CHEMICAL REACTOR ANALYSIS & DESIGN

Froment & Bischoff

Chemical Reactor Analysis and Design

Gilbert F. Froment
Rijksuniversiteit Gent, Belgium

Kenneth B. Bischoff
University of Delaware

John Wiley & Sons
New York Chichester Brisbane Toronto

Library of Congress Cataloging in Publication Data

Froment, Gilbert F.
Chemical reactor analysis and design.

Includes index.
1. Chemical reactors. 2. Chemical reactions.
3. Chemical engineering. I. Bischoff, Kenneth B.,
joint author. II. Title.

TP157.F76 660'.29'9 78-12465

ISBN 0-471-02447-3

Printed in the United States of America

10 9 8 7 6 5 4 3

Chemical Reactor Analysis and Design

Board of Advisors, Engineering

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

To our wives:
Mia and Joyce

Preface

This book provides a comprehensive study of chemical reaction engineering, beginning with the basic definitions and fundamental principles and continuing all the way to practical application. It emphasizes the real-world aspects of chemical reaction engineering encountered in industrial practice. A rational and rigorous approach, based on mathematical expressions for the physical and chemical phenomena occurring in reactors, is maintained as far as possible toward useful solutions. However, the notions of calculus, differential equations, and statistics required for understanding the material presented in this book do not extend beyond the usual abilities of present-day chemical engineers. In addition to the practical aspects, some of the more fundamental, often more abstract, topics are also discussed to permit the reader to understand the current literature.

The book is organized into two main parts: applied or engineering kinetics and reactor analysis and design. This allows the reader to study the detailed kinetics in a given "point," or local region first and then extend this to overall reactor behavior.

Several special features include discussions of chain reactions (e.g., hydrocarbon pyrolysis), modern methods of statistical parameter estimation and model discrimination techniques, pore diffusion in complex media, general models for fluid-solid reactions, catalyst deactivation mechanisms and kinetics, analysis methods for chemical processing aspects of fluid-fluid reactions, design calculations for plug flow reactors in realistic typical situations (e.g., thermal cracking), fixed bed reactors, fluidized bed reactor design, and multiphase reactor design. Several of these topics are not usually covered in chemical reaction engineering texts, but are of high current interest in applications.

Comprehensive and detailed examples are presented, most of which utilize real kinetic data from processes of industrial importance and are based on the authors' combined research and consulting experience.

We firmly believe, based on our experience, that this book can be taught to both undergraduate and graduate classes. If a distinction must be made between undergraduate and graduate material it should be in the extension and the depth of coverage of the chapters. But we emphasize that to prepare the student to solve the problems encountered in industry, as well as in advanced research, the approach must be the same for both levels: there is no point in ignoring the more complicated areas that do not fit into idealized schemes of analysis.

Several chapters of the book have been taught for more than 10 years at the

Rijksuniversiteit Gent, at the University of Maryland, Cornell University, and the University of Delaware. Some chapters were taught by G.F.F. at the University of Houston in 1973, at the Centre de Perfectionnement des Industries Chimiques at Nancy, France, from 1973 onwards and at the Dow Chemical Company, Terneuzen, The Netherlands in 1978. K.B.B. used the text in courses taught at Exxon and Union Carbide and also at the Katholieke Universiteit Leuven, Belgium, in 1976. Substantial parts were presented by both of us at a NATO-sponsored Advanced Study Institute on "Analysis of Fluid–Solid catalytic Systems" held at the Laboratorium voor Petrochemische Techniek, Rijksuniversiteit, Gent, in August 1974.

We thank the following persons for helpful discussions, ideas, and critiques: among these are dr. ir. L. Hosten, dr. ir. F. Dumez, dr. ir. J. Lerou, ir. J. De Geyter and ir. J. Beeckman, all from the Laboratorium voor Petrochemische Techniek of Rijksuniversiteit Gent; Prof. Dan Luss of the University of Houston and Professor W. D. Smith of the University of Rochester.

Gilbert F. Froment
Kenneth B. Bischoff

Notation

Two consistent sets of units are listed in the following pages: one that is currently the most common in engineering calculations (including, for example, m, hr, atm, kcal) and the S.I. units, which are only slowly penetrating into everyday use. In some formulas other units had to be used: the chemical engineering literature contains many correlations that are not based on dimensionless groups and they require the quantities to be expressed in certain given units only. This has been carefully indicated in the text, however.

