ARIS

INTRODUCTION TO THE ANALYSIS OF CHEMICAL REACTORS

PRENTICE-HALL INTERNATIONAL SERIES IN THE PHYSICAL AND CHEMICAL ENGINEERING SCIENCES

Introduction to the Analysis of Chemical Reactors

RUTHERFORD ARIS

Department of
Chemical Engineering
University of Minnesota

PRENTICE-HALL, INC.

Englewood Cliffs, New Jersey

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*

Library of Congress Catalog Card Number: 65—14945

Current printing (last digit):
11 10 9 8 7 6 5 4 3

Printed in the United States of America

C47787

Introduction to the Analysis of Chemical Reactors

PRENTICE-HALL INTERNATIONAL SERIES
IN THE PHYSICAL AND CHEMICAL ENGINEERING SCIENCES

AMUNDSON *Mathematical Methods in Chemical Engineering*
ARIS *Elementary Chemical Reactor Analysis*
ARIS *Introduction to the Analysis of Chemical Reactors*
ARIS *Vectors, Tensors, and the Basic Equations of Fluid Mechanics*
BOUDART *Kinetics of Chemical Processes*
FREDRICKSON *Principles and Applications of Rheology*
HAPPEL AND BRENNER *Low Reynolds Number Hydrodynamics*
HIMMELBLAU *Basic Principles and Calculations in Chemical Engineering*, 2nd ed.
HOLLAND *Multicomponent Distillation*
HOLLAND *Unsteady State Processes with Applications in Multicomponent Distillation*
KOPPEL *Introduction to Control Theory: With Applications to Process Control*
LEVICH *Physicochemical Hydrodynamics*
PETERSEN *Chemical Reaction Analysis*
PRAUSNITZ *Molecular Thermodynamics of Fluid-Phase Equilibria*
PRAUSNITZ AND CHUEH *Computer Calculations for High-Pressure Vapor-Liquid Equilibria*
PRAUSNITZ, ECKERT, ORYE, O'CONNELL *Computer Calculations for Multicomponent Vapor-Liquid Equilibria*
WHITAKER *Introduction to Fluid Mechanics*
WILDE *Optimum Seeking Methods*

PRENTICE-HALL, INC.
PRENTICE-HALL INTERNATIONAL, INC., UNITED KINGDOM AND EIRE
PRENTICE-HALL OF CANADA, LTD., CANADA

To N. R. AMUNDSON

to whom this book owes more than its title
and the author much more than its contents

Preface

This book has grown out of the severe task of taking over an undergraduate course entitled "Chemical Reactor Analysis," which had been taught for some years by Professor N. R. Amundson. It is to be hoped that, in the effort to organize the material, I gained something of what the students lost by this transition and that the results are not out of keeping with the tradition of the department. The "philosophy" of the subject (as our contemporary usage, rather amusingly, styles it) is outlined in the first chapter and need not be repeated here. Suffice it to say that the attempt has been made to bring into the undergraduate curriculum some of the more recent results of research in this field, and to describe them, even where their full analysis is too difficult to give in detail. Read in conjunction with the original references, the book may also be of value to graduate students.

As always I am indebted to more people for more things than I can possibly remember and I must ask the forgiveness of any I overlook in the following specific acknowledgements. To my colleagues and particularly to N. R. Amundson, J. S. Dahler, A. G. Fredrickson and L. E. Scriven, I am obliged for much patience in discussing details and encouragement in general. Professional colleagues outside this university who deserve special mention are: M. Boudart, who gave me free use of his notes on kinetics from the first and has maintained a constant interest in the progress of the writing; E. E. Petersen, for the loan of his manuscript of "Chemical Reaction Analysis" and his willingness to share Fig. 6.7; F. Horn, for some very valuable discussions and cogent criticisms; W. Regenass, for help with the computations underlying Figs. 9.17–9.20 and discussions on other points; J. D. Maloney provided a very stimulating evening of conversation on structure in writing and I hope that the first figures of some of the chapters will not disappoint him.

The graduate students who assisted in the course over the last five years have been of great help. They were P. Becker, H. Chien, A. Chou, R. Singer, R. B. Warden; and of these Adam Chou deserves special thanks for his labors on the computer problems. Other graduate students who have worked on problems in this area and some of whose results are quoted are N. Blakemore, K. Y. Lee, C. D. Siebenthal, G. T. Westbrook and D. Yesberg.

For permission to use a score of problems from Cambridge University Tripos and Qualifying Examinations I am indebted to the Syndics of the Cambridge University Press. They are denoted by the initials C.U. For permission to use figures from journal articles I am obliged to the following authors and journal editors and publishers:

N. R. Amundson; A.I.Ch.E. Journal. Figs. 7.19; 9.15.
N. R. Amundson; Chemical Engineering Science. Figs. 7.21–24.
K. Y. Lee; Industrial and Engineering Chemistry. Figs. 8.17–20.
G. T. Westbrook; Industrial and Engineering Chemistry. Fig. 7.11, 12
R. H. Wilhelm; Pure and Applied Chemistry. Fig. 9.3.

