

**Transport  
Phenomena  
for Chemical  
Reactor Design**

*Laurence A. Belfiore*

**TRANSPORT  
PHENOMENA  
FOR CHEMICAL  
REACTOR DESIGN**

# TRANSPORT PHENOMENA FOR CHEMICAL REACTOR DESIGN

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**Laurence A. Belfiore**

Department of Chemical Engineering  
Colorado State University  
Fort Collins, CO



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*This book is dedicated to Alphonse and all the women in my life: Olivia, Carol, Lorraine, Jenny, Sarah, and Sally. Buddy and Pookie were also inspirational. It is an environmentally friendly book because all proceeds will be used to support motorless motion in Colorado's clean air above 10,000 feet, particularly the ascent of Mount Evans at 14,260 feet from Bergen Park (i.e., the highest paved road on the planet), which, along with col de la Bonette at 2830 meters northwest of St. Etienne de Tinee and southeast of Barcelonnette (i.e., the highest paved road in Europe), is one of the most awesome bike rides on the planet.*

# CONTENTS

<b>PREFACE</b>	<b>xix</b>
<b>PART I ELEMENTARY TOPICS IN CHEMICAL REACTOR DESIGN</b>	<b>1</b>
<b>1 Multiple Chemical Reactions in Plug Flow Tubular Reactors and Continuous Stirred Tank Reactors</b>	<b>3</b>
1-1 Gas-Phase Plug-Flow Tubular Reactors That Produce Triethanolamine from Ethylene Oxide and Ammonia,	3
1-2 Multiple Chemical Reactions in a Liquid-Phase CSTR,	11
1-3 Multiple Chemical Reactions in a CSTR Train, Problems,	19 26
<b>2 Start Up Behavior of a Series Configuration of Continuous Stirred Tank Reactors</b>	<b>33</b>
2-1 Analysis of Multiple Reactions in Two CSTRs: Illustrative Problem,	34
2-2 Analysis of a Train of Five CSTRs: Illustrative Problem, Problems,	38 46

<b>3</b>	<b>Adiabatic Plug-Flow Tubular Reactor That Produces Methanol Reversibly in the Gas Phase from Carbon Monoxide and Hydrogen</b>	<b>47</b>
3-1	Temperature-Averaged Specific Heats,	48
3-2	Conversion Dependence of Mass Fraction and Heat Capacity of the Mixture,	50
3-3	Plug-Flow Mass Balance in Terms of CO Conversion,	51
3-4	Thermal Energy Balance for a Differential Reactor,	52
3-5	Thermodynamics of Multicomponent Mixtures,	53
3-6	Coupled Heat and Mass Transfer,	55
3-7	Kinetics and Thermodynamics of Elementary Reversible Reactions in the Gas Phase,	56
3-8	Integration of the Nonisothermal PFR Design Equation,	60
	Problems,	62
<b>4</b>	<b>Coupled Heat and Mass Transfer in Nonisothermal Liquid-Phase Tubular Reactors with Strongly Exothermic Chemical Reactions</b>	<b>65</b>
4-1	Strategies to Control Thermal Runaway,	65
4-2	Parametric Sensitivity Analysis,	83
4-3	Endothermic Reactions in a Cocurrent Cooling Fluid,	87
4-4	Countercurrent Cooling in Tubular Reactors with Exothermic Chemical Reactions,	95
4-5	Manipulating the Inlet/Outlet Temperature of a Countercurrent Cooling Fluid: Multiple Stationary-State Behavior in Exothermic PFRs,	97
	Problems,	104
<b>5</b>	<b>Multiple Stationary States in Continuous Stirred Tank Reactors</b>	<b>105</b>
5-1	Mass Balance,	106
5-2	Chemical Kinetics,	106
5-3	Thermal Energy Balance,	107
5-4	Multiple Stationary States,	110

5-5	Endothermic Chemical Reactions,	115
	Problems,	117
<b>6</b>	<b>Coupled Heat and Mass Transfer with Chemical Reaction in Batch Reactors</b>	<b>123</b>
6-1	Isothermal Analysis of Experimental Rate Data,	123
6-2	Formalism for Multiple Reactions,	129
6-3	Adiabatic Operation,	130
6-4	Nonisothermal Analysis of a Constant-Volume Batch Reactor,	131
	Problems,	136
<b>7</b>	<b>Total Pressure Method of Reaction-Rate Data Analysis</b>	<b>139</b>
7-1	Elementary Reversible Gas-Phase Reactions in a Constant-Volume Flask,	139
7-2	Generalized Linear Least-Squares Analysis for a Second-Order Polynomial with One Independent Variable,	142
	Problems,	145
<b>PART II</b>	<b>TRANSPORT PHENOMENA: FUNDAMENTALS AND APPLICATIONS</b>	<b>153</b>
<b>8</b>	<b>Applications of the Equations of Change in Fluid Dynamics</b>	<b>155</b>
8-1	Important Variables,	155
8-2	Physical Properties in Fluid Dynamics,	156
8-3	Fundamental Balance in Momentum Transport,	158
8-4	Equation of Motion,	167
8-5	Exact Differentials,	173
8-6	Low-Reynolds-Number Hydrodynamics,	175
8-7	Potential Flow Theory,	205
	Problems,	222
<b>9</b>	<b>Derivation of the Mass Transfer Equation</b>	<b>253</b>
9-1	Accumulation Rate Process,	253
9-2	Rate Processes Due to Mass Flux Across the Surface That Bounds the Control Volume,	254



