CHEMICAL REACTOR DESIGN

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About The Author

E. Bruce Nauman is Professor of Chemical Engineering at Rensselaer Polytechnic Institute. Dr. Nauman has served as Department Chairman and now acts as Director of the Industrial Liaison Program in addition to leading a large and active research group in chemical and polymer reaction engineering. Prior to joining RPI, Dr. Nauman spent seventeen years at Union Carbibe and Xerox Corporation in a variety of research and general management positions. He has also held academic appointments at the University of Tennessee, the University of Rochester, and the State University of New York at Buffalo. He is an active consultant and is a member of several corporate boards in addition to a variety of academic and editorial advisory boards. Dr. Nauman has written a previous Wiley text, *Mixing in Continuous Flow Systems*, with B. A. Buffman, and has published more than fifty rersearch articles. The author of several patents, he has invented a new technique for microparticulation, which is being widely licensed in the polymer industry. Dr. Nauman founded the ongoing series of Engineering Foundation Conferences on Chemical Reaction Engineering and has chaired the Conference on Mixing.

Preface

Some areas of science and technology are led by academians. Others are paced by industrialists. Chemical reaction engineering has benefited from both inputs; and, at least in the research areas, is practiced at a high level of competence. However, undergraduate education has not yet reflected the remarkable changes that have occurred in academic and industrial reaction engineering over the last decade. The transport phenomena revolution of the 1950s and 1960s has fully permeated chemical engineering. Digital computation has become incredibly cheap in the 1970s and 1980s. This combination has led to a quantitative emphasis in chemical reactor design that far surpasses the standard undergraduate texts.

An emphasis throughout this text is numerical computation; it should be understood that this is not an absolute emphasis but one relative to other texts in the field. Physical insights remain of primary concern. The numerical methods used in this book are not sophisticated. Computers are cheap and becoming cheaper. Nowadays, a model too complex to be computable is probably too complex to be real. The student of chemical reactor design can come up with hard numbers rather than qualitative arguments. Obviously, the numbers will be no better than the physical insights that generated them. Horror stories can always be told of numerical precision disguising physical inaccuracy. However, at least one source of error is eliminated when the consequences of a model can be evaluated exactly. To me at least, this is a big step forward.

Simple methods which retain physical transparency are stressed. References are cited to more sophisticated techniques. These should be used for detailed design and optimization studies with complex models. In my judgment, the simplest possible numerical scheme is best at the beginning. Thus Euler's method is used for ordinary differential equations, fully explicit marching techniques are used for partial differential equations, and generous use is made of Richardson extrapolation. These methods are simple and robust, and they rarely mislead.

Two traditional topics, the analysis of rate data and chemical thermodynamics, have been postponed until fairly late in the text. They appear at the end of Chapter 4 which introduces heat balances. This postponement can be rationalized in several ways, but the real motivation was pedagogical. My personal feeling is that students prefer to start a new course by seeing what is distinctly different from previous courses. Should you disagree with this approach, Section 4.3 and Appendix 4.1 can be introduced earlier without significant difficulty.

A standard undergraduate course should include Chapters 1–4, 6 and 7. Chapter 5 constitutes a rather open-ended project where the student can get some feel for process integration and optimization. It, together with a distributed reactor problem from Chapters 6 or 7, is an integral part of RPI's one semester course in chemical reactor design. Also included in that one semester is Chapter 8 and either of Chapters 9 and 10. However, any of Chapters 8 through 12 can be used to round out the undergraduate course depending on the student's interests and abilities.

The book can also be used for a first graduate course, particularly if supplemented by a text, such as that by Aris,[1] which places greater stress on fundamentals. Most students will benefit from a quick tour of Chapters 1 through 4. Although they will have been exposed previously to kinetics and reactor design, few will be comfortable with the relatively heavy emphasis on computation that characterizes this text. Chapters 6 and 7 need to be covered in some detail, since few undergraduate programs give the necessary background in distributed parameter systems. However, it is still possible to cover all of Chapters 8 through 12 in a one-semester graduate course. These chapters include introductions to unsteady reactors and control systems, residence time and micromixing theory, heterogeneous catalysis, microbial processes, multiphase reactors, electronic device fabrication, and polymer reaction engineering. These introductions are intended to be just that. I have had the good fortune to work and consult in most of the mentioned areas. Hopefully, I have managed to distill the essence of these topics without succumbing to the temptation of writing far more than can be covered in an introductory course. Courses beyond this level, whether formal or informal, can be best served by the research literature and specialized monographs.

