Fundamentals of Chemical Reaction Engineering

Fundamentals of Chemical Reaction Engineering

Mark E. Davis
California Institute of Technology

Robert J. Davis
University of Virginia

Boston Burr Ridge, IL Dubuque, IA Madison, WI New York San Francisco St. Louis
Bangkok Bogotá Caracas Kuala Lumpur Lisbon London Madrid Mexico City
Milan Montreal New Delhi Santiago Seoul Singapore Sydney Taipei Toronto

McGraw-Hill Higher Education
A Division of The McGraw-Hill Companies

FUNDAMENTALS OF CHEMICAL REACTION ENGINEERING

This book is printed on acid-free paper.

International 1 2 3 4 5 6 7 8 9 0 DOC/DOC 0 9 8 7 6 5 4 3 2
Domestic 1 2 3 4 5 6 7 8 9 0 DOC/DOC 0 9 8 7 6 5 4 3 2

ISBN 0–07–245007–X
ISBN 0–07–119260–3 (ISE)

Publisher: *Elizabeth A. Jones*
Sponsoring editor: *Suzanne Jeans*
Developmental editor: *Maja Lorkovic*
Marketing manager: *Sarah Martin*
Project manager: *Jane Mohr*
Production supervisor: *Sherry L. Kane*
Senior media project manager: *Tammy Juran*
Coordinator of freelance design: *Rick D. Noel*
Cover designer: *Maureen McCutcheon*
Compositor: ***TECH**BOOKS*
Typeface: *10/12 Times Roman*
Printer: *R. R. Donnelley/Crawfordsville, IN*

Cover image: *Adapted from artwork provided courtesy of Professor Ahmed Zewail's group at Caltech. In 1999, Professor Zewail received the Nobel Prize in Chemistry for studies on the transition states of chemical reactions using femtosecond spectroscopy.*

Library of Congress Cataloging-in-Publication Data

Davis, Mark E.
Fundamentals of chemical reaction engineering / Mark E. Davis, Robert J. Davis. — 1st ed.
p. cm. — (McGraw-Hill chemical engineering series)
Includes index.
ISBN 0–07–245007–X (acid-free paper) — ISBN 0–07–119260–3 (acid-free paper : ISE)
1. Chemical processes. I. Davis, Robert J. II. Title. III. Series.

TP155.7 .D38 2003
660'.28—dc21 2002025525
CIP

INTERNATIONAL EDITION ISBN 0–07–119260–3

www.mhhe.com

McGraw-Hill Chemical Engineering Series

Bailey and Ollis
Biochemical Engineering Fundamentals

Bennett and Myers
Momentum, Heat and Mass Transfer

Coughanowr
Process Systems Analysis and Control

de Nevers
Air Pollution Control Engineering

de Nevers
Fluid Mechanics for Chemical Engineers

Douglas
Conceptual Design of Chemical Processes

Edgar and Himmelblau
Optimization of Chemical Processes

Gates, Katzer, and Schuit
Chemistry of Catalytic Processes

King
Separation Processes

Luyben
Process Modeling, Simulation, and Control for Chemical Engineers

Marlin
Process Control: Designing Processes and Control Systems for Dynamic Performance

McCabe, Smith, and Harriott
Unit Operations of Chemical Engineering

Middleman and Hochberg
Process Engineering Analysis in Semiconductor Device Fabrication

Perry and Green
Perry's Chemical Engineers' Handbook

Peters and Timmerhaus
Plant Design and Economics for Chemical Engineers

Reid, Prausnitz, and Poling
Properties of Gases and Liquids

Smith, Van Ness, and Abbott
Introduction to Chemical Engineering Thermodynamics

Treybal
Mass Transfer Operations

To Mary, Kathleen, and our parents Ruth and Ted.

CONTENTS

PREFACE

This book is an introduction to the quantitative treatment of chemical reaction engineering. The level of the presentation is what we consider appropriate for a one-semester course. The text provides a *balanced* approach to the understanding of: (1) *both* homogeneous and heterogeneous reacting systems and (2) *both* chemical reaction engineering and chemical reactor engineering. We have emulated the teachings of Prof. Michel Boudart in numerous sections of this text. For example, much of Chapters 1 and 4 are modeled after his superb text that is now out of print (*Kinetics of Chemical Processes*), but they have been expanded and updated. Each chapter contains numerous worked problems and vignettes. We use the vignettes to provide the reader with discussions on real, commercial processes and/or uses of the molecules and/or analyses described in the text. Thus, the vignettes relate the material presented to what happens in the world around us so that the reader gains appreciation for how chemical reaction engineering and its principles affect everyday life. Many problems in this text require numerical solution. The reader should seek appropriate software for proper solution of these problems. Since this software is abundant and continually improving, the reader should be able to easily find the necessary software. This exercise is useful for students since they will need to do this upon leaving their academic institutions. Completion of the entire text will give the reader a good introduction to the fundamentals of chemical reaction engineering and provide a basis for extensions into other nontraditional uses of these analyses, for example, behavior of biological systems, processing of electronic materials, and prediction of global atmospheric phenomena. We believe that the emphasis on chemical *reaction* engineering as opposed to chemical *reactor* engineering is the appropriate context for training future chemical engineers who will confront issues in diverse sectors of employment.