9-3	Rate Processes Due to Multiple Chemical Reactions,	255
9-4	Constructing Integral and Microscopic Descriptions of the Mass Transfer Equation,	256
9-5	Diffusional Fluxes in Multicomponent Mixtures,	257
9-6	Diffusional Fluxes and Linear Transport Laws in Binary and Pseudo-Binary Mixtures,	260
9-7	Simplification of the Mass Transfer Equation for Pseudo-Binary Incompressible Mixtures with Constant Physical Properties,	261
<b>10</b>	<b>Dimensional Analysis of the Mass Transfer Equation</b>	<b>265</b>
10-1	Dimensional Scaling Factors for the Mass Transfer Rate Processes,	265
10-2	Dimensionless Form of the Generalized Mass Transfer Equation with Unsteady-State Convection, Diffusion, and Chemical Reaction,	266
10-3	Functional Dependence of the Molar Density of Species $i$ Via Dimensional Analysis,	269
10-4	Maximum Number of Dimensionless Groups That Can Be Calculated for a Generic Mass Transfer Problem,	271
	Problems,	272
<b>11</b>	<b>Laminar Boundary Layer Mass Transfer around Solid Spheres, Gas Bubbles, and Other Submerged Objects</b>	<b>275</b>
11-1	Boundary Layer Mass Transfer Analysis,	275
11-2	Tangential Velocity Component $v_\theta$ Within the Mass Transfer Boundary Layer,	284
11-3	Boundary Layer Solution of the Mass Transfer Equation,	287
11-4	Interphase Mass Transfer at the Solid–Liquid Interface,	298
11-5	Laminar Boundary Layer Mass Transfer Across a Spherical Gas–Liquid Interface,	303
11-6	Boundary Layer Solution of the Mass Transfer Equation Around a Gas Bubble,	306

11-7	Interphase Mass Transfer at the Gas–Liquid Interface, 313	
	Problems, 328	
<b>12</b>	<b>Dimensional Analysis of the Equations of Change for Fluid Dynamics Within the Mass Transfer Boundary Layer</b>	<b>361</b>
12-1	Generalized Dimensionless Form of the Equation of Motion for Incompressible Fluids Undergoing Laminar Flow, 362	
12-2	Incompressible Newtonian Fluids in the Creeping Flow Regime, 362	
12-3	Locally Flat Momentum Boundary Layer Problem for Laminar Flow Around Solid Spheres, 363	
12-4	Renormalization of the Dimensionless Variables Reveals Explicit Dependence of $g^*$ on $Re$ , 365	
<b>13</b>	<b>Diffusion and Chemical Reaction Across Spherical Gas–Liquid Interfaces</b>	<b>369</b>
13-1	Molar Density Profile, 369	
13-2	Molar Flux Analysis, 372	
<b>PART III</b>	<b>KINETICS AND ELEMENTARY SURFACE SCIENCE</b>	<b>381</b>
<b>14</b>	<b>Kinetic Mechanisms and Rate Expressions for Heterogeneous Surface-Catalyzed Chemical Reactions</b>	<b>383</b>
14-1	Converting Reactants to Products, 383	
14-2	Isotherms, 384	
14-3	Single-Site Adsorption of Each Component in a Multicomponent Mixture, 392	
14-4	Dual-Site Adsorption of Submolecular Fragments, 394	
14-5	Summary of Adsorption Isotherms for Pure Gases, 397	
14-6	Hougen–Watson Kinetic Models, 399	
14-7	Pressure Dependence of the Kinetic Rate Constant Via Elements of Transition State Theory, 420	
14-8	Interpretation of Heterogeneous Kinetic Rate Data Via Hougen–Watson Models, 424	
	Problems, 428	

