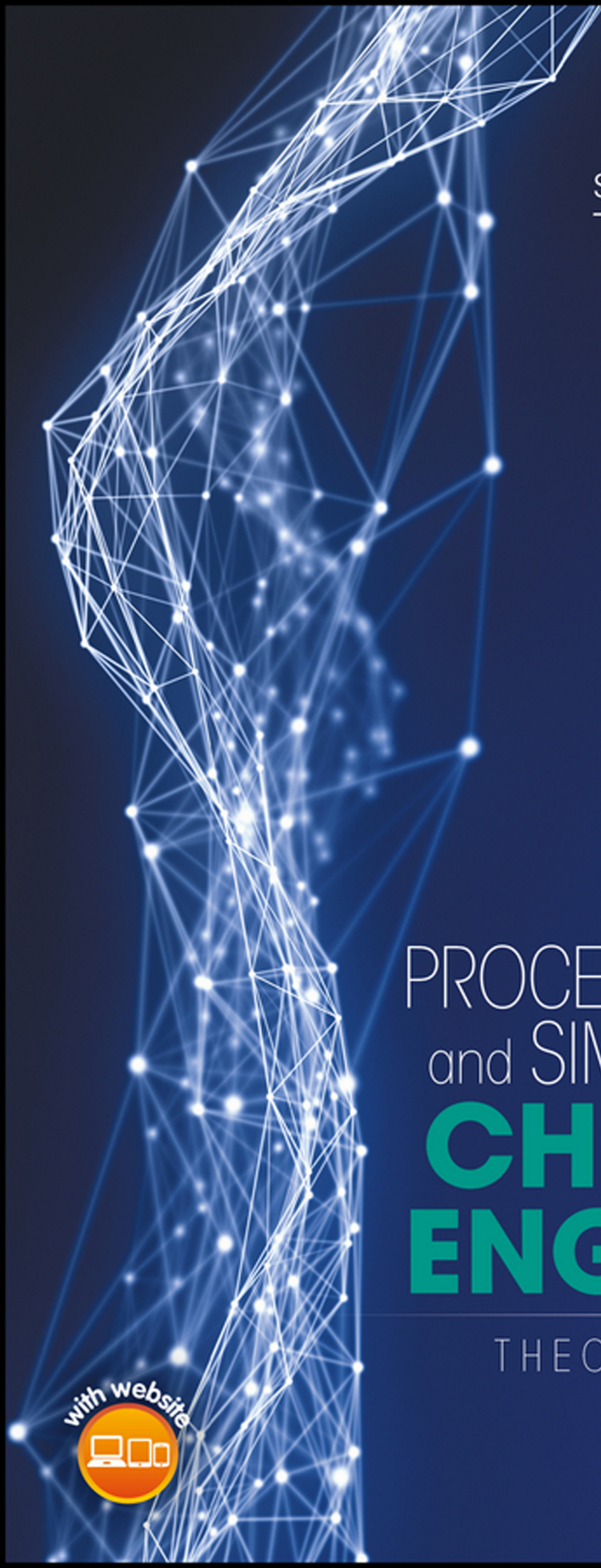


An abstract graphic on the left side of the cover, consisting of a complex web of white lines connecting numerous small white dots, resembling a molecular structure or a network diagram, set against a dark blue background.

SIMANT RANJAN UPRETI

PROCESS MODELING
and SIMULATION FOR
**CHEMICAL
ENGINEERS**

THEORY AND PRACTICE



WILEY

PROCESS MODELING AND SIMULATION FOR CHEMICAL ENGINEERS

PROCESS MODELING AND SIMULATION FOR CHEMICAL ENGINEERS

THEORY AND PRACTICE

Simant Ranjan Upreti

*Department of Chemical Engineering,
Ryerson University,
Toronto, Canada*

WILEY

This edition first published 2017
© 2017 John Wiley & Sons Ltd

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by law. Advice on how to obtain permission to reuse material from this title is available at <http://www.wiley.com/go/permissions>.

The right of Simant Ranjan Upreti to be identified as the author of this work has been asserted in accordance with law.

Registered Offices

John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA
John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, UK

Editorial Office

The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, UK

For details of our global editorial offices, customer services, and more information about Wiley products visit us at www.wiley.com.

Wiley also publishes its books in a variety of electronic formats and by print-on-demand. Some content that appears in standard print versions of this book may not be available in other formats.