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[1] R. Aris, Introduction to the Analysis of Chemical Reactors, Prentice-Hall, Englewood Cliffs, NJ, 1965.

problems. Colleagues who read and used the manuscript deserve credit for its strengths: Robert Adler, Alfred Engel, L. T. Fan, John Friedly, A. H. Johannes, and F. Shadman. They share none of the blame for its weaknesses. Also deserving credit for the book's strengths are the Wiley editors Don Ford and Christina Mediate. Occasionally, I had the good judgment to heed their advice.

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Troy, New York
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A Note on Notation

Occasionally, chemical reactions will be spelled out in detail, for example,

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O \tag{0.1}$$

and the concentrations (in moles per unit volume) of the various species will be represented using square brackets, for example,

$$K_{\text{equil}} = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} \tag{0.2}$$

This notation quickly becomes cumbersome when the molecules are complicated. Thus we normally use shorthand:

$$A + B \rightleftharpoons C + D \tag{0.3}$$

$$K_{\text{equil}} = \frac{[C][D]}{[A][B]} \tag{0.4}$$

or

$$K_{\text{equil}} = \frac{C_C C_D}{C_A C_B} \tag{0.5}$$

or

$$K_{\text{equil}} = \frac{cd}{ab} \tag{0.6}$$

All the concentration notations in Equations 0.4 through 0.6 are found in the literature. We shall usually use the lowercase letters $a, b, c, \ldots$ to denote concentrations of components A, B, C, ... as illustrated in Equation 0.6. This form is easy to write and lends itself to subscripts: a_0, a_{in}, a_{out}.

When the capital letters A, B, C, ... appear as subscripts, they denote a particular component. Thus N_A is the number of moles of A present in the system and $\mathscr{R}_A$ is the rate of formation of A (in moles per unit volume per unit time). Roman numeral subscripts are used to distinguish between different reactions. Thus $\mathscr{R}_{A,\text{II}}$ is the rate of formation of component A by Reaction II.

Two types of averages are used in this text. The spatial average of a is denoted as $\hat{a}$ and the convected mean is denoted as $\bar{a}$.

List of Symbols

Roman Symbols

Symbol		*Reference Equation*
a	Concentration of component A	1.4
a_0	Initial concentration of A	1.30
$a(0+)$	Concentration of A immediately after reactor inlet	7.8
$\mathbf{a}$	Vector of concentrations	2.74
$\mathbf{a}_0$	Vector of initial concentrations	2.74
$\hat{a}$	Spatial average concentration	1.4
$\bar{a}$	Mixing cup or convected mean concentration	12.82
a_b	Concentration of A in the bubble phase	11.74
a_{batch}	Concentration of A after batch reaction	9.82
a_c	Specific surface area of catalyst	10.13
a_e	Concentration of A in the emulsion phase	11.73
a_g	Concentration of A in the gas phase	11.1
a_g^*	Concentration of A in gas phase at interface	11.1
a_i	Concentration of A inside a pore	10.4
a_{in}	Concentration of A at reactor inlet	1.3
a_j	Concentration of A at jth step of calculation	3.5
a_l	Concentration of A in liquid phase	11.1
a_l^*	Concentration of A in liquid phase at interface	11.1

