PREFACE		xvii
ABOUT THE AU	VTHOR	xxxiii
CHAPTER 1 M	MOLE BALANCES	1
1.1	The Rate of Reaction, $-r_A$ 4	
1.2	The General Mole Balance Equation 8	
1.3 1.4	Batch Reactors (BRs) 10 Continuous-Flow Reactors 12	
1.4	1.4.1 Continuous-Stirred Tank Reactor (CSTR) 12	
	1.4.2 Tubular Reactor 14	
	1.4.3 Packed-Bed Reactor (PBR) 18	
1.5	Industrial Reactors 22	
CHAPTER 2 C	CONVERSION AND REACTOR SIZING	31
2.1	Definition of Conversion 32	
2.2	Batch Reactor Design Equations 32	
2.3	Design Equations for Flow Reactors 35	
	2.3.1 CSTR (Also Known as a Backmix Reactor or a Vat) 36	
	2.3.2 Tubular Flow Reactor (PFR) 36	
2.4	2.3.3 Packed-Bed Reactor (PBR) 37	
2.4 2.5	Sizing Continuous-Flow Reactors 38 Reactors in Series 47	
2.3	2.5.1 CSTRs in Series 48	
	2.5.2 PFRs in Series 52	
	2.5.3 Combinations of CSTRs and PFRs in Series 53	
	2.5.4 Comparing the CSTR and PFR Reactor Volumes and Reactor	
	Sequencing 57	

Viii Contents

	2.6	Some Further Definitions 58	
		2.6.1 Space Time 58	
		2.6.2 Space Velocity 60	
CHAPTER 3	B RA	ATE LAWS	69
	3.1	Basic Definitions 70	
		3.1.1 Relative Rates of Reaction 71	
	3.2	The Reaction Order and the Rate Law 72	
		3.2.1 Power Law Models and Elementary Rate Laws 72	
		3.2.2 Nonelementary Rate Laws 76	
		3.2.3 Reversible Reactions 80	
	3.3	Rates and the Reaction Rate Constant 83	
		3.3.1 The Rate Constant k 83	
		3.3.2 The Arrhenius Plot 90	
	3.4	Present Status of Our Approach to Reactor Sizing and Design 93	
CHAPTER 4	4 ST	COICHIOMETRY	105
	4.1	Batch Systems 107	
	7.1	4.1.1 Batch Concentrations for the Generic Reaction,	
		Equation (2-2) 109	
	4.2	Flow Systems 113	
	7.2	4.2.1 Equations for Concentrations in Flow Systems 114	
		4.2.2 Liquid-Phase Concentrations 114	
		4.2.3 Gas-Phase Concentrations 115	
	4.3	Reversible Reactions and Equilibrium Conversion 126	
CHAPTER 5	5 ISO	OTHERMAL REACTOR DESIGN: CONVERSION	139
	150	OTTENHE RELIEF OR BESTOTT COTTY BROTOTT	10)
	5.1	Design Structure for Isothermal Reactors 140	
	5.2	Batch Reactors (BRs) 144	
		5.2.1 Batch Reaction Times 145	
	5.3	Continuous-Stirred Tank Reactors (CSTRs) 152	
		5.3.1 A Single CSTR 152	
		5.3.2 CSTRs in Series 155	
	5.4	Tubular Reactors 162	
	5.5	Pressure Drop in Reactors 169	
		5.5.1 Pressure Drop and the Rate Law 169	
		5.5.2 Flow Through a Packed Bed 170	
		5.5.3 Pressure Drop in Pipes 174	
		5.5.4 Analytical Solution for Reaction with Pressure Drop 177	
		5.5.5 Robert the Worrier Wonders: What If 181	
	5.6	Synthesizing the Design of a Chemical Plant 190	