Limit of Liability/Disclaimer of Warranty

The publisher and the authors make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of fitness for a particular purpose. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for every situation. In view of ongoing research, equipment modifications, changes in governmental regulations, and the constant flow of information relating to the use of experimental reagents, equipment, and devices, the reader is urged to review and evaluate the information provided in the package insert or instructions for each chemical, piece of equipment, reagent, or device for, among other things, any changes in the instructions or indication of usage and for added warnings and precautions. The fact that an organization or website is referred to in this work as a citation and/or potential source of further information does not mean that the author or the publisher endorses the information the organization or website may provide or recommendations it may make. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read. No warranty may be created or extended by any promotional statements for this work. Neither the publisher nor the author shall be liable for any damages arising herefrom.

Library of Congress Cataloging-in-Publication Data

Names: Upreti, Simant Ranjan, author.

Title: Process modeling and simulation for chemical engineers : theory and practice / Simant Ranjan Upreti.

Description: Chichester, UK ; Hoboken, NJ : John Wiley & Sons, 2017. |

Includes bibliographical references and index.

Identifiers: LCCN 2016053339 | ISBN 9781118914687 (cloth) | ISBN 9781118914663 (epub)

Subjects: LCSH: Chemical processes—Mathematical models. | Chemical processes—Data processing.

Classification: LCC TP155.7 .U67 2017 | DDC 660/.284401—dc23

LC record available at <https://lccn.loc.gov/2016053339>

Cover image: shulz/Gettyimages

Cover design by Wiley

Set in 10/12pt, NimbusRomNo by SPi Global, Chennai, India.

to my wife and kids

CONTENTS

Preface	xiii
Notation	xv
1 Introduction	1
1.1 System	1
1.1.1 Uniform System	2
1.1.2 Properties of System	2
1.1.3 Classification of System	3
1.1.4 Model	3
1.2 Process	3
1.2.1 Classification of Processes	4
1.2.2 Process Model	5
1.3 Process Modeling	6
1.3.1 Relations	7
1.3.2 Assumptions	7
1.3.3 Variables and Parameters	8
1.4 Process Simulation	9
1.4.1 Utility	9
1.4.2 Simulation Methods	10
1.5 Development of Process Model	11
1.6 Learning about Process	13
1.7 System Specification	14
Bibliography	16
Exercises	16
2 Fundamental Relations	17
2.1 Basic Form	17
2.1.1 Application	19
2.2 Mass Balance	21

2.2.1	Microscopic Balances	21
2.2.2	Equation of Change for Mass Fraction	23
2.3	Mole Balance	24
2.3.1	Microscopic Balances	24
2.3.2	Equation of Change for Mole Fraction	25
2.4	Momentum Balance	26
2.4.1	Convective Momentum Flux	27
2.4.2	Total Momentum Flux	28
2.4.3	Macroscopic Balance	29
2.4.4	Microscopic Balance	31
2.5	Energy Balance	33
2.5.1	Microscopic Balance	33
2.5.2	Macroscopic Balance	35
2.6	Equation of Change for Kinetic and Potential Energy	38
2.6.1	Microscopic Equation	38
2.6.2	Macroscopic Equation	40
2.7	Equation of Change for Temperature	41
2.7.1	Microscopic Equation	41
2.7.2	Macroscopic Equation	42
2.A	Enthalpy Change from Thermodynamics	44
2.B	Divergence Theorem	48
2.C	General Transport Theorem	50
2.D	Equations in Cartesian, Cylindrical and Spherical Coordinate Systems	53
2.D.1	Equations of Continuity	54
2.D.2	Equations of Continuity for Individual Species	54
2.D.3	Equations of Motion	55
2.D.4	Equations of Change for Temperature	56
	Bibliography	57
	Exercises	57
3	Constitutive Relations	59
3.1	Diffusion	59
3.1.1	Multicomponent Mixtures	60
3.2	Viscous Motion	60
3.2.1	Newtonian Fluids	61
3.2.2	Non-Newtonian Fluids	62
3.3	Thermal Conduction	63
3.4	Chemical Reaction	63
3.5	Rate of Reaction	65