All the numerical calculations in the text are in the above mentioned engineering units, but the intermediate and final results are also given in S.I. units. We feel that this reflects—and even simplifies—the practical reality that is going to last for many more years, and we have preferred this pragmatic approach to preserve the feeling for orders of magnitude gained from years of manipulation of the engineering units. Finally, great attention has been given to the detailed definition of the units of the different quantities: for example, when a dimension of length is used, it is always clarified as to whether this length concerns the catalyst or the reactor. We have found that this greatly promotes insight into the mathematical modeling of a phenomenon.

		Engineering units	S.I. units
A	reaction component		
A_b	heat exchange surface, packed bed side	m^2	m^2
A_j	reacting species in a reaction system		
A_k	heat exchange surface in a batch reactor, on the side of the reaction mixture	m^2	m^2
A_m	logarithmic mean of A_k and A_r or of A_b and A_u	m^2	m^2
A_r	heat exchange surface for a batch reactor on the side of the heat transfer medium	m^2	m^2
A_t	total heat exchange surface	m^2	m^2

		Engineering units	S.I. units
A_a	heat exchange surface for a packed bed on the side of the heat transfer medium	m^2	m^2
A_v	gas-liquid interfacial area per unit liquid volume	m_i^2/m_L^3	m_i^2/m_L^3
A_{vt}	interfacial area per unit tray surface	m_i^2/m^2	m_i^2/m^2
A_0	frequency factor		
A'	absorption factor, L'/mF		
A'_v	gas-liquid interfacial area per unit gas + liquid volume	m_i^2/m_{L+G}^3	m_i^2/m_{L+G}^3
a	stoichiometric coefficient		
a_0, a_1	parameters (Sec. 8.3.b)		
a_g	surface to volume ratio of a particle	m_p^2/m_p^3	m_p^2/m_p^3
a_m	external particle surface area per unit catalyst mass	m_p^2/kg cat.	m_p^2/kg cat.
a_r	external particle surface area per unit reactor volume	m_p^2/m_r^3	m_p^2/m_r^3
a'	order of reaction with respect to A		
a'_j	order of reaction with respect to A_j		
a'_v	gas-liquid interfacial area per unit packed volume	m_i^2/m_r^3	m_i^2/m_r^3
a''_v	liquid-solid interfacial area per unit packed volume	m_i^2/m_r^3	m_i^2/m_r^3
B	reaction component		
B_m	fictitious component		
B	vector of fictitious components		
b	stoichiometric coefficient		
b'	order of reaction with respect to B		
C_A, C_B, C_j	molar concentration of species A, B, j	kmol/m^3	kmol/m^3
$C_{Ab}, C_{Bb} \ldots$	molar concentrations of species $A, B \ldots$ in the bulk fluid	kmol/m_f^3	kmol/m_f^3
$C_{Al}, C_{Bl} \ldots$	molar concentrations of adsorbed $A, B \ldots$	kmol/kg cat.	kmol/kg cat.
C_D	drag coefficient for spheres		

		Engineering units	S.I. units
C_S	molar concentration of reacting component S of solid	kmol/m_p^3	kmol/m_p^3
C_c	coke content of catalyst	kg coke/kg cat.	kg coke/kg cat.
C_l	molar concentration of vacant active sites of catalyst	kmol/kg cat.	kmol/kg cat.
C_t	total molar concentration of active sites	kmol/kg cat.	kmol/kg cat.
C_0	inlet concentration	kmol/m^3	kmol/m^3
$\mathbf{C}$	vector of concentrations	kmol/m^3	kmol/m^3
C_{Aeq}	molar concentration of A at equilibrium	kmol/m^3	kmol/m^3
C_{A_i}	molar concentration of A in front of the interface	kmol/m_f^3	kmol/m_f^3
C_{A_s}, C_s	molar concentration of fluid reactant inside the solid	kmol/m_f^3	kmol/m_f^3
C_{P_s}, $C_{P_s}{}^c$	molar concentration of sorbed poison inside catalyst, with respect to core boundary	kmol/m_f^3	kmol/m_f^3
$C_{P_{s,}}$	equilibrium molar concentration of sorbed poison inside catalyst	kmol/m_f^3	kmol/m_f^3
C_{s0}	reactant molar concentration at centerline of particle (Chapter 3)	kmol/m_f^3	kmol/m_f^3
$\overline{C_A}$	Laplace transform of C_A		
$C_{A_s}{}^s$, $C_s{}^s$	molar concentration of fluid reactant in front of the solid surface	kmol/m_f^3	kmol/m_f^3
C'_{A_s}	molar concentration of A inside completely reacted zone of solid	kmol/m_f^3	kmol/m_f^3
c_p	specific heat of fluid	kcal/kg K	kJ/kg K
c_{p_s}	specific heat of solid	kcal/kg K	kJ/kg K
Da	Damköhler number for poisoning, $k_{sP}R/D_{eP}$		
D_A, D_B	molecular diffusivities of A, B in liquid film	m^3/m_L hr	m^3/m_L s
D_{AB}	molecular diffusivity for A in a binary mixture of A and B	m_f^3/m hr	m_f^3/m s