<b>PART IV</b>	<b>MASS TRANSFER AND CHEMICAL REACTION IN ISOTHERMAL CATALYTIC PELLETS</b>	<b>447</b>
<b>15</b>	<b>Diffusion and Heterogeneous Chemical Reaction in Isothermal Catalytic Pellets</b>	<b>449</b>
15-1	Complex Problem Descriptions Without Invoking Any Assumptions, 449	
15-2	Diffusion and Pseudo-Homogeneous Chemical Reactions in Isothermal Catalytic Pellets, 452	
15-3	Pseudo-First-Order Kinetic Rate Expressions That Can Replace Hougen–Watson Models and Generate Linearized Ordinary Differential Equations for the Mass Balance, 453	
15-4	Diffusion and Heterogeneous Chemical Reactions in Isothermal Catalytic Pellets, 458	
	Problem, 459	
<b>16</b>	<b>Complete Analytical Solutions for Diffusion and Zeroth-Order Chemical Reactions in Isothermal Catalytic Pellets</b>	<b>461</b>
16-1	Catalytic Pellets with Rectangular Symmetry, 461	
16-2	Long, Cylindrically Shaped Catalysts, 464	
16-3	Spherical Pellets, 466	
16-4	Redefining the Intrapellet Damkohler Number So That Its Critical Value Might Be the Same for All Pellet Geometries, 468	
	Problems, 470	
<b>17</b>	<b>Complete Analytical Solutions for Diffusion and First-Order Chemical Reactions in Isothermal Catalytic Pellets</b>	<b>473</b>
17-1	Catalytic Pellets with Rectangular Symmetry, 473	
17-2	Long, Cylindrically Shaped Catalysts, 475	
17-3	Spherical Pellets, 476	
	Problems, 480	
<b>18</b>	<b>Numerical Solutions for Diffusion and <math>n</math>th-Order Chemical Reactions in Isothermal Catalytic Pellets</b>	<b>483</b>
18-1	Kinetic Rate Law and Diffusional Flux, 483	

18-2	Mass Transfer Equation in Three Coordinate Systems, 484	
18-3	Numerical Results for Second-Order Irreversible Chemical Kinetics, 487	
18-4	Equivalent Examples with Different Characteristic Length Scales, 488	
<b>19</b>	<b>Numerical Solutions for Diffusion and Hougen–Watson Chemical Kinetics in Isothermal Catalytic Pellets</b>	<b>491</b>
19-1	Dimensionless Kinetic Rate Law, 491	
19-2	Mass Balance for Reactant A, 493	
19-3	Dimensionless Correlation for the Effectiveness Factor in Terms of the Intrapellet Damkohler Number, 497	
19-4	Dimensionless Correlation for Porous Wafers with Rectangular Symmetry, 500	
19-5	Numerical Results for $A_2 + B \rightarrow C + D$ in Flat-Slab Wafers with Rectangular Symmetry, 501	
	Problems, 505	
<b>20</b>	<b>Internal Mass Transfer Limitations in Isothermal Catalytic Pellets</b>	<b>509</b>
20-1	Reactor Design Strategy, 509	
20-2	Correlations for Catalysts with Different Macroscopic Symmetry, 512	
20-3	Effectiveness Factors, 515	
20-4	Dimensionless Correlation between the Effectiveness Factor and the Intrapellet Damkohler Number, 521	
	Problems, 527	
<b>21</b>	<b>Diffusion Coefficients and Damkohler Numbers Within the Internal Pores of Catalytic Pellets</b>	<b>539</b>
21-1	Dependence of Intrapellet Pore Diffusion on Molecular Size, 539	
21-2	Knudsen Diffusion in Straight Cylindrical Pores, 543	
21-3	Ordinary Molecular Diffusion in Binary and Pseudo-Binary Mixtures, 544	
21-4	Estimating Tortuosity Factors and Intrapellet Porosity Based on the Distribution in Orientation and Size of Catalytic Pores Via the Parallel-Pore Model, 553	
	Problems, 558	

<b>PART V</b>	<b>ISOTHERMAL CHEMICAL REACTOR DESIGN</b>	<b>561</b>
<b>22</b>	<b>Isothermal Design of Heterogeneous Packed Catalytic Reactors</b>	<b>563</b>
22-1	Simplification of the Generalized Mass Transfer Equation for a One-Dimensional Plug Flow Model,	564
22-2	Differential Form of the Design Equation for Ideal Packed Catalytic Tubular Reactors Without Interpellet Axial Dispersion,	567
22-3	Design of a Packed Catalytic Tubular Reactor for the Production of Methanol from Carbon Monoxide and Hydrogen,	573
22-4	Design of Non-Ideal Heterogeneous Packed Catalytic Reactors with Interpellet Axial Dispersion,	579
22-5	Mass Transfer Peclet Numbers Based on Interpellet Axial Dispersion in Packed Catalytic Tubular Reactors,	592
22-6	Applications to a Packed Chromatographic or Ion-Exchange Column,	596
22-7	Factors That Must Be Considered in the Design of a Packed Catalytic Tubular Reactor,	597
	Problems,	601
<b>23</b>	<b>Heterogeneous Catalytic Reactors with Metal Catalyst Coated on the Inner Walls of the Flow Channels</b>	<b>611</b>
23-1	Convective Diffusion in Catalytic Reactors of Noncircular Cross Section and Nonuniform Catalyst Activity,	611
23-2	Fully Developed Fluid Velocity Profiles in Regular Polygon Ducts,	614
23-3	Mass Transfer Equation,	619
23-4	Details of the Numerical Algorithm,	624
23-5	Second-Order Correct Finite-Difference Expressions for First Derivatives on the Boundary of the Flow Cross Section,	627
23-6	Viscous Flow,	632
	Problems,	645
<b>24</b>	<b>Designing a Multicomponent Isothermal Gas–Liquid CSTR for the Chlorination of Benzene to Produce Monochlorobenzene</b>	<b>655</b>
24-1	Strategy to Solve This Problem,	656