3.5.1	Equations of Change for Moles	66
3.5.2	Equations of Change for Temperature	67
3.5.3	Macroscopic Equation of Change for Temperature	69
3.6	Interphase Transfer	71
3.7	Thermodynamic Relations	72
3.A	Equations in Cartesian, Cylindrical and Spherical Coordinate Systems	74
3.A.1	Equations of Continuity for Binary Systems	74
3.A.2	Equations of Motion for Newtonian Fluids	75
3.A.3	Equations of Change for Temperature	76
	References	77
	Bibliography	77
	Exercises	78
4	Model Formulation	79
4.1	Lumped-Parameter Systems	80
4.1.1	Isothermal CSTR	80
4.1.2	Flow through Eccentric Reducer	83
4.1.3	Liquid Preheater	84
4.1.4	Non-Isothermal CSTR	87
4.2	Distributed-Parameter Systems	90
4.2.1	Nicotine Patch	90
4.2.2	Fluid Flow between Inclined Parallel Plates	93
4.2.3	Tapered Fin	96
4.2.4	Continuous Microchannel Reactor	99
4.2.5	Oxygen Transport to Tissues	103
4.2.6	Dermal Heat Transfer in Cylindrical Limb	106
4.2.7	Solvent Induced Heavy Oil Recovery	108
4.2.8	Hydrogel Tablet	112
4.2.9	Neutron Diffusion	117
4.2.10	Horton Sphere	119
4.2.11	Reactions around Solid Reactant	122
4.3	Fluxes along Non-Linear Directions	127
4.3.1	Saccadic Movement of an Eye	128
4.A	Initial and Boundary Conditions	131
4.A.1	Initial Condition	131
4.A.2	Boundary Condition	131
4.A.3	Periodic Condition	132
4.B	Zero Derivative at the Point of Symmetry	133
4.C	Equation of Motion along the Radial Direction in Cylindrical Coordinates	134
	References	137

Exercises	137
5 Model Transformation	139
5.1 Transformation between Orthogonal Coordinate Systems	139
5.1.1 Scale Factors	139
5.1.2 Differential Elements	142
5.1.3 Vector Representation	143
5.1.4 Derivatives of Unit Vectors	144
5.1.5 Differential Operators	146
5.2 Transformation between Arbitrary Coordinate Systems	155
5.2.1 Transformation of Velocity	155
5.2.2 Transformation of Spatial Derivatives	156
5.2.3 Correctness of Transformation Matrices	156
5.3 Laplace Transformation	161
5.3.1 Examples	162
5.3.2 Properties of Laplace Transforms	164
5.3.3 Solution of Linear Differential Equations	168
5.4 Miscellaneous Transformations	178
5.4.1 Higher Order Derivatives	178
5.4.2 Scaling	178
5.4.3 Change of Independent Variable	179
5.4.4 Semi-Infinite Domain	179
5.4.5 Non-Autonomous to Autonomous Differential Equation	180
5.A Differential Operators in an Orthogonal Coordinate System	180
5.A.1 Gradient of a Scalar	180
5.A.2 Divergence of a Vector	181
5.A.3 Laplacian of a Scalar	184
5.A.4 Curl of a Vector	184
References	186
Bibliography	186
Exercises	186
6 Model Simplification and Approximation	189
6.1 Model Simplification	189
6.1.1 Scaling and Ordering Analysis	190
6.1.2 Linearization	193
6.2 Model Approximation	200
6.2.1 Dimensional Analysis	201
6.2.2 Model Fitting	204
6.A Linear Function	220
6.B Proof of Buckingham Pi Theorem	221

6.C Newton's Optimization Method	223
References	224
Bibliography	224
Exercises	225
7 Process Simulation	227
7.1 Algebraic Equations	227
7.1.1 Linear Algebraic Equations	227
7.1.2 Non-Linear Algebraic Equations	236
7.2 Differential Equations	241
7.2.1 Ordinary Differential Equations	242
7.2.2 Explicit Runge–Kutta Methods	242
7.2.3 Step-Size Control	246
7.2.4 Stiff Equations	247
7.3 Partial Differential Equations	253
7.3.1 Finite Difference Method	255
7.4 Differential Equations with Split Boundaries	263
7.4.1 Shooting Newton–Raphson Method	264
7.5 Periodic Differential Equations	268
7.5.1 Shooting Newton–Raphson Method	268
7.6 Programming of Derivatives	271
7.7 Miscellanea	274
7.7.1 Integration of Discrete Data	274
7.7.2 Roots of a Single Algebraic Equation	276
7.7.3 Cubic Equations	278
7.A Partial Pivoting for Matrix Inverse	281
7.B Derivation of Newton–Raphson Method	281
7.B.1 Quadratic Convergence	282
7.C General Derivation of Finite Difference Formulas	284
7.C.1 First Derivative, Centered Second Order Formula	285
7.C.2 Second Derivative, Forward Second Order Formula	286
7.C.3 Third Derivative, Mixed Fourth Order Formula	287
7.C.4 Common Finite Difference Formulas	289
References	291
Bibliography	291
Exercises	291
8 Mathematical Review	295
8.1 Order of Magnitude	295