My wife has added to her usual forebearance a great deal of hard work in the final preparation of the manuscript for the excellent typing of which I am again indebted to my sister-in-law, Mrs. A. Blair.

RUTHERFORD ARIS

Department of Chemical Engineering
University of Minnesota

Contents

What Is Chemical Reactor Analysis?

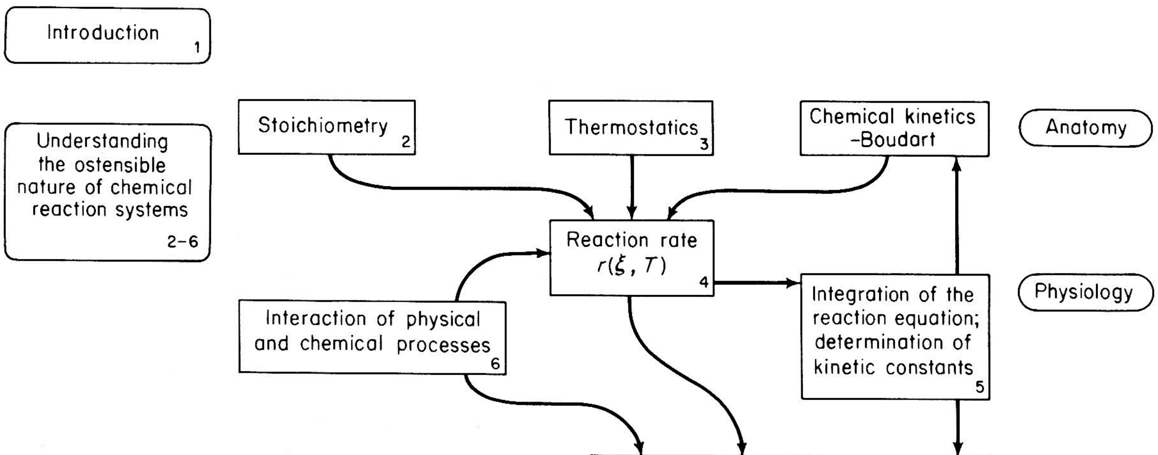
I

1.1 Introductory perspective

Let us attempt to get a bird's eye view of the territory we wish to explore in this book so as to start with some notion of the lie of the land and of its boundaries. To do this is particularly important in an introductory text where we cannot hope to cover all the ground we would wish, nor examine it in the detail it deserves.

The word "analysis" in the title* is characteristic of our viewpoint; that is, we want to take the subject to pieces and examine the relationship of its parts. Out of this analysis there arise a variety of synthetic methods for the design of chemical reactors. The basic problem, however, is to understand the structure of the subject. Since we are attempting to understand chemical reactors and since these are constructed expressly to perform chemical reactions, we must start by eliciting the principles which describe chemical reactions. Here, at the boundary of our subject, lies a neighboring domain—that of pure chemical kinetics. This area which is concerned with the precise mechanisms or molecular process of a chemical reaction, is of profound importance and great interest. For our purposes we must be content to take its results and build with them. Among the vast literature, an excellent introduction is to be found in Boudart's text. Our approach to the reaction itself is phenomenological, dealing with it as it appears on the surface without delving into its inner workings. In this, stoichiometry and thermostatics play a fundamental role,

* The original title of this book, *Chemical Reactor Analysis*, which was the title Amundson gave to the course at the University of Minnesota (whence the dedicatory allusion), has been lengthened to avoid possible confusion with Petersen's *Chemical Reaction Analysis*. The terms "applied reaction kinetics" and "chemical reaction engineering" are also used for this subject.



	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	8.5–7	9.6	10.3
Stability, transient behavior, control	7.5–6	8.8	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.)

for all changes of state must be within their constraints. Within this frame of reference we are in a position to use the information the chemist can give us about the dynamics of these changes, the nature of their driving forces and their velocity. In doing so we take the three elements on the top line of Fig. 1.1 and see how they combine to give a reaction rate expression; but we must always bear in mind that our borrowing from pure kinetics has not been sufficient to give a real entrance into that part of the subject. What we shall attempt to do, however, is to build up an understanding of the way in which the reaction rate is influenced by the state of the reaction mixture. This is genuine experience, for the analyst of any intellectual structure must grow by getting a feel for each part of his subject until he reaches the point of being able to hold it together in his mind in its true proportions. As well as getting a feel for the variation of reaction rate, we need also to experience the shape of the changes that reaction brings about. The chapter on the integration of the rate equation in its isothermal form is intended to provide this, an insight that has some bearing on how the kinetic constants may best be determined. A feature that principally distinguishes applied chemical kinetics from pure kinetics is the interaction of physical and chemical processes. This is adverted to in the sixth chapter, and the steps that are involved in heterogeneous catalysis are examined there.

These subjects constitute the middle group shown in Fig. 1.1, and if the top line may be likened to the anatomy of the subject, the middle group can perhaps be said to form the physiological aspects. With some grounding in anatomy and physiology we shall be able to approach the ecological study of reactions and see how they behave in their several habitats.