a_{mix}	Concentration of A after mixing	3.85
a_n	Concentration of oligometer of length n	12.47
a_{out}	Concentration of A at reactor outlet	1.3, 8.4
a_r	Concentration of A inside a spherical pellet	11.99
a_s	Surface concentration of A	10.3
a_t	Concentration of A at time t	1.30
a_t^*	Estimate of $a(t)$	2.13
A	Subscript denoting reactive species A	1.3
A_{b}	Cross-sectional area of bubble phase	11.74
A_c	Cross-sectional area of reactor	3.7
A_{e}	Cross-sectional area of emulsion phase	11.73
A_{ext}	External surface area of reactor	4.23, 11.43
A'_{ext}	External surface area per unit length of reactor	4.26
A_g	Cross-sectional area of gas phase	11.46
A_i	Interfacial area per unit volume of reactor	11.1
A'_i	Interfacial area per unit height of column	11.45
A_l	Cross-sectional area of liquid phase	11.45
A_s	Cross-sectional area of solid phase	1.111
Av	Avogadro's number, molecules/mol	1.9
b	Concentration of component B	1.7
b_0	Initial concentration of B	1.45
b_{bulk}	Concentration of B in the bulk fluid	11.72
b_{in}	Concentration of B at reactor inlet	1.80
b_j	Concentration of B at jth step in calculation	3.6
b_n	Concentration of oligometer of length n	12.47
b_{out}	Concentration of B at reactor outlet	1.80
b_t	Concentration of B at time t	2.51
B	Subscript denoting reactive species B	2.9
c	Concentration of component C	1.18
c	Concentration of live cells	10.79
c_0	Initial concentration of C	2.53
c_{in}	Concentration of C at reactor inlet	3.32
c_n	Concentration of oligometer, possible cyclic, of length n	12.46, 12.47
c_{out}	Concentration of C at reactor outlet	3.32
C	Constant of integration	1.41
C	Subscript denoting component C	2.9
C	Concentration of nonreactive tracer	9.2
C_{A}	Capacity of ion exchange resin for reactant A	11.103
C_{AB}	Collision rate between A and B molecules	1.9
C_0	Initial concentration of tracer	9.2
C_p	Heat capacity	4.29
d	Concentration of component D	2.10

d_0	Initial concentration of D	2.10
d_{in}	Concentration of component D at reactor inlet	3.63
d_{out}	Concentration of component D at reactor outlet	3.63
d_p	Diameter of packing or of catalyst particle	3.14
d_t	Concentration of component D at time t	2.53
d_s	Diameter of unreacted zone	11.98
d	Diameter of tube	5.3
D	Subscript denoting reactive species D	2.9
D	Axial dispersion coefficient	7.5
D_r	Radial dispersion coefficient	11.95
D_z	Axial dispersion coefficient	11.95
$\mathcal{D}$	Molecular diffusivity	6.1
$\mathcal{D}_{\text{A}}$	Molecular diffusivity of component A	6.13
$\mathcal{D}_{\text{eff}}$	Effective diffusion coefficient inside catalyst particle	10.59
$\mathcal{D}_{\text{K}}$	Knudsen diffusivity	10.52
$\mathcal{D}_{\text{net}}$	Combined Knudsen and bulk diffusivity	10.53
$\mathcal{D}_{\text{P}}$	Molecular diffusivity of component P	10.9
e	Concentration of epoxy	8.40
e	Denotes the emulsion phase	11.73
E	Denotes an enzyme	Section 10.4.1
E	Activation energy	4.1
E	Axial dispersion coefficient for energy	7.26
$\mathcal{E}$	Enhancement factor in reactive gas absorption	11.71
E_{I}, E_{II}	Activation energies for Reactions I, II	Section 4.1.2
E_0	Concentration of reactive enzyme sites	10.64
E_f	Activation energy of forward reaction	4.6
E_r	Activation energy of reverse reaction	4.6
E_r	Radial dispersion coefficient for energy	7.46
$f(\ell)$	Frequency function for chain lengths	12.50
$f(t)$	Frequency function for residence times	9.10
f_G	Frequency function for growing chains	12.66
f_D	Frequency function for dead chains	12.67
$f_{\mathcal{R}}$	Collision efficiency factor	1.8
F	Arbitrary function	3.90
$F(t)$	Cumulative distribution of residence times	9.7
F_1, F_2	Arbitrary functions	3.51, 12.87
Fa	Fanning friction factor	3.13
F_{C}	Mole fraction of component C	3.67
F_j	Gas flow rate for jth tray	11.35
F_{X}, F_{Y}	Mole fractions of components X and Y	12.95
g	Denotes the gas phase	11.1