We gratefully acknowledge Prof. Michel Boudart who encouraged us to write this text and who has provided intellectual guidance to both of us. MED also thanks Martha Hepworth for her efforts in converting a pile of handwritten notes into a final product. In addition, Stacey Siporin, John Murphy, and Kyle Bishop are acknowledged for their excellent assistance in compiling the solutions manual. The cover artwork was provided courtesy of Professor Ahmed Zewail's group at Caltech, and we gratefully thank them for their contribution. We acknowledge with appreciation the people who reviewed our project, especially A. Brad Anton of Cornell University, who provided extensive comments on content and accuracy. Finally, we thank and apologize to the many students who suffered through the early drafts as course notes.

We dedicate this book to our wives and to our parents for their constant support.

Mark E. Davis
Pasadena, CA

Robert J. Davis
Charlottesville, VA

Nomenclature

a_i	activity of species i
a_v	external catalyst particle surface area per unit reactor volume
A_i	representation of species i
A_C	cross sectional area of tubular reactor
A_C^P	cross sectional area of a pore
A_H	heat transfer area
$\overline{A}$	pre-exponential factor
Bo_a	dimensionless group analogous to the axial Peclet number for the energy balance
C_i or $[A_i]$	concentration of species i
C_{iB}	concentration of species i in the bulk fluid
C_{iS}	concentration of species i at the solid surface
C_p	heat capacity per mole
$\overline{C}_p$	heat capacity per unit mass
d_e	effective diameter
d_p	particle diameter
d_t	diameter of tube
D_a	axial dispersion coefficient
D^e	effective diffusivity
D_{ij}	molecular diffusion coefficient
D_{Ki}	Knudsen diffusivity of species i
D_r	radial dispersion coefficient
D_{TA}	transition diffusivity from the Bosanquet equation
Da	Damkohler number
$\overline{Da}$	dimensionless group
E	activation energy
E_D	activation energy for diffusion
$E(t)$	$E(t)$-curve; residence time distribution
$\overline{E}$	total energy in closed system
f_f	friction factor in Ergun equation and modified Ergun equation
f_i	fractional conversion based on species i
f_i^{eq}	fractional conversion at equilibrium

$\bar{f}_i$	fugacity of species i
$\bar{f}_i^0$	fugacity at standard state of pure species i
ff	frictional force
F_i	molar flow rate of species i
g	gravitational acceleration
$(g/g_c)\bar{z}$	gravitational potential energy per unit mass
g_c	gravitational constant
gm	mass of catalyst
ΔG	change in Gibbs function ("free energy")
h	Planck's constant
h_i	enthalpy per mass of stream i
h_t	heat transfer coefficient
H	enthalpy
ΔH	change in enthalpy
ΔH_r	enthalpy of the reaction (often called heat of reaction)
H_w	dimensionless group
$\overline{H}_w$	dimensionless group
$\bar{I}$	ionic strength
J	Colburn J factor
$\bar{J}_i$	flux of species i with respect to a coordinate system
k	rate constant
$\bar{k}$	Boltzmann's constant
$\bar{k}_c$	mass transfer coefficient
K_a	equilibrium constant expressed in terms of activities
K_C	portion of equilibrium constant involving concentration
K_P	portion of equilibrium constant involving total pressure
K_X	portion of equilibrium constant involving mole fractions
$K_{\bar{\phi}}$	portion of equilibrium constant involving activity coefficients
L	length of tubular reactor
L_c	length of microcavity in Vignette 6.4.2
L_p	generalized length parameter
$\bar{L}$	length in a catalyst particle
$\overline{m}_i$	mass of stream i
$\dot{m}_i$	mass flow rate of stream i
M_i	molecular weight of species i
$\overline{M}$	ratio of concentrations or moles of two species
$\overline{MS}$	total mass of system
n_i	number of moles of species i