	SOTHERMAL REACTOR DESIGN: OLES AND MOLAR FLOW RATES	207
6.1 6.2	The Molar Flow Rate Balance Algorithm 208 Mole Balances on CSTRs, PFRs, PBRs, and Batch Reactors 208 6.2.1 Liquid Phase 208 6.2.2 Gas Phase 210	
6.3	Application of the PFR Molar Flow Rate Algorithm to a Microreactor 212	
6.4	Membrane Reactors 217	
6.5	Unsteady-State Operation of Stirred Reactors 225	
6.6	Semibatch Reactors 227	
	 6.6.1 Motivation for Using a Semibatch Reactor 6.6.2 Semibatch Reactor Mole Balances 227 	
CHAPTER 7 C	OLLECTION AND ANALYSIS OF RATE DATA	243
7.1	The Algorithm for Data Analysis 244	
7.2	Determining the Reaction Order for Each of Two Reactants Using the	
7.2	Method of Excess 246	
7.3	Integral Method 247	
7.4	Differential Method of Analysis 251	
7	7.4.1 Graphical Differentiation Method 252	
	7.4.2 Numerical Method 252	
	7.4.3 Finding the Rate-Law Parameters 253	
7.5	Nonlinear Regression 258	
7.6	Reaction-Rate Data from Differential Reactors 264	
7.7	Experimental Planning 271	
CHAPTER 8 M	ULTIPLE REACTIONS	279
8.1	Definitions 280	
0.1	8.1.1 Types of Reactions 280	
	8.1.2 Selectivity 281	
	8.1.3 Yield 282	
8.2	Algorithm for Multiple Reactions 282	
0.2	8.2.1 Modifications to the Chapter 6 CRE Algorithm for Multiple	
	Reactions 284	
8.3	Parallel Reactions 285	
0.3	8.3.1 Selectivity 285	
	8.3.2 Maximizing the Desired Product for One Reactant 285	
	8.3.3 Reactor Selection and Operating Conditions 291	
8.4	Reactions in Series 294	
0.7	Transport in Series 27 :	

X Contents

8.5	8.5.1	Complex Gas-Phase Reactions in a PBR 304	
	8.5.2	Complex Liquid-Phase Reactions in a CSTR 307	
	8.5.3	Complex Liquid-Phase Reactions in a Semibatch	
		Reactor 310	
8.6	Membra	ne Reactors to Improve Selectivity	
	in Multij	ple Reactions 312	
8.7	Sorting 1	it All Out 317	
8.8	The Fun	Part 317	
CHAPTER 9	PEACTION	N MECHANISMS, PATHWAYS, BIOREACTIONS,	
		PEACTORS	333
1	IND DION	LACTORS	333
9.1	Active In	ntermediates and Nonelementary Rate Laws 334	
	9.1.1	Pseudo-Steady-State Hypothesis (PSSH) 335	
	9.1.2	Why Is the Rate Law First Order? 338	
	9.1.3	Searching for a Mechanism 339	
	9.1.4	Chain Reactions 343	
9.2	Enzymat	tic Reaction Fundamentals 343	
	9.2.1	Enzyme–Substrate Complex 344	
	9.2.2	Mechanisms 346	
	9.2.3	Michaelis–Menten Equation 348	
	9.2.4	Batch-Reactor Calculations for Enzyme Reactions 354	
9.3	Inhibitio	n of Enzyme Reactions 356	
	9.3.1	Competitive Inhibition 357	
	9.3.2	Uncompetitive Inhibition 359	
	9.3.3	Noncompetitive Inhibition (Mixed Inhibition) 361	
	9.3.4	Substrate Inhibition 363	
9.4	Bioreact	ors and Biosynthesis 364	
	9.4.1	Cell Growth 368	
	9.4.2	Rate Laws 369	
	9.4.3	Stoichiometry 371	
	9.4.4	Mass Balances 377	
	9.4.5	Chemostats 381	
	9.4.6	CSTR Bioreactor Operation 381	
	9.4.7	Wash-Out 383	
CHAPTER 10	CATALYS	SIS AND CATALYTIC REACTORS	399
10.1	Catalysts	s 399	
10.1	10.1.1	Definitions 400	
	10.1.1	Catalyst Properties 401	
	10.1.3	Catalytic Gas-Solid Interactions 403	
	10.1.3	Classification of Catalysts 404	
10.2		a Catalytic Reaction 405	
10.2	10.2.1	Step 1 Overview: Diffusion from the Bulk to the External	
	10.2.1	Surface of the Catalyst 408	
	10.2.2	Step 2 Overview: Internal Diffusion 409	
	10.2.2	Step 2 Content Internet Digitation 107	