24-2	Gas-Phase Mass Balances with Interphase Mass Transfer,	658
24-3	Liquid-Phase Mass Balances with Chemical Reaction, Interphase Transport, and Reaction-Enhanced Mass Transfer Coefficients,	659
24-4	Interfacial Equilibrium and Equality of Interfacial Fluxes,	665
24-5	Molecular Diffusion in Liquids,	671
24-6	Nonlinear Equation Solver Program,	673
	Problems,	681
<b>PART VI THERMODYNAMICS AND NONISOTHERMAL REACTOR DESIGN</b>		<b>685</b>
<b>25</b>	<b>Classical Irreversible Thermodynamics of Multicomponent Mixtures</b>	<b>687</b>
25-1	Strategy to Analyze Nonequilibrium Systems,	688
25-2	Microscopic Equation of Change for Kinetic Energy,	689
25-3	Re-Expressed Equation of Change for Kinetic Energy,	690
25-4	Microscopic Equation of Change for Internal Energy Via the First Law of Thermodynamics,	692
25-5	Microscopic Equation of Change for Total Energy,	693
25-6	Identification of the Molecular Flux of Thermal Energy in the Equation of Change for Total Energy,	695
25-7	Equation of Change for Entropy,	696
25-8	Rate of Entropy Production in Multicomponent Systems with Chemical Reaction,	697
25-9	Linear Relations Between Fluxes and Forces That Obey the Curie Restriction,	701
25-10	Coupling Between Diffusional Mass Flux and Molecular Flux of Thermal Energy in Binary Mixtures: The Onsager Reciprocal Relations,	703
25-11	Identification of Fourier's Law in the Molecular Flux of Thermal Energy and the Requirement That Thermal Conductivities Are Positive,	705

25-12	Complete Expression for the Diffusional Mass Flux of Component A in a Binary Mixture,	706
25-13	Thermodynamic Evaluation of $(\partial\varphi_A/\partial\omega_A)_{T,p}$ in Binary Mixtures,	708
25-14	Connection between Transport Phenomena and Thermodynamics for Diffusional Mass Fluxes and Diffusivities in Binary Mixtures,	709
25-15	Liquid-Phase Diffusivities and the Stokes–Einstein Diffusion Equation for Binary Mixtures,	710
	Problems,	712
<b>26</b>	<b>Molecular Flux of Thermal Energy in Binary and Multicomponent Mixtures Via the Formalism of Nonequilibrium Thermodynamics</b>	<b>717</b>
26-1	Three Contributions to $\mathbf{q}$ in Binary Systems,	717
26-2	Thermodynamic Analysis of $\varphi_A - T(\partial\varphi_A/\partial T)_{p,\omega_A}$ ,	719
26-3	Analysis of the Interdiffusional Flux of Thermal Energy in Binary Mixtures and Generalization to Multicomponent Mixtures,	723
	Problems,	724
<b>27</b>	<b>Thermal Energy Balance in Multicomponent Mixtures and Nonisothermal Effectiveness Factors Via Coupled Heat and Mass Transfer in Porous Catalysts</b>	<b>727</b>
27-1	Equation of Change for Specific Internal Energy That Satisfies the First Law of Thermodynamics,	727
27-2	Multicomponent Transport in Porous Catalysts,	731
27-3	Nonisothermal Effectiveness Factors in Porous Catalysts,	733
27-4	Physicochemical Properties of Gases Within Catalytic Pellets,	737
27-5	Estimates of the Maximum Temperature Rise Within Catalytic Pellets for Exothermic Chemical Reactions,	740
27-6	Design of a Nonisothermal Packed Catalytic Tubular Reactor,	745
	Problems,	748