$g(\ell)$	Chain length distribution by weight fractions	12.54
$g(t)$	Transient response function	9.63
G	Arbitrary function	3.90
G_0, G_1, G_2	Control system constants	8.38
h	Concentration of possibly hypothetical component H	2.82
h_i	Heat transfer coefficient at interphase	11.43
h_i	Inside heat transfer coefficient	5.3
h_r	Wall heat transfer coefficient in a packed bed	7.50
H	Reactive component having a stoichiometric coefficient of +1	2.82
H	Enthalphy	4.25
H_g	Enthalphy of gas phase	11.43
H_{in}	Enthalphy at reactor inlet	4.12
H_l	Enthalphy of liquid phase	11.44
H_{out}	Enthalphy at reactor outlet	4.12
i	Step index in the radial direction	6.12
I	Number of steps in the radial direction	6.12
I_2	Denotes initiator molecule	12.17
$\mathrm{I}\cdot$	Denotes initiator free radical	12.17
$I(r)$	Integral	6.68
j	Step index in axial direction	3.5
j	Index denoting experimental observation	4.82
J	Number of steps in the axial direction	3.5
J	Number of observations	4.82
J_{min}	Minimum number of axial steps needed for stability	Example 6.3
k	Reaction rate constant	1.7
k_0	Pre-exponential reaction rate constant	4.1
k_∞	Asymptotic cell birth rate constant	10.83
$k_{\mathrm{I}}, k_{\mathrm{II}}$	Rate constants for Reactions I and II	2.1
$k_{-\mathrm{I}}$	Rate constant for reverse of Reaction I	2.20
k'	Constant	3.68
k_a^+	Forward rate constant for absorption step	10.24
k_d^-	Reverse rate constant for absorption step	10.24
k_b	Rate constant for cell births	10.79
k_B	Constant	10.40
k_c	Rate constant for termination by combination	12.22
k_d	Rate constant for cell deaths	10.79
k_d	Rate constant for termination by disproportionation	12.23
k_d^+	Forward rate constant for desorption	10.24
k_d^-	Reverse rate constant for desorption	10.24
k_f	Rate constant for forward reaction step	1.15, 11.49

k_l	Gas-side mass transfer coefficient	11.3
k_g	Liquid-side mass transfer coefficient	11.3
k_M, k_P	Rate constants	11.14, 11.15
k_r	Rate constant for reverse reaction step	1.15, 11.49
k_{H}	Henry's law constant	11.2
k_{I}	Rate constant for initiator decomposition	12.17
k_n	Rate constant involving molecule of length n	12.1
k_{mn}	Rate constant for reaction between molecules of lengths m and n	12.2
k_p	Propagation rate constant	12.20
$k_{\mathscr{R}}$	Rate constant	10.37
$k_{\mathscr{R}}^{+}$	Forward rate constant for surface reaction	10.24
$k_{\mathscr{R}}^{-}$	Reverse rate constant for surface reaction	10.24
k_s	Mass transfer coefficient for catalyst particle	10.3
k_t	Termination rate constant	12.21
k_{XX}	Propagation rate constant for X–X homopolymerization	12.28
k_{XY}	Propagation rate constant for X–Y copolymerization	12.28
k_{YX}	Propagation rate constant for Y–X copolymerization	12.28
k_{YY}	Propagation rate constant for Y–Y homopolymerization	12.28
K	Equilibrium constant	4.69
K_{I}, K_{II}	Equilibrium constants for Reactions I and II	10.72
K_a	Adsorption equilibrium constant	10.34
K_d	Desorption equilibrium constant	10.31
K_{equil}	Equilibrium constant	1.16
K_P	Reciprocal desorption constant	10.38
$K_{\mathscr{R}}$	Equilibrium constant for surface reaction	10.30
l	Denotes liquid phase	11.1
ℓ	Distance down a pore	10.46
ℓ	Chain length	12.50
$\bar{\ell}$, $\bar{\ell}_n$	Number-average chain length	12.52
$\bar{\ell}_w$	Weight-average chain length	12.55
L	Length of tubular reactor	1.71
$\mathscr{L}$	Length of a pore	10.46
m	Constant in Arrhenius temperature dependence	4.1
m	Concentration of monoalkylate	11.15
m	Number of monomer units	12.2
m_{A}, m_{B}	Molecular masses, kg/molecule, of components A, B	1.9
$M\cdot$	Denotes free radical of monomer	12.1
$\bar{M}_n$	Number-average molecular weight	12.56