8.2	Big-O Notation	295
8.3	Analytical Function	295
8.4	Vectors	296
8.4.1	Vector Operations	297
8.4.2	Cauchy–Schwarz Inequality	302
8.5	Matrices	302
8.5.1	Terminology	303
8.5.2	Matrix Operations	304
8.5.3	Operator Inequality	305
8.6	Tensors	306
8.6.1	Multilinearity	306
8.6.2	Coordinate-Independence	306
8.6.3	Representation of Second Order Tensor	307
8.6.4	Einstein or Index Notation	308
8.6.5	Kronecker Delta	310
8.6.6	Operations Involving Vectors and Second Order Tensors	310
8.7	Differential	318
8.7.1	Derivative	318
8.7.2	Partial Derivative and Differential	318
8.7.3	Chain Rule of Differentiation	319
8.7.4	Material and Total Derivatives	321
8.8	Taylor Series	322
8.8.1	Multivariable Taylor Series	323
8.8.2	First Order Taylor Expansion	323
8.9	L'Hôpital's Rule	326
8.10	Leibniz's Rule	326
8.11	Integration by Parts	327
8.12	Euler's Formulas	327
8.13	Solution of Linear Ordinary Differential Equations	327
8.13.1	Single First Order Equation	327
8.13.2	Simultaneous First Order Equations	328
	Bibliography	332

PREFACE

I am delighted to present this book on process modeling and simulation for chemical engineers. It is a humble attempt to assimilate the amazing contributions of researchers and academicians in this area.

The goal of this book is to provide a rigorous treatment of fundamental concepts and techniques of this subject. To that end, the book includes all requisite mathematical analyses and derivations, which could be sometimes hard to find. Target readers are those at the graduate level. This book endeavors to equip them to model sophisticated processes, develop requisite computational algorithms and programs, improvise existing software, and solve research problems with confidence.

Chapter 1 provides the groundwork by introducing the terminology of process modeling and simulation. Chapter 2 presents the fundamental relations for this subject. Chapter 3 incorporates important constitutive relations for common systems. Chapter 4 presents model formulation with the help of several examples. Transformation techniques are introduced in Chapter 5. Model simplification and approximation methods are discussed in Chapter 6. The numerical solution of process models is the theme of Chapter 7. Review of important mathematical concepts is provided in Chapter 8.

This book can be used as a primary text for a one-semester course. Alternatively, it could serve as a supplementary text in graduate courses related to modeling and simulation. Readers could also study the book on their own. During an initial reading, one could very well skim quickly through a derivation, accept the result for the time being, and learn more from applications. Computer programs for the solutions of book examples can be obtained from the publisher's website, www.wiley.com/go/upreti/pms.for.chemicalengineers.

I am grateful to the editorial team at John Wiley & Sons for providing excellent support from start to finish.

Finally, I am deeply indebted to my wife Deepa, and children Jahnavi and Pranav. I could not have completed this book without their unsparing support and understanding.

Ryerson University, Toronto

Simant R. Upreti

Notation

Symbol	Description	Units
a	surface area per unit volume	m^{-1}
A_{m}	area of moving surfaces	m^2
A_{p}	area of a port of flow	m^2
A	area	m^2
$\mathbf{A}$	area vector	m^2
c	average concentration of a mixture	kmol m^{-3}
c_i	concentration of the i^{th} species	kmol m^{-3}
$\hat{C}_{\text{P}}$	specific heat capacity of mixture	$\text{J kg}^{-1}\text{K}^{-1}$
$\hat{C}_{\text{P}i}$	$\hat{C}_{\text{P}}$ of the i^{th} species in pure form	$\text{J kg}^{-1}\text{K}^{-1}$
$\underline{C}_{\text{P},i}$	molar specific heat capacity of the i^{th} species in a mixture	$\text{J kmol}^{-1}\text{K}^{-1}$
$\tilde{C}_{\text{P},i}$	partial specific heat capacity of the i^{th} species in a mixture	$\text{J kmol}^{-1}\text{K}^{-1}$
$\text{d}x$	differential change in x	of x
D	diffusivity of species	$\text{m}^2 \text{s}^{-1}$
D_{AB}	binary diffusivity of A in a mixture of A and B	$\text{m}^2 \text{s}^{-1}$
$\mathbf{D}$	matrix of multicomponent diffusivities	$\text{m}^2 \text{s}^{-1}$
e_i	the i^{th} component of energy flux	$\text{J m}^{-2} \text{s}^{-1}$
E	sum of the squared errors in y in a population	of y^2
E	total energy of a system	J
E	activation energy of reaction	J kmol^{-1}
$\hat{E}$	energy per unit mass	J kg^{-1}
f_i	fugacity of the i^{th} species	Pa
F	volumetric flow rate	$\text{m}^3 \text{s}^{-1}$
$\mathbf{f}_i$	mass flux of the i^{th} species	$\text{kg m}^{-2} \text{s}^{-1}$
$\mathbf{f}$	overall mass flux of a mixture	$\text{kg m}^{-2} \text{s}^{-1}$