<b>28</b>	<b>Statistical Thermodynamics of Ideal Gases</b>	<b>757</b>
28-1	Generalized Postulates, 757	
28-2	Introduction to Quantum Statistical Mechanics, 758	
28-3	The Ergodic Problem, 760	
28-4	$\mathcal{H}$ Theorem of Statistical Thermodynamics, 761	
28-5	Consistency with Classical Thermodynamics, 763	
28-6	Internal Energy and Heat Capacity of Monatomic Ideal Gases, 768	
28-7	Diatomic Gases, 768	
28-8	Entropy and Chemical Potential, 776	
	Problems, 780	
<b>29</b>	<b>Thermodynamic Stability Criteria for Single-Phase Homogeneous Mixtures</b>	<b>785</b>
29-1	Energy Representation of the Fundamental Equation and Exact Differentials, 785	
29-2	Legendre Transformations, 787	
29-3	Euler's Integral Theorem for Homogeneous Functions of Order $m$ , 790	
29-4	Gibbs–Duhem Equation, 794	
29-5	Analysis of Partial Derivatives Via Jacobian Transformations, 795	
29-6	Thermodynamic Stability Relations, 798	
<b>30</b>	<b>Coupled Heat and Mass Transfer in Packed Catalytic Tubular Reactors That Account for External Transport Limitations</b>	<b>821</b>
30-1	Intrapellet and Bulk Species Concentrations, 823	
30-2	Intrapellet and Bulk Gas Temperature, 825	
30-3	Evaluation of $C_{A, \text{surface}}$ Via the Effectiveness Factor: Complete Strategy for Packed Catalytic Tubular Reactors, 830	
30-4	Reactor Design, 835	
30-5	Maximum Conversion in Non-Ideal Packed Catalytic Tubular Reactors Under Isothermal Conditions, 842	



30-6	Analysis of First-Order Irreversible Chemical Kinetics in Ideal Packed Catalytic Tubular Reactors When The External Resistances to Heat and Mass Transfer Cannot Be Neglected,	845
	Problems,	852
	References	<b>861</b>
	Index	<b>865</b>

# PREFACE

In this book, the design of chemical reactors is approached from microscopic heat and mass transfer principles. The content is influenced heavily by my training at Stevens Institute of Technology, Yale University, and the University of Wisconsin. Several ideas presented herein crystallized out of thin air, just like snowflakes, in the Colorado high country above 10,000 feet, where phones, faxes, e-mail, junk mail, and all other media disturbances were nonexistent. A few problems were synthesized in les hautes Alpes, where the ascent of any premiere col with  $42 \times 24$  low gearing is a test of strength and perseverance. Isothermal design strategies begin with the microscopic mass transfer equation, and assumptions are invoked until a one-dimensional mass balance can be integrated to produce macroscopic results. We focus on packed catalytic tubular reactors in which reactant gases must diffuse into the pores of the pellets and adsorb on active catalytic sites before chemical reaction occurs. Hence, Langmuir adsorption isotherms, Langmuir–Hinshelwood mechanisms, and Hougen–Watson kinetic rate expressions are employed to design heterogeneous catalytic reactors. Once the kinetics are understood and rate laws can be generated, isolated catalytic pellets are analyzed in terms of pseudo-homogeneous models with diffusion and chemical reaction. This section of the book treats zeroth-order, first-order,  $n$ th-order, and Hougen–Watson chemical kinetics with the overall goal of generating dimensionless correlations between the effectiveness factor and the intrapellet Damkohler number. Quantitative methods are described to estimate effective intrapellet diffusivities as well as axial dispersion coefficients in packed beds. Effective intrapellet diffusion coefficients appear in the denominator of the intrapellet Damkohler number, and axial dispersion coefficients are required to calculate the mass transfer Peclet number and the interpellet Damkohler number when convection, axial dispersion, and chemical reaction are operative in non-ideal packed catalytic

tubular reactors. Nonisothermal effects in isolated pellets are addressed within the framework of classical irreversible thermodynamics. The complete expression for the molecular flux of thermal energy in multicomponent systems, excluding the Dufour effect, is used to predict intrapellet temperature profiles that are coupled to reactant concentration profiles within the catalyst. Complete details are provided to calculate nonisothermal effectiveness factors, and examples are discussed which illustrate key dimensionless parameters that exhibit strong influence on the effectiveness factor. The complete design of a heterogeneous catalytic tubular reactor combines all the previous information when nonisothermal effects are important and the external resistances to heat and mass transfer cannot be neglected. Convective diffusion in regular polygon channels with expensive metal catalyst coated on the inner walls of the flow channel is described and compared with packed reactors. Optimal catalyst deposition strategies are incorporated into a three-dimensional mass transfer model.