N_i	flux of species i
$NCOMP$	number of components
$NRXN$	number of independent reactions
P	pressure
Pe_a	axial Peclet number
Pe_r	radial Peclet number
PP	probability
q	heat flux
Q	heat transferred
$\dot{Q}$	rate of heat transfer
r	reaction rate
r_t	turnover frequency or rate of turnover
$\bar{r}$	radial coordinate
$\bar{r}_t$	radius of tubular reactor
R	recycle ratio
R_g	universal gas constant
R_p	radius of pellet
R_{pore}	radius of pore
$\bar{R}$	dimensionless radial coordinate in tubular reactor
$\bar{R}_{cc}$	correlation coefficient
Re	Reynolds number
s_i	instantaneous selectivity to species i
ΔS	change in entropy
S_c	sticking coefficient
S_i	overall selectivity to species i
S_p	surface area of catalyst particle
$\bar{S}$	number of active sites on catalyst
SA	surface area
Sc	Schmidt number
SE	standard error on parameters
Sh	Sherwood number
t	time
$\langle t \rangle$	mean residence time
$\bar{t}^*$	student t-test value
T	temperature
T_B	temperature of bulk fluid
T_S	temperature of solid surface
TB	third body in a collision process
u	linear fluid velocity (superficial velocity)

$\bar{u}(\bar{r})$	laminar flow velocity profile
U	overall heat transfer coefficient
$\bar{U}_i$	internal energy
v	volumetric flow rate
V	volume
V_i	mean velocity of gas-phase species i
V_p	volume of catalyst particle
V_R	volume of reactor
V_{total}	average velocity of all gas-phase species
W_c	width of microcavity in Vignette 6.4.2
x	length variable
x_p	half the thickness of a slab catalyst particle
X_i	mole fraction of species i
$\bar{X}^2$	defined by Equation (B.1.5)
y	dimensionless concentration
Y_i	yield of species i
z	axial coordinate
$\bar{z}$	height above a reference point
Z	dimensionless axial coordinate
$\bar{Z}_i$	charge of species i
α_i	when used as a superscript is the order of reaction with respect to species i
$\bar{\alpha}_i$	coefficients; from linear regression analysis, from integration, etc.
$\alpha\alpha_1$	parameter groupings in Section 9.6
$\alpha\alpha_2$	parameter groupings in Section 9.6
β	Prater number
β_T	dimensionless group
$\beta\beta_i$	dimensionless groups
γ	Arrhenius number
$\bar{\gamma}_i$	activity coefficient of species i
Γ	dimensionless temperature in catalyst particle
$\bar{\Gamma}$	dimensionless temperature
$\delta(t)$	Dirac delta function
$\bar{\delta}$	thickness of boundary layer
ε_i	molar expansion factor based on species i
$\bar{\varepsilon}$	deviation of concentration from steady-state value
$\bar{\varepsilon}_B$	porosity of bed
$\bar{\varepsilon}_p$	porosity of catalyst pellet

η	intraphase effectiveness factor
η_o	overall effectiveness factor
$\overline{\eta}$	interphase effectiveness factor
θ	dimensionless time
θ_i	fractional surface coverage of species i
$\overline{\theta}$	dimensionless temperature
λ	universal frequency factor
λ^e	effective thermal conductivity in catalyst particle
λ_λ	parameter groupings in Section 9.6
$\overline{\lambda}_r$	effective thermal conductivity in the radial direction
μ_i	chemical potential of species i
$\overline{\mu}$	viscosity
ξ	number of moles of species reacted
ρ	density (either mass or mole basis)
ρ_B	bed density
ρ_p	density of catalyst pellet
σ_i	standard deviation
$\overline{\sigma}_i$	stoichiometric number of elementary step i
τ	space time
$\overline{\tau}$	tortuosity
υ_i	stoichiometric coefficient of species i
ϕ	Thiele modulus
ϕ_0	Thiele modulus based on generalized length parameter
$\overline{\phi}_i$	fugacity coefficient of species i
Φ	extent of reaction
χ	dimensionless length variable in catalyst particle
ψ	dimensionless concentration in catalyst particle for irreversible reaction
$\overline{\psi}$	dimensionless concentration in catalyst particle for reversible reaction
Ψ	dimensionless concentration
ω	dimensionless distance in catalyst particle

Notation used for stoichiometric reactions and elementary steps

	Stoichiometric reaction	Elementary step
Irreversible (one-way)	$\Longrightarrow$	$\longrightarrow$
Reversible (two-way)	$\rightleftharpoons$	$\rightleftharpoons$
Equilibrated	$\rightleftharpoons$	$\rightleftharpoons$
Rate-determining		$\overset{\longrightarrow}{\wedge}$ or $\overset{\rightleftharpoons}{\wedge}$