Symbol	Description	Units
$\mathbf{F}_i$	molar flux of the i^{th} species	$\text{kmol m}^{-2} \text{s}^{-1}$
$\mathbf{F}$	overall molar flux of a mixture	$\text{kmol m}^{-2} \text{s}^{-1}$
$\mathbf{F}$	force vector	N
G	Gibbs free energy	J
$\hat{G}_i$	Gibbs free energy per unit mass of the i^{th} species	J kg^{-1}
$\mathbf{g}$	gravity, 9.806 65	m s^{-2}
h	heat transfer coefficient	$\text{W m}^{-2} \text{K}^{-1}$
H	enthalpy	J
$\hat{H}$	enthalpy per unit mass	J kg^{-1}
H_i	Henry's law constant for the i^{th} species	Pa
$\hat{H}_i$	enthalpy per unit mass of the i^{th} species	J kg^{-1}
$\bar{H}_i$	partial specific enthalpy of the i^{th} species in a mixture	J kg^{-1}
$\bar{\bar{H}}_i$	partial molar enthalpy of the i^{th} species in a mixture	J kmol^{-1}
$\underline{H}_i$	molar enthalpy of the i^{th} species in pure form	J kmol^{-1}
$\underline{H}_i^\circ$	standard $\underline{H}_i$	J kmol^{-1}
$\mathbf{H}$	Hessian matrix	
$\mathbf{I}$	identity matrix	
$\mathbf{j}_i$	diffusive mass flux of the i^{th} species	$\text{kg m}^{-2} \text{s}^{-1}$
$\bar{\mathbf{j}}$	vector of $\mathbf{j}_i$	$\text{kg m}^{-2} \text{s}^{-1}$
$\mathbf{J}$	Jacobian matrix	
$\mathbf{J}_i$	diffusive molar flux of the i^{th} species	$\text{kmol m}^{-2} \text{s}^{-1}$
$\bar{\mathbf{J}}$	vector of $\mathbf{J}_i$	$\text{kmol m}^{-2} \text{s}^{-1}$
k	reaction rate coefficient	as per reaction
k	thermal conductivity	$\text{W m}^{-1} \text{K}^{-1}$
k_0	frequency factor	as per reaction
k_c	mass transfer coefficient	m s^{-1}
K	equilibrium constant of a chemical reaction	
$\mathbf{L}$	lower triangular matrix	
m	mass	kg
m_i	mass of the i^{th} species	kg
M_i	molecular weight of the i^{th} species	kg kmol^{-1}
N_c	number of components or species	

Symbol	Description	Units
N_i	number of moles of the i^{th} species	
N_r	number of chemical reactions	
$\hat{\mathbf{n}}, \tilde{\mathbf{n}}, \underline{\mathbf{n}}$	unit vectors	
p_i	partial pressure of the i^{th} species	Pa
P	pressure	Pa
P_c	critical pressure	Pa
$\mathbf{p}$	momentum	kg m s^{-1}
q	rate of heat transfer	J s^{-1}
q_i	the i^{th} component of conductive heat flux	$\text{J m}^{-2} \text{s}^{-1}$
Q	heat, i.e., energy in transit	J
$\mathbf{q}$	conductive heat flux	$\text{J m}^{-2} \text{s}^{-1}$
r	correlation coefficient	
r	rate of reaction	$\text{kg(kmol)} \text{m}^{-3} \text{s}^{-1}$
r	radial direction in cylindrical and spherical coordinates	m
r^2	coefficient of determination	
R	universal gas constant, $8.314\,46 \times 10^3$	$\text{J kmol}^{-1} \text{K}^{-1}$
$r_{\text{gen},i}$	mass rate of i^{th} species generated per unit volume	$\text{kg m}^{-3} \text{s}^{-1}$
$R_{\text{gen},i}$	molar rate of i^{th} species generated per unit volume	$\text{kmol m}^{-3} \text{s}^{-1}$
s_y	standard deviation in values of y	of y
S	entropy	J K^{-1}
$\hat{S}_i$	entropy per unit mass of the i^{th} species	$\text{J K}^{-1} \text{kg}^{-1}$
S	sum of the squared errors from the average of y in a population	of y^2
t	time	s
T	temperature	K, °C
T_c	critical temperature	°C
U	internal energy	J
$\hat{U}$	internal energy per unit mass	J kg^{-1}
$\hat{U}_i$	internal energy per unit mass of the i^{th} species	J kg^{-1}
$\mathbf{U}$	upper triangular matrix	
v	magnitude of velocity	m s^{-1}
v_i	the i^{th} component of $\mathbf{v}$, or average velocity along the x_i -direction	m s^{-1}