In an attempt to broaden the scope of the book, several examples of heat and mass transfer with multiple chemical reactions in continuous stirred tanks and plug-flow reactors, including start up behavior, adiabatic operation, and gas-liquid dispersed systems, are discussed primarily in the introductory section (i.e., Part I). Novel examples of multiple stationary states in exothermic tubular reactors with countercurrent cooling are presented quantitatively and compared with similar phenomena in continuous-stirred tanks. Thermal energy effects in batch reactors are also discussed. Most problems and examples require numerical methods to obtain quantitative results. The appropriate software is employed to solve coupled ordinary differential equations, in some cases with split boundary conditions, and results are presented graphically or in tabular form. Various segments of this book can be incorporated into several chemical engineering courses at both the graduate and undergraduate levels. Complementary topics in transport phenomena and thermodynamics that provide support for chemical reactor analysis are included for completeness. These are (1) fluid dynamics in the creeping and potential flow regimes around solid spheres and gas bubbles, (2) the corresponding mass transfer problems that employ velocity profiles derived in the fluid dynamics section to calculate interphase heat and mass transfer coefficients, (3) heat capacities of ideal gases via statistical thermodynamics to calculate Prandtl numbers, and (4) thermodynamic stability criteria for homogeneous mixtures which reveal that binary molecular diffusion coefficients must be positive. Topics 1 and 2 are based on information from Professor Ed Lightfoot's intermediate transport phenomena course at the University of Wisconsin. Complementary topic 3 was extracted from a statistical mechanics course in the chemistry department at Wisconsin taught by Professor Charles F. Curtiss, and the information in topic 4 was presented by Professor Curtiss in a chemical thermodynamics course. The primary use of the entire treatise follows a complete year of graduate courses in transport phenomena and chemical reactor design. In this mode, Part I works well as a review of the required undergraduate reactor design course, and topics 1 through 4, described briefly above, provide useful information that complements the main focus of this book.

There are a few instructors from my undergraduate and graduate education that I must thank personally, because they introduced me to the topics discussed in this book and provided me with the tools to address these issues. Professor George B. DeLancey at Stevens Institute of Technology presented most of the material in the introductory review section when I was a senior in his chemical reactor design course in 1975. These problems were intriguing, with practical implications, and they required numerical analysis via Newton–Raphson root finding or Runge–Kutta–Gill integration of coupled ordinary differential equations. In 1975, it was necessary to write Fortran code on punchcards or at remote teletypes to obtain numerical solutions. Most of these problems in the introductory section have been modified and reworked via Engineering Equation Solver or Polymath. One of the most versatile problems discussed by Professor DeLancey was the chlorination of benzene in a gas–liquid continuous-stirred tank. This material is presented in Chapter 24. These results can be used to analyze the effect of interphase mass transfer on the design of a gas–liquid CSTR. Without algebraic equation solvers, Professor DeLancey presented an elaborate substitution approach which involved nonlinear analysis due to second-order irreversible chemical reaction between benzene and dissolved chlorine in the liquid phase. More recently, the solution is obtained with much less tedium via nonlinear algebraic equation solvers. The solution to the first review problem on multiple chemical reactions in gas-phase plug-flow tubular reactors in Chapter 1 was developed in its entirety by undergraduate student Terrence Pikul at Colorado State University during the 2.5-hour chemical reactor final exam in December 1994. While I was grading Terrence’s exam, it was immediately obvious that his solution was much better than mine. So I swallowed my ego, gave him 10 or 20 points extra credit, and adopted his approach. At the University of Wisconsin, Professor Bob Bird presented Laplace transform and matrix analyses of the start up behavior of a CSTR train with first-order irreversible chemical reaction in a 1977 fall semester course offering of mathematical methods in chemical engineering. This review problem has been extended to multiple chemical reactions in Chapter 2, and it also appeared on a reactor design final exam at Colorado State University. Professor Stuart W. Churchill at the University of Pennsylvania is acknowledged for reviewing the multiple-stationary-states introductory problem in plug-flow tubular reactors with countercurrent cooling. Professor Churchill convinced me that, indeed, multiple steady states are possible in tubular reactors.

Professor Stanley H. Langer’s personal notes on Langmuir adsorption, Langmuir–Hinshelwood mechanisms, and Hougen–Watson kinetic models were extremely helpful. I obtained this information from a 1976 fall semester graduate course on kinetics and catalysis at the University of Wisconsin. In a 1978 spring semester graduate course offering of physicochemical hydrodynamics presented by Professor Bird, I learned the fundamentals of irreversible thermodynamics in binary mixtures with chemical reaction. After extending this information to multicomponent mixtures, I employed the results to analyze nonisothermal effectiveness factors via the complete expression for the molecular flux of thermal

energy, which includes Fourier's law, the Dufour effect (this was neglected), and the interdiffusional flux. Laurent Simon, a graduate student in advanced mass transfer at Colorado State, is acknowledged for checking some of my numerical results on this topic, which require the solution of three coupled first-order ordinary differential equations with split boundary conditions. Professor Lightfoot is acknowledged for introducing me to boundary layer heat and mass transfer around solid spheres and gas bubbles in a 1976 graduate course in intermediate transport phenomena. This information provides the general scaling behavior of Nusselt and Sherwood numbers in terms of the Reynolds and Prandtl or Schmidt numbers when the thermal and concentration boundary layers are thin. Heat and mass transfer coefficients based on these correlations are used to estimate external transport resistances between catalytic pellets and the bulk fluid phase moving through a packed catalytic tubular reactor. Correlations for flow around gas bubbles are employed to estimate the magnitude of mass transfer coefficients in gas-liquid dispersed systems for the chlorination of benzene in Chapter 24.