	10.2.3 Adsorption Isotherms 410	
	10.2.4 Surface Reaction 416	
	10.2.5 Desorption 418	
	10.2.6 The Rate-Limiting Step 419	
10.3	Synthesizing a Rate Law, Mechanism, and Rate-Limiting Step 421	
	10.3.1 Is the Adsorption of Cumene Rate-Limiting? 424	
	10.3.2 Is the Surface Reaction Rate-Limiting? 427	
	10.3.3 Is the Desorption of Benzene Rate-Limiting? 429	
	10.3.4 Summary of the Cumene Decomposition 430	
	10.3.5 Reforming Catalysts 431	
	10.3.6 Rate Laws Derived from the Pseudo-Steady-	
	State Hypothesis (PSSH) 435	
	10.3.7 Temperature Dependence of the Rate Law 436	
10.4	Heterogeneous Data Analysis for Reactor Design 436	
	10.4.1 Deducing a Rate Law from the Experimental Data 438	
	10.4.2 Finding a Mechanism Consistent with Experimental	
	Observations 439	
	10.4.3 Evaluation of the Rate-Law Parameters 440	
	10.4.4 Reactor Design 443	
10.5	Reaction Engineering in Microelectronic Fabrication 446	
	10.5.1 Overview 446	
	10.5.2 Chemical Vapor Deposition 448	
10.6	Model Discrimination 451	
10.7	Catalyst Deactivation 454	
	10.7.1 Types of Catalyst Deactivation 456	
	10.7.2 Reactors That Can Be Used to Help Offset Catalyst	
	<i>Decay</i> 465	
	10.7.3 Temperature–Time Trajectories 465	
	10.7.4 Moving-Bed Reactors 467	
	10.7.5 Straight-Through Transport Reactors (STTR) 472	
CHAPTER 11 N	NONISOTHERMAL REACTOR DESIGN—THE STEADY-	
	STATE ENERGY BALANCE AND ADIABATIC	
		402
Ρ	PFR APPLICATIONS	493
11.1	Rationale 494	
11.2	The Energy Balance 495	
	11.2.1 First Law of Thermodynamics 495	
	11.2.2 Evaluating the Work Term 496	
	11.2.3 Overview of Energy Balances 498	
11.3	The User-Friendly Energy Balance Equations 502	
	11.3.1 Dissecting the Steady-State Molar Flow Rates	
	to Obtain the Heat of Reaction 502	
	11.3.2 Dissecting the Enthalpies 504	
	11.3.3 Relating $\Delta H_{\rm Rx}(T)$, $\Delta H_{\rm Rx}^{\circ}(T_{\rm R})$, and $\Delta C_{\rm P}$ 505	
11.4	Adiabatic Operation 508	
	11.4.1 Adiabatic Energy Balance 508	
	11.4.2 Adiabatic Tubular Reactor 509	

Xİİ Contents

11.5	Adiabatic Equilibrium Conversion 518	
	11.5.1 Equilibrium Conversion 518	
11.6	Reactor Staging 522	
	11.6.1 Reactor Staging with Interstage Cooling or Heating 522	
	11.6.2 Exothermic Reactions 523	
	11.6.3 Endothermic Reactions 523	
11.7	Optimum Feed Temperature 526	
CHAPTER 12 S	TEADY-STATE NONISOTHERMAL REACTOR	
D	DESIGN—FLOW REACTORS WITH HEAT EXCHANGE	539
12.1	Steady-State Tubular Reactor with Heat Exchange 540	
	12.1.1 Deriving the Energy Balance for a PFR 540	
	12.1.2 Applying the Algorithm to Flow Reactors with Heat	
	Exchange 542	
12.2	Balance on the Heat-Transfer Fluid 543	
	12.2.1 Co-current Flow 543	
	12.2.2 Countercurrent Flow 544	
12.3	Algorithm for PFR/PBR Design with Heat Effects 545	
	12.3.1 Applying the Algorithm to an Exothermic Reaction 548	
	12.3.2 Applying the Algorithm to an Endothermic Reaction 555	
12.4	CSTR with Heat Effects 564	
	12.4.1 Heat Added to the Reactor, \dot{Q} 564	
12.5	Multiple Steady States (MSS) 574	
	12.5.1 Heat-Removed Term, $R(T)$ 575	
	12.5.2 Heat-Generated Term, $G(T)$ 576	
	12.5.3 Ignition-Extinction Curve 578	
12.6	Nonisothermal Multiple Chemical Reactions 581	
	12.6.1 Energy Balance for Multiple Reactions in Plug-Flow	
	Reactors 581	
	12.6.2 Parallel Reactions in a PFR 582	
	12.6.3 Energy Balance for Multiple Reactions in a CSTR 585	
	12.6.4 Series Reactions in a CSTR 585	
	12.6.5 Complex Reactions in a PFR 588	
12.7	Radial and Axial Variations in a Tubular Reactor 595	
	12.7.1 Molar Flux 596	
	12.7.2 Energy Flux 597	
	12.7.3 Energy Balance 598	
12.8	Safety 603	
12.0		
CHAPTER 13 U	INSTEADY-STATE NONISOTHERMAL REACTOR DESIGN	629
CHAPTER 13 C	INSTEADT-STATE NONISOTHERWAL REACTOR DESIGN	029
13.1	Unsteady-State Energy Balance 630	
13.2	Energy Balance on Batch Reactors 632	
13.2	13.2.1 Adiabatic Operation of a Batch Reactor 633	
	13.2.2 Case History of a Batch Reactor with Interrupted Isothermal	
	Operation Causing a Runaway Reaction 640	