Symbol	Description	Units
V	volume	m^3
$\bar{V}$	molar volume	$\text{m}^3 \text{ kmol}^{-1}$
$\hat{V}$	specific volume	$\text{m}^3 \text{ kg}^{-1}$
$\hat{V}_i$	specific volume of the i^{th} species	$\text{m}^3 \text{ kg}^{-1}$
$\mathbf{v}$	mass average velocity	m s^{-1}
$\tilde{\mathbf{v}}$	molar average velocity	m s^{-1}
W_s	shaft work	J
$\dot{x}$	change of x per unit time	$x\text{-units s}^{-1}$
x_{ext}	amount of x from external source	of x
x_{gen}	generated amount of x	of x
X	extent of chemical reaction	
$\tilde{X}$	extent of chemical reaction per unit volume	m^{-3}
$\mathbf{x}^{\top}$	transpose of $\mathbf{x}$ (vector or matrix)	
$\hat{\mathbf{x}}_i$	unit vector along the x_i -direction	
$\ \mathbf{x}\ $	norm or magnitude of $\mathbf{x}$ (vector or matrix)	
z	axial direction in cylindrical coordinates	m

Greek Symbols

$\dot{\gamma}$	rate-of-strain tensor	s^{-1}
δ_{ij}	Kronecker delta	
δQ	net Q involved in differential changes, dU and dS	J
δ	unit dyadic (unit tensor)	
ΔH_i°	standard heat of formation of the i^{th} species	J kmol^{-1}
ΔH_r	heat of reaction	J kmol^{-1}
ΔH_r°	standard heat of reaction	J kmol^{-1}
Δx	small amount of, or change in x	of x
$\Delta[x]$	loss of x from a system through its ports	of x
∇	gradient operator (a vector)	
η	Non-Newtonian viscosity	Pa s
θ	θ -direction in cylindrical and spherical coordinates	$\text{rad}, ^{\circ}$
κ	dilatational viscosity	Pa s
μ	viscosity	Pa s

Symbol	Description	Units
ν_i	stoichiometric coefficient of i^{th} species in a chemical reaction	
π	molecular stress tensor	Pa
Π	dimensionless number	
ρ	density, mass concentration	kg m^{-3}
ρ_i	density, mass concentration of the i^{th} species	kg m^{-3}
$\tau_{ij}, \pi_{ij}, \phi_{ij}$	the j^{th} component of stress acting on the i^{th} area component	Pa
τ	time period	s
$\boldsymbol{\tau}$	viscous stress tensor	Pa
ϕ	ϕ -direction in spherical coordinates	rad, $^{\circ}$
$\boldsymbol{\phi}$	overall stress tensor	Pa
$\hat{\Phi}$	potential energy per unit mass	J kg^{-1}
ω	mass fraction	
ω	acentric factor	
$\boldsymbol{\omega}$	vorticity tensor	s^{-1}

1

Introduction

Process modeling and simulation is our intellectual endeavor to explain real-world processes, foresee their effects, and improve them to our satisfaction. Using foundational rules and the language of mathematics, we describe a process, i.e., develop its model. Depending on what needs to be known, we pose the model as a problem. Its solution provides the needed information, thereby simulating the process as it would unfold in the real world.

This chapter lays the groundwork for process modeling and simulation. We explain the basic concepts, and introduce the involved terminology in a methodical manner. Our starting point is the definition of a system.