		Engineering units	S.I. units
D_K	Knudsen diffusivity	$m_f^3/m \cdot hr$	$m_f^3/m\ s$
D_e, D_{eA}, D_{eB}	effective diffusivities for transport in a (pseudo-) continuum, or (Chapter 13) in emulsion phase	m_f^3/m hr or m_f^3/m_r hr	m_f^3/m s or m_f^3/m_r s
D_{eG}	gas phase effective diffusivity in axial direction in a multiphase packed bed	m_G^3/m_r hr	m_G^3/m_r s
D_{eL}	liquid phase effective diffusivity in axial direction in a multiphase packed bed	m_L^3/m_r hr	m_L^3/m_r s
D_{eP}	effective pore diffusivity for poison	m_f^3/m cat. hr	m_f^3/m cat. s
D_{ea}, D_{er}	effective diffusivities in axial, respectively radial directions in a packed bed	m_f^3/m_r hr	m_f^3/m_r s
D_{eg}	effective diffusivity for transport of A through a grain (Sec. 4.4)	m_f^3/m_p hr	m_f^3/m_p s
D_{ep}	effective diffusivity for transport of A in the pores between the grains (Sec. 4.4)	m_f^3/m_p hr	m_f^3/m_p s
$D_{i,n}$	measure of divergence between rival models for the nth experiment in the ith grid point		
$D_{j,l}$	eddy diffusivity for species j in the 1 direction	m_f^3/m hr	m_f^3/m s
D_l	eddy diffusivity in the l direction	m_f^3/m hr	m_f^3/m s
D'_e	effective diffusivity for transport through completely reacted solid (Chapter 4)	m_f^3/m_p hr	m_f^3/m_p s
D_{jm}	effective molecular diffusivity of j in a multicomponent mixture	m_f^3/m hr	m_f^3/m s
d	wall thickness	m	m
d_b	bubble diameter	m	m
d_c	coil diameter	m	m
d_p	particle diameter	m	m
d_r	reactor diameter	m	m

		Engineering units	S.I. units
d_s	stirrer diameter	m	m
d_t	internal tube diameter also tower diameter (Chapter 14)	m	m
E	activation energy	kcal/kmol	kJ/kmol
E_C	Murphree tray efficiency corrected for entrainment		
$E_i(x)$	exponential integral		
E'	Murphree tray efficiency		
$\bar{E}$	overall tray efficiency		
$\dot{E}$	point tray efficiency along gas streamline		
Eö_b	Eötvös number, based on bubble diameter, $\frac{d_b \rho_L g}{\sigma}$		
$\text{erf}(\eta)$	error function		
$\text{erfc}(\eta)$	complementary error function, 1-erf(η)		
F	total molar flow rate	kmol/hr	kmol/s
F_A	enhancement factor		
F_{A_0}, F_{j_0}	molar feed rate of reactants A and j	kmol/hr	kmol/s
F_k	force exerted per unit cross section	kgf/m^2 or atm	N/m^2
$\mathscr{F}$	objective function		
F'	volumetric gas flow rate	m^3/hr	m^3/s
F'_0	volumetric gas feed rate	m^3/hr	m^3/s
F''	volumetric gas flow rate (Chapter 14)	ft^3/ft^2 min	m^3/m^2 s
f	friction factor in Fanning equation		
f_b	fraction of total fluidized bed volume occupied by bubble gas		
f_e	fraction of total fluidized bed volume occupied by emulsion gas		
G	superficial mass flow velocity	kg/m_r^2 hr	kg/m_r^2 s
$\mathbf{G}$	matrix of partial derivatives of model with respect to the parameters		
$\mathbf{G}^T$	transpose of $\mathbf{G}$		