M_w	Weight-average molecular weight	12.56
M_{A}	Molecular weight of component A	3.22, 5.1
M_{B}	Molecular weight of component B	3.22, 5.1
n	Concentration of dialkylate	11.16
n	Index of summation	3.82
n	Order of moment	9.29
n	Order of reaction	2.15, 9.92
n	Number of monomer units	12.1
N	Number of sitrred tanks in series	3.82, 9.46
N	Number of piston flow reactors in parallel	12.85
$\mathbf{N}$	Vector of moles present	2.78
$\mathbf{N}_0$	Vector of moles present initially	2.78
$N_{\mathrm{A}}, N_{\mathrm{B}}$	Number of moles of components A and B	1.51
$(N_{\mathrm{A}})_0, (N_{\mathrm{B}})_0$	Number of moles of components A and B initially	1.51
p	Concentration of component P	2.12
p_0	Initial concentration of monomer	12.61
p_n	Concentration of polymer of length n	12.45, 12.61
P	Subscript denoting component P	2.12
P	Pressure	2.63
Pe	Peclet number	7.10
P_e	Peclet number for emulsion phase	11.75
P_{in}	Pressure at reactor inlet	3.66
P_j	Pressure at point j	3.20
P_ℓ	Denotes polymer molecule of length ℓ	12.42
P_n	Denotes polymer molecule of length n	12.1
P_{out}	Pressure at reactor outlet	3.66
$P_{\mathscr{R}}$	Reaction probability	9.64
$\overline{P}_{\mathscr{R}}$	Average reaction probability	9.65
q	Flow rate in recycle loop	3.85
q	Fractional flow rate in parallel reactors	9.50
q	Concentration of component Q	10.40
Q	Subscript denoting species Q	10.40
Q	Volumetric flow rate	1.65
Q_1, Q_2	Flow rates of reactors in parallel	3.75
Q_{b}	Volumetric flow rate in bubble phase	11.79
Q_{e}	Volumetric flow rate in emulsion phase	11.79
Q_g	Volumetric flow rate in gas phase	11.6
Q_{in}	Inlet flow rate	1.3
Q_l	Volumetric flow rate in liquid phase	11.5
Q_{out}	Outlet flow rate	1.3
Q_{slug}	Flow rate at which slugging occurs	11.81
r	Radial coordinate	6.2
r_p	Radial coordinate within a catalyst particle	10.58
$r_{\mathrm{X}}, r_{\mathrm{Y}}$	Copolymer reactivity ratios	12.31
$\mathscr{r}$	Dimensionless radial coordinate	6.14