In the summers of 1975 and 1976, I participated in an undergraduate research program at Yale University hosted by its Department of Engineering and Applied Science. Professor Daniel E. Rosner of Yale's Chemical Engineering Department chose me to work on a simulation-based project focusing on convection, diffusion, and heterogeneous chemical reaction in flow channels with noncircular cross section and metal catalyst coated on the inner walls. This "tube-wall" reactor problem is described in detail in Chapter 23. I used some of the methodology presented by Professor DeLancey for tray-by-tray calculations in multicomponent distillation columns and employed the Thomas algorithm to solve a partial differential mass balance using linear algebraic finite-difference equations characterized by a tridiagonal coefficient matrix. When the flow cross section is annular, the inner cylindrical wall is catalytically active, and the outer wall is inert, numerical simulations were performed in parallel with nitrogen atom recombination experiments on a metal wire. The overall objective of this research was to understand thermal energy transfer to the heat shield of the Space Shuttle upon re-entry into the Earth's atmosphere. Most of the numerical results in Chapter 23 were extracted from the 1988 M.S. thesis of Seong Young Lee at Colorado State University, entitled "Convective Diffusion in Heterogeneous Catalytic Reactors with Rectangular Cross Section and Nonuniform Catalyst Activity."

Diffusion and zeroth-order chemical reaction in porous catalysts are presented in detail for pellets with rectangular, cylindrical, and spherical symmetry. These effectiveness factor problems represent a logical extension of Section 18.7 in Bird, Stewart, and Lightfoot's *Transport Phenomena*, Second Edition (pp. 563–567). However, with no guiding light, I stumbled several times before correcting all of my mistakes. I must acknowledge Mark Heinrich, a student in graduate reactor design at Colorado State during the spring of 1994, for informing me that my initial approach to diffusion and zeroth-order chemical reaction produced effectiveness factor vs. intrapellet Damkohler number, correlations that intersected curves for other reaction orders instead of defining the asymptotes at large and small Damkohler numbers. Then Brandon Vail, a senior in transport phenomena at Colorado State during the

spring of 1997, refined my definition of the critical spatial coordinate in porous catalysts below which reactants do not penetrate when the intrapellet Damkohler number is larger than its critical value. This crutch is required for zeroth-order kinetics because there is no automatic method of “turning off” the rate of reactant consumption when the central core of the catalyst is starved of reactants. Zeroth-order chemical kinetics generate mathematically simple problem definitions, but these problems are conceptually challenging. Diffusion and Hougen–Watson chemical kinetics posed another stumbling block because the rate law contains molar densities of several reactants and products, and I couldn’t relate all of these molar densities within the pores of the catalyst. Coupled solution of several second-order ODEs with split boundary conditions was not the preferred approach because trial and error was required for each ODE via the “shooting” method. Hence, a modification of stoichiometry and the steady-state mass balance with convection and chemical reaction was required because, now, diffusion and chemical reaction were important. Professor DeLancey’s notes from a 1976 graduate course in mass transfer provided the solution to this bottleneck moments before the graduate reactor design class at Colorado State was scheduled to meet one morning in the spring of 1994.

Finally, I must thank students and colleagues in Colorado State’s Department of Chemical Engineering for their assistance. Professor David B. McWhorter introduced me to a porous media approach to estimate axial dispersion coefficients. These are required to calculate mass transfer Peclet numbers and interpellet Damkohler numbers, and to compare ideal and non-ideal simulations in packed catalytic tubular reactors. Jeremiah J. Way’s M.S. thesis in 2003 under my guidance, entitled “Interpellet Axial Dispersion and External Mass Transfer Resistance in Heterogeneous Packed Catalytic Tubular Reactors: A Simulation-Based Study,” has identified the critical value of the mass transfer Peclet number above which packed catalytic tubular reactors perform ideally. Jeremiah’s correlations and tabular data reveal that the critical value of the mass transfer Peclet number depends on the interpellet Damkohler number, the effectiveness factor, and the catalyst filling factor for a packed bed. These results are summarized in Chapter 22. Of particular importance, correlations are presented that allow one to predict deviations from ideal reactor performance when one operates at subcritical mass transfer Peclet numbers. Jeremiah is also acknowledged for clarifying some intrapellet diffusion concepts about the orientation part of the distribution function and the corresponding tortuosity factors in the parallel-pore model. Professor Ranil Wickramasinghe provided useful information about commercial chromatographic separation columns and maximum filling factors for spherically shaped catalysts (i.e., 66 to 74%) in packed beds. Professor Terry G. Lenz provided thermodynamic comments on the nonisothermal batch and adiabatic tubular reactor introductory problems in Part I which employ a reversible reaction scheme for the production of methanol from carbon monoxide and hydrogen. Professor Lenz was extremely helpful in his identification of energy changes for chemical reaction in the thermal energy balance, based on partial molar properties instead of pure-component molar properties. Professor Naz Karim provided assistance with