1.1 System

A **system** is defined as a set of one or more units relevant to the knowledge that is sought. Eventually, that knowledge is obtained as system characteristics, and their behavior in time and space.

We specify a system based on what we want to know about it. Consider for example a well-mixed reactor shown in Figure 1.1 below. The reactor is fed certain amounts of non-volatile species A and B in a liquid phase. Inside the reactor, the species react to form a non-volatile liquid product C. Given that we wish to know the concentration of C in the liquid phase,

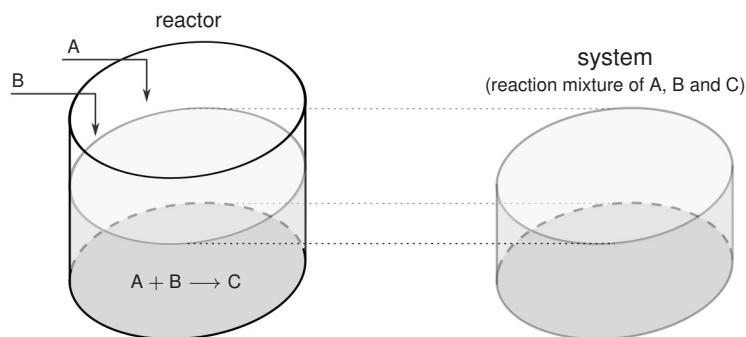


Figure 1.1 A system of reaction mixture in a reactor

the system is precisely the reaction mixture as shown in the figure. Anything not relevant – such as the reactor wall, and the vapor phase over the mixture – is not included in the system.

Everything external to a system constitute its **surroundings**. A region of zero thickness in the system separating it from the surroundings is called the **boundary**. Any interaction between a system and its surroundings requiring physical contact takes place across the boundary. For instance, this interaction could be transfer of mass.

For the above system of reaction mixture, the surroundings comprise the reactor wall, and the vapor phase over the reaction mixture. The system boundary is made of the surface of mixture in contact with (i) the reactor wall, and (ii) air. An example of interaction between this system and its surroundings is the evaporation of the species from the mixture through its top surface (i.e., across the boundary) to air.

1.1.1 Uniform System

A system is said to be **uniform** or homogenous if it stays the same, regardless of any recombination of its parts. As an illustration, consider a system in the shape of a cube. We split it into a set of arbitrary number of small cubes of identical size. Next, we recombine them in all possible ways to form the initial cube. The system would be uniform if each recombination (for each set of small cubes) resulted in the original system. If even one recombination produced a different system, the system would be non-uniform or heterogenous.

1.1.2 Properties of System

We associate a system with the properties it possesses. By **property** we mean any measurable characteristic that is related to matter, energy, space, or time. Some common examples of property are mass, concentration, temperature, enthalpy, pressure, volume, diffusivity, etc. With the help of the properties of a system, we can keep track of it, and compare it to other systems of interest.

System properties can be classified into intensive and extensive properties. Given a uniform system, an **extensive property** is proportional to the size or extent of the system. Examples of extensive properties are mass and volume. Thus, the mass of a fraction (say, $1/10^{\text{th}}$) of a system is the same fraction ($1/10^{\text{th}}$) of the total mass of the system. On the other hand, an **intensive property** of a uniform system does not depend on its size or extent, and is the same, i.e., has the same value, for each part of the system. Examples of intensive property are concentration, temperature and pressure.

Thus, if a uniform system is at a certain pressure then any part of the system is at the same pressure. Equivalently, if all intensive properties of a system do not vary then the system is uniform. An example is the reaction mixture of Figure 1.1 on the previous page. The mixture has

1. the same value of concentration of the species A throughout the system (or uniform concentration of A),
2. uniform concentration of each of the remaining species B and C, and
3. a similar uniformity of any other intensive property, e.g., temperature.

For a non-uniform system, one or more intensive properties vary within the system. More precisely, the properties vary with space inside the system. For example, if the reaction mixture of Figure 1.1 on p. 1 were not well-mixed then the species concentrations, and temperature would not be the same throughout the mixture. In that situation, the mixture would be a non-uniform system.

1.1.3 Classification of System

Based on whether or not the intensive properties of a system vary with space, we can call a system uniform, or non-uniform. A non-uniform system is also known as a **distributed-parameter** system. If the intensive properties have variations that are small enough to be insignificant then the system may be considered as a uniform system by taking into account the space-averaged values of intensive properties. This system is then called a **lumped-parameter** system. Thus, the reaction mixture of Figure 1.1 would be a lumped-parameter system if the temperature varied slightly within the mixture but the latter was considered to be at some average temperature throughout.

