: Verlag Chemie, 1958. Translated by D. A. Diener and J. A. Weaver as *Fundamentals of Chemical Reaction Engineering*. Reading, Mass.: Addison-Wesley Publishing Co., 1965.

K. Dialer, F. Horn, and L. Küchler, "Chemische Reaktionstechnik" in *Chemische Technologie*, Vol. I. München: Carl Hanser Verlag, 1958.

J. C. Jungers et al., *Cinétique Chimique Appliquée*. Paris: Technip, 1958.

O. Levenspiel, *Chemical Reaction Engineering*. New York: John Wiley & Sons, Inc., 1962.

H. Kramers and K. R. Westerterp, *Elements of Chemical Reactor Design and Operation*. New York: Academic Press Inc., 1963.

K. G. Denbigh, *Chemical Reactor Theory*. New York: Cambridge University Press, 1965.

E. E. Petersen, *Chemical Reaction Analysis*. Englewood Cliffs, N. J.: Prentice-Hall, Inc., 1965.

The volumes of Academic Press' series *Advances in Chemical Engineering* should also be consulted. For example, Vol. 3 (1962) contains an article:

J. Beek, "Design of Packed Catalytic Reactors";

and in Vol. 4 (1963) is found:

O. Levenspiel and K. B. Bischoff, "Patterns of Flow in Chemical Process Vessels."

An introduction to fluidized beds is given in Levenspiel's book quoted above and in his forthcoming:

O. Levenspiel and D. Kunii, *Fluidization Engineering*. New York: John Wiley & Sons, Inc., 1968.

See also:

J. F. Davidson and D. Harrison, *Fluidized Particles*. New York: Cambridge University Press, 1963.

On the pure kinetics side, the *Advances in Catalysis* series, also published by Academic Press, is of particular interest; Walas has a convenient listing of their contents at the end of his book. Of texts in this cognate area we will only mention:

M. Boudart, *The Kinetics of Chemical Processes*. Englewood Cliffs, N. J.: Prentice-Hall, Inc., 1968.

This contains an excellent exposition of chemical kinetics and an entry into its vast literature.

Stoichiometry 2

2.1 What It Is and Why We Need It

The strict meaning of the word "stoichiometry" is measurement of the elements, but it is commonly used to refer to all manner of calculations regarding the composition of a chemical system. We shall give it a broad meaning here for we are concerned as much with the algebra of the relationship between the chemical species as with the arithmetical calculations that are implied. Stoichiometry is essentially the bookkeeping of the material components of the chemical system.

Its importance lies in the fact that the changes in composition in a reactor are not haphazard, but are of two distinct kinds. First, there are the advective changes due to material brought into the system or removed from it; this may be by forced flow, convection, or diffusion. Second, there is the internal change of composition by reaction; this change would be seen in a well-stirred batch reactor, for example, where advection has been deliberately eliminated. The advection will have to be expressed by certain terms in the material balance for a particular reactor, but the reactive changes are common to all types and deserve study first.

To see the nature of the restrictions on possible changes in composition let us recall a universally known reaction

$$2\,H_2 + O_2 = 2\,H_2O. \tag{2.1.1}$$

An equation such as this can have two meanings. It may be a kinetic description of the reaction and imply that two molecules of hydrogen combine directly with one of oxygen to form two molecules of water. In this particular case, Eq. (2.1.1) is not true as a kinetic description. On the other hand, it may be a stoichiometric description of the reaction, and the equation will then mean that the numbers of hydrogen and oxygen molecules combining to form water are in the ratio 2 : 1. It is clear that if a reaction expression is true in a kinetic sense it is also true in a stoichiometric sense, but the converse statement is false. We shall only be concerned in passing with the kinetic meaning of the reaction expression. The proportions 2 : 1 in the stoichiometric description are absolutely definite and an equation such as $3\,H_2 + O_2 = 3\,H_2O$ is nonsense. It follows that the changes in composition will be definite, for every time a given number of molecules of water are formed, the same number of hydrogen and half that number of oxygen molecules will disappear.

In keeping with our need to understand the structure of these changes, we shall not want to talk about particular reactions except by way of illustration, and our first task is to devise a suitably general notation.

2.2 Entire Reactions and Reaction Mechanisms

From a chemical engineer's point of view, the important thing about a reaction like the one above is that three chemical species (here hydrogen, oxygen, and water) are observed to react in certain proportions. If he can account for the rate at which this takes place in terms of the concentrations of the observed chemical species, he has all he needs to know about the reactions so far as designing a reactor is concerned. Such a reaction and its reaction rate expression will be called *entire*. It is the chemist who is interested in the fact that the entire reaction does not provide a kinetic description of what is taking place, and in devising a *mechanism* for a reaction he looks for elementary steps such that the stoichiometric equation of each step does correspond to the kinetics. In doing so he may be led to hypothesize certain intermediate species or radicals which are present in only trace quantities. This activity of the chemical kineticist is most important if valid and intelligible reaction rate expressions are to be built up, but it is part of pure chemical kinetics and we shall only have occasion to refer to it in passing.

We want our notation to reflect these facts and to be suitably general. Let us start with a set of S chemical species and denote them by $A_1, A_2, \ldots, A_S$ or A_j, where $j = 1, 2, \ldots, S$. Thus if $A_1 \equiv H_2O$, $A_2 \equiv H_2$, and $A_3 \equiv O_2$, the reaction given by Eq. (2.1.1) would be $2A_2 + A_3 = 2A_1$. It is convenient to write all the chemical species on one side of the equation and to give a positive sign to the species which are regarded as the products of the reaction. Thus if water is being formed we would write

$$2\,H_2O - 2\,H_2 - O_2 = 0 \quad \text{or} \quad 2A_1 - 2A_2 - A_3 = 0. \qquad (2.2.1)$$