Once again, let us point out the boundaries of the area of interest. We shall make some passing reference to, but will have no primary interest in, the constructional details of a reactor. These are too special to an industry or even to a particular company to afford much intellectual discipline. What we shall be concerned with is to set up a reasonable mathematical model and so obtain reasonable design procedures. Reasonableness in this context requires that we include in the model all the essential features of the reactor but do not overload it with so much detail that analysis and design become impossible. For example, the model of a stirred tank assumes perfect mixing and leads to a reasonable design procedure and analysis of stability and control. We return later to see just how mixing may be described and what the effect of imperfect mixing may be. However, we do not consider the form of the stirring paddle or the way in which the tank should be baffled.

The four types of reactor that are treated are shown in Fig. 1.1; the study of fluidized beds, important though it be, is omitted for reasons of space. The development of each follows the same lines though it varies in amplitude from one type to another. First, the equations of a reasonable model are set up and from these the nature of the design problem becomes clear. Whenever possible, the optimal design is also considered and this is often not much more difficult to obtain than any other design. Even though the optimum may not be practically attainable, it always provides an objective standard against which other designs may be measured. While design is primarily a matter of solving the steady state equations, it is important not to overlook the transient behaviour of the reactor, for a steady state that is unstable must either be rejected or be stabilized by the addition of a controller. We return at the end of each chapter to reconsider some of the idealizations that have been made in setting up the model and the effect that these may have on the design and performance.

The four types of reactor considered are not unrelated physically or mathematically. The mixed or stirred tank reactor and the tubular or packed bed flow reactor are different both in construction and in their equations; but with sufficient backmixing the flow reactor approaches the mixed type. The batch reactor is a stirred tank with no flow, but it is described, in the simplest model, by the same equations as the tubular reactor. The term adiabatic refers to the mode of operation of the reactor rather than to its form, for it may be a tubular, batch or stirred tank. The same detail of treatment cannot be given to each topic for each reactor, partly because the areas have not been equally fully studied and partly because the analysis of some is too difficult for this level of presentation. For example, the transient equations of the stirred tank are ordinary differential equations and we can take their analysis quite far. However, the steady state equations of the tubular reactor are already ordinary differential equations and those for the transient behavior are partial differential equations which makes their analysis distinctly more difficult. Wherever possible, I have attempted to present some of the results of the deeper analysis by description and diagram with sufficient detail to make them appear reasonable, though not obvious.

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 thing, but as including function and interaction. Analysis is not 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 problems and prerequisites

In no area of chemical engineering does the formulation of good problems present greater difficulty. They tend to be either trite or impossibly lengthy. I do not pretend to be satisfied with those given here, and I suggest that they be supplemented by reference to other texts. While some of them do refer to actual reactions and processes, I make no apology for the prevalence of the reactions $\Sigma \alpha_{ij} A_j = 0$ nor even for the time honored $A \rightarrow B$ and $A \rightarrow B \rightarrow C$. A problem is futile if it leads the student into a morass of details; the principles involved can often be seen most clearly if the detail is omitted, however important this may be in another context. With a clear grasp of principles the engineer is equipped to tackle the problems of the real world; without them he is lost unless a relevant recipe is at hand. In teaching the course to fourth year students, an attempt has been made to get around the impossible lengthiness of many useful problems by simultaneously teaching computer programming. An appendix gives some examples and further reference to what has been done in this area.

A working knowledge of elementary calculus is presumed as well as some acquaintance with ordinary differential equations. Experience suggests that the latter cannot be taken for granted, and some particularly important types are reviewed in Section 5.1. A nodding acquaintance with linear algebra is helpful in Chapter 2. A thorough course in thermodynamics, one of the staples of the undergraduate chemical engineer's diet, should precede a course on chemical reactors, and Chapter 3 is little more than a summary of required results cast in the notation of this book. It is hoped that the large number of diagrams will help in following the argument and teach the student to extract as much information about the general behavior of the solution as possible before turning to computation. Present day computers have an unrivalled capacity for producing reams of waste paper when presented with problems whose structure is not first well understood.

REFERENCES

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

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

Two particularly valuable supplements to *Chemical Engineering Science* have been issued. They are the papers given at the first two European Symposia on Chemical Reaction Engineering in 1957 and 1960. The first was issued as a monograph and as Vol. 8; the second as Vol. 14. A third symposium was held in September 1964.

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).

Also

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

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

W. Brötz, *Grundriss der chemischen Reaktionstechnik*. Weinheim: Verlag Chemie, 1958.

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

J. C. Jungers and others, *Cinétique Chimique Appliquée*. Paris: Technip, 1958.

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

Two recent and very good texts are:

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*. London: Cambridge University Press. 1965.

To appear shortly is

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

This is at a graduate level, but the enterprising undergraduate will want to tackle it.

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 Vol. 4. (1963) O. Levenspiel and K. B. Bischoff's "Patterns of Flow in Chemical Process Vessels."

On the pure kinetics side, the *Advances in Catalysis* series, put out by the same house, 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., 1964.

where an excellent exposition of chemical kinetics and an entry into its vast literature will be found.