R	Radius of tube	3.11, 6.1
Re	Reynolds number	3.13
R_g	Gas law constant	1.9, 4.1
$\boldsymbol{\mathscr{R}}$	Vector of reaction rates	2.74
$\mathscr{R}$	Reaction rate	1.14
$\mathscr{R}_{\mathrm{I}}, \mathscr{R}_{\mathrm{II}}$	Reaction rate for Reactions I, II	1.21, 1.22
$\mathscr{R}_{\mathrm{A}}$	Rate of formation of component A	1.5
$\hat{\mathscr{R}}_{\mathrm{A}}$	Spatial average formation rate of component A	1.5
$\mathscr{R}_{\mathrm{B}}$	Rate of formation of component B	2.9
$R_n \cdot$	Denotes free radical of length n	12.21
$\mathscr{R}_{\mathrm{X}}, \mathscr{R}_{\mathrm{Y}}$	Rate of formation of components X, Y	12.28
s	Dimensionless transform parameter	7.11, 12.67
$s_{\mathrm{I}}, s_{\mathrm{II}}$	Roots of quadratic equation	2.22
ss	Subscript denoting steady state operation	Figure 8.3
$\mathscr{S}$	Source term in energy equation	7.26
S	Denotes a surface site	10.6
S	Denotes a special constraint	4.79
S_0	Concentration of surface sites	10.22
S_2	Sum of squares	4.91
S_{AB}	Stoichiometric ratio	12.5
Sc	Schmidt number	Figure 7.1
t	Residence time	1.30, 9.3
$\bar{t}$	Mean residence time	1.70, 9.30
$\bar{t}_1, \bar{t}_2$	Mean residence times in subsystems	3.73, 9.51
t_b	Residence times in segregated flow model	9.81
t_c	Contact time	10.13
$\bar{t}_e$	Mean residence time in emulsion phase	11.75
$\bar{t}_g$	Mean residence time in gas phase	
$\bar{t}_l$	Mean residence time in liquid phase	11.33
t_n	Residence time in segregated flow element	12.85
$\bar{t}_s$	Mean residence time based on superficial velocity	7.56
T	Temperature	4.1
$T(0+)$	Temperature immediately after reactor inlet	7.28
$\hat{T}$	Spatial average temperature	4.16
T_{ext}	Temperature of external environment	4.23, 7.27
T_{in}	Inlet temperature	7.36
T_{out}	Outlet temperature	4.20, 8.33
T_s	External surface temperature	Section 10.3.3
T_{wall}	Wall temperature of tubular reactor	7.50
$\bar{u}$	Mean axial velocity in tubular reactor	1.66
u_0	Axial velocity at centerline	6.67
u_{b}	Axial velocity of bubble phase	11.74
u_{e}	Axial velocity of emulsion phase	11.73
$\bar{u}_{\mathrm{g}}$	Mean axial velocity of gas phase	11.46

$\bar{u}_l$	Mean axial velocity of liquid phase	11.45
$u_{\max}$	Axial velocity at centerline	6.6
$\bar{u}_s$	Superficial velocity in a packed bed	3.14, 7.43
U	Overall heat transfer coefficient	4.17, 7.27
$\hat{U}$	Average heat transfer coefficient	4.12
U_m	Overall mass transfer coefficient	11.4, 11.73
v_0	Axial velocity at centerline	12.76
v_z	Axial component of velocity	6.2, 12.68
v_r	Radial component of velocity	6.76
V	Volume of reactor	1.3
$\mathbf{V}$	Velocity vector	7.1
V_g	Volume of gas phase	11.6
V_l	Volume of liquid phase	11.5
V_0	Initial volume of reactor	4.60
V_t	Volume of reactor at time t	4.60
W	Washout function	9.3
W_b	Washout function for segregated ball model	9.8
x	Denotes concentration of comonomer X	12.28
x	Variable	3.49
x_{p}	Mole fraction of component X in polymer	12.29
X	Denotes comonomer X	12.27
X	Conversion	12.57
X_{A}	Conversion of component A	1.38, 12.6
X_{B}	Conversion of component B	Figure 12.1
$X_n\cdot$	Denotes an X-terminated radical of length n	12.27
y	Denotes concentration of comonomer Y	12.28
y	Variable	3.49
y_{p}	Mole fraction of component Y in polymer	12.29
Y	Denotes comonomer Y	12.27
$\mathrm{Y}_n\cdot$	Denotes a Y-terminated radical of length n	12.27
z	Axial coordinate	1.65, 6.13
z	Dimensionless axial coordinate	6.14

Greek Symbols

α	Exponent in rate equation	4.53, 10.41
α	Age in a reactor	1.31, 1.57
α_T	Thermal diffusivity	6.19
β	Exponent in rate equation	4.53, 10.41
β	Chain length dependence of reaction rate	12.61
γ	Exponent in rate equation	10.41
γ	Constant used to take numerical partial derivative	3.97
δ	Film thickness	Figure 10.1, 11.63