13.3 13.4	Semibatch Reactors with a Heat Exchanger 646 Unsteady Operation of a CSTR 651	
	13.4.1 Startup 651	
13.5	Nonisothermal Multiple Reactions 656	
CHAPTER 14 N	MASS TRANSFER LIMITATIONS IN REACTING SYSTEMS	679
14.1	Diffusion Fundamentals 680	
	14.1.1 Definitions 681	
	14.1.2 Molar Flux 682	
14.2	14.1.3 Fick's First Law 683 Binary Diffusion 684	
14.2	14.2.1 Evaluating the Molar Flux 684	
	14.2.2 Diffusion and Convective Transport 685	
	14.2.3 Boundary Conditions 685	
	14.2.4 Temperature and Pressure Dependence of D _{AB} 686	
	14.2.5 Steps in Modeling Diffusion without Reaction 687	
	14.2.6 Modeling Diffusion with Chemical Reaction 687	
14.3	Diffusion Through a Stagnant Film 688	
14.4	The Mass Transfer Coefficient 690	
	14.4.1 Correlations for the Mass Transfer Coefficient 690 14.4.2 Mass Transfer to a Single Particle 693	
	14.4.3 Mass Transfer—Limited Reactions in Packed Beds 697	
	14.4.4 Robert the Worrier 700	
14.5	What If ? (Parameter Sensitivity) 705	
CHAPTER 15 I	DIFFUSION AND REACTION	7 19
15.1	Diffusion and Reactions in Homogeneous Systems 720	
15.2	Diffusion and Reactions in Spherical Catalyst Pellets 720	
	15.2.1 Effective Diffusivity 721 15.2.2 Derivation of the Differential Equation Describing Diffusion	
	15.2.2 Derivation of the Differential Equation Describing Diffusion and Reaction in a Single Catalyst Pellet 723	
	15.2.3 Writing the Diffusion with the Catalytic Reaction Equation in	
	Dimensionless Form 726	
	15.2.4 Solution to the Differential Equation for a First-Order Reaction 729	
15.3	The Internal Effectiveness Factor 730	
13.3	15.3.1 Isothermal First-Order Catalytic Reactions 730	
	15.3.2 Effectiveness Factors with Volume Change with	
	Reaction 733	
	15.3.3 Isothermal Reactors Other Than First Order 733	
	15.3.4 Weisz–Prater Criterion for Internal Diffusion 734	
15.4	Falsified Kinetics 737	
15.5	Overall Effectiveness Factor 739 Estimation of Diffusion, and Position Limited Regimes 743	
15.6	Estimation of Diffusion- and Reaction-Limited Regimes 743 15.6.1 Means Criterion for External Diffusion Limitations 743	

XİV Contents

15.7	Mass Transfer and Reaction in a Packed Bed 744	
15.8	Determination of Limiting Situations from Reaction-Rate Data 750	
15.9	Multiphase Reactors in the Professional Reference Shelf 751	
	15.9.1 Slurry Reactors 752	
	15.9.2 Trickle Bed Reactors 752	
15.10	Fluidized Bed Reactors 753	
	Chemical Vapor Deposition (CVD) 753	
CHAPTER 16 F	RESIDENCE TIME DISTRIBUTIONS OF	
		= /=
C	CHEMICAL REACTORS	767
16.1	General Considerations 767	
10.1		
16.2	,	
10.2		
	16.2.1 Pulse Input Experiment 770	
16.2	16.2.2 Step Tracer Experiment 775	
16.3	Characteristics of the RTD 777	
	16.3.1 Integral Relationships 777	
	16.3.2 Mean Residence Time 778	
	16.3.3 Other Moments of the RTD 778	
	16.3.4 Normalized RTD Function, $E(\Theta)$ 782	
	16.3.5 Internal-Age Distribution, $I(\alpha)$ 783	
16.4	RTD in Ideal Reactors 784	
	16.4.1 RTDs in Batch and Plug-Flow Reactors 784	
	16.4.2 Single-CSTR RTD 785	
	16.4.3 Laminar-Flow Reactor (LFR) 786	
16.5	PFR/CSTR Series RTD 789	
16.6	Diagnostics and Troubleshooting 793	
	16.6.1 General Comments 793	
	16.6.2 Simple Diagnostics and Troubleshooting Using the RTD for	
	Ideal Reactors 794	
CHADTED 17 I	PREDICTING CONVERSION DIRECTLY FROM THE	
		00=
K	RESIDENCE TIME DISTRIBUTION	807
4.7.4	M. 111 M. 11 I.D	
17.1	Modeling Nonideal Reactors Using the RTD 808	
	17.1.1 Modeling and Mixing Overview 808	
	17.1.2 Mixing 808	
17.2	Zero-Adjustable-Parameter Models 810	
	17.2.1 Segregation Model 810	
	17.2.2 Maximum Mixedness Model 820	
17.3	Using Software Packages 827	
	17.3.1 Comparing Segregation and Maximum Mixedness	
	Predictions 829	
17.4	RTD and Multiple Reactions 830	
	17.4.1 Segregation Model 830	
	17.4.2 Maximum Mixedness 831	