		Engineering units	S.I. units
g	acceleration of gravity	m/hr^2	m/s^2
$g_{j,l}$	external force on species j in the l direction per unit mass of j	kcal/kg m	N/kg
$g_{u,i}$	partial derivative of reaction rate with respect to the parameter K_i at the uth set of experimental conditions		
H	Henry's law coefficient	m^3atm/kmol	Nm/kmol
$H_{G,n}$	enthalpy of gas on plate n	kcal/kmol	kJ/kmol
H_L	liquid height	m	m
$H_{L,n}$	enthalpy of liquid on plate n	kcal/kmol	kJ/kmol
H_{fj}	heat of formation of species j	kcal/kmol	kJ/kmol
H_i	height of stirrer above bottom	m	m
$\bar{H}_j$	molar enthalpy of species j	kcal/kmol	kJ/kmol
$-\Delta H$	heat of reaction	kcal/kmol	kJ/kmol
h_f	heat transfer coefficient for film surrounding a particle	kcal/m_p^2 hr °C	kJ/m_p^2 s K
I	initiator; also intermediate species; inert;		
$\mathbf{I}$	unit matrix		
$J_{j,l}$	molar flux of species j in l direction, with respect to mass average velocity	kmol/m^2 hr	kmol/m^2 s
J_s	pressure drop in straight tubes	kgf/m^2 or atm	N/m^2
j_D	j-factor for mass transfer, $\frac{k_g M_m P_{fA}}{G} Sc^{2/3}$		
j_H	j-factor for heat transfer, $\frac{h_f}{c_p G}(\mathrm{Pr})^{2/3}$		
$K, K_A, K_1 \ldots$	equilibrium constants	atm^{-1} or m^3/kmol	m^2/N or m^3/kmol
$\mathbf{K}$	matrix of rate coefficients		
$\hat{K}$	kinetic energy per unit mass	m^2/hr^2	m^2/s^2
$\hat{K}_1$	flow averaged kinetic energy per unit mass	m^2/hr^2	m^2/s^2
k	reaction rate coefficient	see k_c, k_y, k_p	

		Engineering units	S.I. units
k	rate coefficient with respect to unit solid mass for a reaction with order n with respect to fluid reactant A and order m with respect to solid component S	$m_f^{3n}(\text{kmol } A)^{1-n}$ $(\text{kmol } S)^{-m}$ $m_p^{3(m-1)}\,\text{hr}^{-1}$	$m_f^{3n}(\text{kmol } A)^{1-n}$ $(\text{kmol } s)^{-m}$ $m_p^{3(m-1)}\,\text{s}^{-1}$
k_C	coking rate coefficient	kg coke/kg cat. hr atm or hr^{-1}	kg coke/kg cat. $\text{s}(\text{N/m}^2)$ or s^{-1}
k_G	gas phase mass transfer coefficient referred to unit interfacial area	$m_G^3\, m_i^2\,\text{hr}$	$m_G^3/m_i^2\,\text{s}$
k_L	liquid phase mass transfer coefficient referred to unit interfacial area	$m_L^3/m_i^2\,\text{hr}$	$m_L^3/m_i^2\,\text{s}$
k_T	mass transfer coefficient (including interfacial area) between flowing and stagnant liquid in a multiphase reactor	$m_L^3/m_r^3\,\text{hr}$	$m_L^3/m_r^3\,\text{s}$
k_{T1}, k_{T2}	mass transfer coefficient (including interfacial area) beween regions 1 and 2 of flow model (Chapter 12)	$m_L^3/m_r^3\,\text{hr}$	$m_L^3/m_r^3\,\text{s}$
k_c	rate coefficient based on concentrations	$\text{hr}^{-1}\{\text{kmol/m}^3\}^{1-(a'+b'\ldots)}$	$\text{s}^{-1}\{\text{kmol/m}^3\}^{1-(a'+b'\ldots)}$
k_g	gas phase mass transfer coefficient; when based on concentrations; when based on mole fractions; when based on partial pressures; in a fluidized bed	$m_f^3/m_p^2\,\text{hr}$; $\text{kmol/m}_p^2\,\text{hr}$; $\text{kmol/m}_p^2\,\text{hr atm}$ $m_f^3/m_c^3\,\text{hr}$	$m_f^3/m_p^2\,\text{s}$; $\text{kmol/m}_p^2\,\text{s}$; $\text{kmol/m}_p^2\,\text{s}\,(\text{N/m}^2)$; $m_f^3/m_c^3\,\text{s}$
k_{gP}	interfacial mass transfer coefficient for catalyst poison	$m_f^3/m_p^2\,\text{hr}$	$m_f^3/m_p^2\,\text{s}$
k_l	mass transfer coefficient between liquid and catalyst surface, referred to unit interfacial area	$m_L^3/m_i^2\,\text{hr}$	$m_L^3/m_i^2\,\text{s}$
k_p	reaction rate coefficient based on partial pressures	$\text{hr}^{-1}\text{kmol/m}^3$ $\text{atm}^{-(a'+b'\ldots)}$	$\text{s}^{-1}\text{kmol/m}^3$ $(\text{N/m}^2)^{-(a'+b'\ldots)}$
k_{pr}	rate coefficient for propagation reaction in addition polymerization	$\text{m}^3/\text{kmol hr}$	$\text{m}^3/\text{kmol s}$