the matrix analysis of start up behavior for multiple tanks (i.e., CSTRs) in series. Professors Vince Murphy, Jim Linden, and Ken Reardon fine-tuned a biochemical engineering cell culture problem based on principles discussed in Chapter 24, which focuses on gas–liquid continuous-stirred tanks. Professors Vince Murphy and David Dandy are acknowledged for providing reference material and answering my “off-the-wall” questions, whenever asked. Professor Dandy supports my choice of boundary conditions at the inlet to a packed catalytic tubular reactor with significant interpellet axial dispersion. In other words, the dimensionless molar density of reactant A at the tube inlet is, by definition, unity. This boundary condition is appropriate in the design of an ideal tubular reactor in which axial dispersion is negligible at high mass transfer Peclet numbers. However, I also employ this boundary condition to simulate non-ideal reactor performance, whereas most of the chemical reactor community has settled on a modification of this boundary condition because axial dispersion is important beyond the inlet plane, but absent prior to the inlet plane. Professors Branka Ladanyi and Marshall Fixman of the Colorado State Chemistry Department and Professor Vince Murphy are acknowledged for helping me analyze the pressure dependence of kinetic rate constants in terms of the volume of activation, which is described best as a difference between partial molar volumes of the activated complex and all the reactants. As a senior at Colorado State, Mark Heinrich was enrolled in an undergraduate transport phenomena course in the fall of 1991 when he suggested that the finite-difference formula for first and second derivatives, presented in Chapter 23, should be developed in general for non-equispaced data points. Mark Heinrich and Tony Rainsberger, in the same class, suggested that coupled heat and mass transfer in nonisothermal tubular reactors in Chapter 4 should be analyzed with cocurrent cooling fluids. Then, in the spring of 1994, as a graduate student in advanced reactor design at Colorado State, Mark Heinrich helped me finalize an approximate method to estimate multicomponent diffusivities and resistances in porous catalysts. Dimensionless correlations between the effectiveness factor and the intrapellet Damkohler number in various shaped catalysts were prepared by graduate students Chris Cannizzaro, Bill Nagle, David Oelschlager, and Ken Tunnicliff in the spring of 1994. Bill Nagle suggested a modification of the Danckwerts boundary condition in the exit stream of a non-ideal plug-flow tubular reactor such that ideal and non-ideal reactors satisfy the same boundary conditions in the inlet and exit streams. This idea is described in detail in Chapter 22. When David John Phillips was enrolled in undergraduate chemical reactor design at Colorado State in the fall of 1999, he generated the idea for Problem 5-3. In other words, he questioned the number of steady states that exist in a nonisothermal CSTR when the rate of thermal energy removal vs. temperature coincides with the steepest section of the rate of thermal energy generation such that there is essentially a continuum of operating points that are common to both curves. Graduate student Neema Saxena corrected some mathematical errors in Chapter 27 by replacing total derivatives with partial derivatives when the “dot” product of unit normal vectors with temperature and concentration gradients is constructed. Neema also clarified one of the momentum boundary conditions

at gas–liquid interfaces, where continuity of the velocity vector is imposed. In other words, “perfect slip” is more appropriate than “no slip,” and the velocity component tangential to the interface in the liquid phase induces circulation within bubbles. Graduate student Anthony Tartaglione helped me generate ideal and non-ideal reactor simulations when the external resistance to mass transfer cannot be neglected. Jeremiah Way completed the analysis of external mass transfer resistance in packed catalytic tubular reactors and discovered the following simulation-based phenomena: (1) Higher conversion of reactants to products is achieved at shorter residence times, over a restricted range of mass transfer Peclet numbers; and (2) non-ideal reactors perform better than ideal reactors, based on the conditions required to achieve maximum conversion of reactants to products, because the ideal simulations are not valid when the mass transfer Peclet number is smaller than its critical value. These nontraditional results are attributed to the interplay between external mass transfer resistance and average residence-time effects in packed catalytic tubular reactors. Graduate student Eric M. Indra deserves a special thanks for proofreading a major portion of the manuscript during the “early years,” and Dr. Pronab Das and Dr. Mary Pat McCurdie also read various chapters. It gives me great pleasure to express sincere appreciation for many fruitful discussions with two colleagues, Drs. Rajiv Bhadra and Allen Rakow, who knew about, but are no longer here to witness the impact of, this textbook. Their intellectual enthusiasm and sense of humor are greatly missed. I apologize to anyone else, who provided assistance directly or indirectly, whose name was forgotten.

Fort Collins, Colorado  
November 22, 2002  
belfiore@engr.colostate.edu

L.A.B.