CHAPTER 1	18 1	MODELS FOR NONIDEAL REACTORS	845
	18.1	Some Guidelines for Developing Models 846	
		18.1.1 One-Parameter Models 847	
		18.1.2 Two-Parameter Models 848	
	18.2	The Tanks-in-Series (T-I-S) One-Parameter Model 848	
		18.2.1 Developing the E-Curve for the T-I-S Model 849	
		18.2.2 Calculating Conversion for the T-I-S Model 851	
		18.2.3 Tanks-in-Series versus Segregation for a First-Order Reaction 852	
	18.3	Dispersion One-Parameter Model 852	
	18.4	Flow, Reaction, and Dispersion 854	
		18.4.1 Balance Equations 854	
		18.4.2 Boundary Conditions 855	
		18.4.3 Finding D _a and the Peclet Number 858	
		18.4.4 Dispersion in a Tubular Reactor with Laminar Flow 858 18.4.5 Correlations for D ₂ 860	
		18.4.5 Correlations for D_a 860 18.4.6 Experimental Determination of D_a 862	
	18.5	Tanks-in-Series Model versus Dispersion Model 869	
	18.6	Numerical Solutions to Flows with Dispersion and Reaction 870	
	18.7	Two-Parameter Models—Modeling Real Reactors with Combinations of	
	101.	Ideal Reactors 871	
		18.7.1 Real CSTR Modeled Using Bypassing and Dead Space 872	
		18.7.2 Real CSTR Modeled as Two CSTRs with Interchange 878	
	18.8	Use of Software Packages to Determine the Model Parameters 880	
	18.9	Other Models of Nonideal Reactors Using CSTRs and PFRs 882	
	18.10	Applications to Pharmacokinetic Modeling 883	
APPENDIX	A 1	NUMERICAL TECHNIQUES	897
	A 1	Useful Integrals in Reactor Design 897	
	A.1 A.2	Useful Integrals in Reactor Design 897 Equal-Area Graphical Differentiation 898	
	A.3	Solutions to Differential Equations 900	
	л.5	A.3.A First-Order Ordinary Differential Equations 900	
		A.3.B Coupled Differential Equations 900	
		A.3.C Second-Order Ordinary Differential Equations 901	
	A.4	Numerical Evaluation of Integrals 901	
	A.5	Semilog Graphs 903	
	A.6	Software Packages 903	
APPENDIX	B	IDEAL GAS CONSTANT AND CONVERSION FACTORS	905
APPENDIX	C	THERMODYNAMIC RELATIONSHIPS INVOLVING	
		THE EQUILIBRIUM CONSTANT	909

XVİ

APPENDIX D	SOFTWARE PACKAGES	915
D.1 D.2 D.3	D.I.A About Polymath 915 D.I.B Polymath Tutorials 916 2 MATLAB 916 3 Aspen 916	
D.4	4 COMSOL Multiphysics 917	
APPENDIX E	RATE LAW DATA	919
APPENDIX F	NOMENCLATURE	921
APPENDIX G	OPEN-ENDED PROBLEMS	925
G.1 G.2 G.3 G.4 G.5 G.5 G.8 G.9	2 Effective Lubricant Design 925 3 Peach Bottom Nuclear Reactor 925 4 Underground Wet Oxidation 926 5 Hydrodesulfurization Reactor Design 926 6 Continuous Bioprocessing 926 7 Methanol Synthesis 926 8 Cajun Seafood Gumbo 926 9 Alcohol Metabolism 927	
APPENDIX H	USE OF COMPUTATIONAL CHEMISTRY SOFTWARE PACKAGES	929
APPENDIX I	HOW TO USE THE CRE WEB RESOURCES	931
I.1 I.2	CRE Web Resources Components 931 How the Web Can Help Your Learning Style 933 1.2.1 Global vs. Sequential Learners 933 1.2.2 Active vs. Reflective Learners 934	
I.3	Navigation 934	
INDEX		937