		Engineering units	S.I. units
k_r	reaction rate coefficient (Chapter 3)	m_f^3/m^2 cat. hr	m_f^3/m^2 cat. s
k_{rA}, k_{rB}	rate coefficient for catalytic reaction subject to poisoning	m_f^3/m^2 cat. hr	m_f^3/m^2 cat. s
k_{rP}	rate coefficient for first-order poisoning reaction at core boundary	m_f^3/m^2 cat. hr	m_f^3/m^2 cat. s
k_s	surface-based rate coefficient for catalytic reaction (Chapter 5)	m_f^3/m^2 cat. hr	m_f^3/m^2 cat. s
k_t, k_{tr}	rate coefficients for termination reactions	m^3/kmol hr or hr^{-1}	m^3/kmol s or s^{-1}
k_v, k_v°	volume-based rate coefficient for catalytic reaction during poisoning, resp. in absence of poison	m_f^3/m^3 cat. hr	m_f^3/m^3 cat. s
k_y	rate coefficient based on mole fractions	kmol/m^3 hr	kmol/m^3 s
k_1	elutriation rate coefficient (Chapter 13)	kg/m^2 hr	kg/m^2 s
$k_1, k_2 \ldots$	reaction rate coefficients	see k_c, k_y, k_p	
k_A°	rate coefficient of catalytic reaction in absence of coke	depending on rate dimensions	
k_g°	mass transfer coefficient in case of equimolar counterdiffusion, $k_g y_{f_A}$	see k_g	
k_l'	mass transfer coefficient between stagnant liquid and catalyst surface in a multiphase reactor	m_L^3/m_r^3 hr	m_L^3/m_r^3 s
k_s'	surface based reaction rate coefficient for gas-solid reaction	$\left(\frac{m_p}{hr}\right)\Big/\left(\frac{kmol\ A}{m_f^3}\right)$	$\left(\frac{m_p}{s}\right)\Big/\left(\frac{kmol\ A}{m_f^3}\right)$
$(k_{bc})_b$	mass transfer coefficient from bubble to interchange zone, referred to unit bubble volume	m_f^3/m_b^3 hr	m_f^3/m_b^3 s
$(k_{bc})_b$	overall mass transfer coefficient from bubble to emulsion, referred to unit bubble volume	m_G^3/m_b^3 hr	m_G^3/m_b^3 s

		Engineering units	S.I. units
$(k_{ce})_b$	mass transfer coefficient from interchange zone to emulsion, referred to unit bubble volume	m_f^3/m_b^3 hr	m_f^3/m_b^3 s
$(k_{ce})_c$	mass transfer coefficient from bubble + interchange zone to emulsion, referred to unit bubble + interchange zone volume	m_G^3/m_c^3 hr	m_G^3/m_c^3 s
L	volumetric liquid flow rate	m_L^3/hr	m_L^3/s
	also distance from center to surface of catalyst pellet (Chapter 3)	m	m
	also distance between pores in a solid particle (Sec. 4.5) and thickness of a slab (Sec. 4.6)	m	m
L_f	total height of fluidized bed	m	m
L_{mf}	height of a fluidized bed at minimum fluidization	m	m
L'	molar liquid flow rate	kmol/hr	kmol/s
Lw'	modified Lewis number, $\lambda_e/\rho_s c_{p_s} D_e$		
l	vacant active site		
M	ratio of initial concentrations C_{B_0}/C_{A_0}		
M_j	molecular weight of species j	kg/kmol	kg/kmol
M_m	mean molecular weight	kg/kmol	kg/kmol
M_1	monomer (Sec. 1.4-6)		
m	Henry's coefficient based on mole fractions, also order of reaction		
m_t	total mass	kg	kg
$\dot{m}$	total mass flow rate	kg/hr	kg/s
$\dot{m}_j$	mass flow rate of component j	kg/hr	kg/s
N	stirrer revolution speed; also runaway number, $2U/R_t \rho c_p k_v$ (Sec. 11.5.c)	hr^{-1}	s^{-1}
$\dot{N}_A$	molar rate of absorption per unit gas-liquid interfacial area	$kmol/m_i^2$ hr	$kmol/m_i^2$ s