Depending on the degree of separation from the surroundings, systems are also classified into open, closed and isolated systems. An **open system** allows exchanges of mass and energy with the surroundings. On the other hand, a **closed system** allows only the exchange of energy. An **isolated system** does not allow any exchange of mass, or energy.

Thus, the reaction mixture shown in Figure 1.1 would be an open system if it were heated, or cooled, and the species volatilized to the air. The mixture would be a closed system if it were heated, or cooled, but the top surface were covered to prevent any escape of the species. With the top surface covered and perfectly insulated along with the reactor vessel, the mixture would become an isolated system.

1.1.4 Model

The reason we conceive a system is that we want to learn about it. This learning is synonymous with figuring out relations between system properties. These relations give rise to a model. In mathematical terms, a **model** is a set of equations that involve system properties. A simple example of a model is the ideal gas law,

$$P\bar{V} = RT$$

where P , $\bar{V}$ and T are, respectively, the pressure, molar volume, and temperature (properties) of a system at sufficiently low pressure, and R is the universal gas constant. The properties in the model do not depend on time, and the associated system is unchanging or at equilibrium to be exact.

When a system undergoes a change, it appears as an effect on one or more of the system properties. This is where the notion of process emerges.

1.2 Process

A **process** is defined as a set of activities taking place in a system, and resulting in certain effects on its properties. A process is either natural, or man-made. Natural processes – such

as blood circulation in a human body, photosynthesis in plants, or planetary motion in the solar system – happen without human volition, and are responsible for certain effects on the associated systems. For instance, the process of blood circulation in a human body primarily involves pulmonary circulation between the heart and lungs, and systemic circulation between the heart and the rest of the body excluding lungs. This process results in, among other things, specific levels of oxygen and carbon dioxide concentrations in different parts of the body, i.e., the system.

Man-made processes on the other hand are contrived by human beings to produce results of utility. Common examples include processes to produce various synthetic chemicals and materials, to extract and refine natural resources, to treat gaseous emissions and wastewaters, and to control climate in living spaces. The reactor shown in Figure 1.1 on p. 1 enables a man-made process. It involves a chemical reaction between the reactants A and B, which results in the product C.

1.2.1 *Classification of Processes*

Based on how system properties change with time, processes are classified into unsteady state and steady state processes. A process that changes any property of a system with time is called an **unsteady state process**, and the system is called unsteady. Thus, the process of chemical reaction in the reactor of Figure 1.1 is an unsteady state process. It causes the reactant and product concentrations to, respectively, decrease and increase with time.

In contrast, a **steady state process** does not result in any change in system properties with time. The reason is that any decrease in a property gets instantaneously offset by an equal increase in the same.

A simple example of a steady state process is the filling of a tank with a non-volatile liquid, and its simultaneous drainage from the tank at the same flow rate as that of filling. Here, the system and the property of interest are, respectively, the liquid and its volume inside the tank. Due to equal inflow and outflow rates, the volume does not change with time.

Another example of a steady state process is a chemical reaction that continues after a transient period in a constant volume stirred tank reactor with constant flow rates of incoming reactants, and the outgoing mixture of residual reactants and products. In this process, the species concentrations, and the volume of the reaction mixture inside the tank do not change with time.

Steady State versus Equilibrium

It may be noted that the time derivatives of all properties are zero in a system under the influence of a steady state process. That is also true for a system at equilibrium. But there is a subtle difference. A system at equilibrium does not sustain any process since the gradients (i.e., spatial derivatives) of all potentials in the system have decayed to zero. For this reason, the properties in such a system do not have any propensity to change. However, the properties in a system under a steady state process undergo simultaneous increments and decrements in such a way that the net change in each property is zero. In other words, the properties end up being time-invariant. If a steady state process is stopped then the properties of the system would begin to change with time until the system eventually arrived at equilibrium.

1.2.2 Process Model

A **process model** is a set of equations or relations involving properties of the system under the influence of a process. The properties represent observable occurrences or phenomena classifiable into the categories of (i) initiating events, (ii) specifications, and (iii) effects. Thus, a process model is a scheme according to which a process with given specifications and initiating events would generate effects in the system.

Figure 1.2 below shows the concept of the model as a triangle, each side of which represents the relations between the two ends or vertices denoting the categories. If we know these relations, i.e., the process model, we can use it to unravel one or more unknown phenomena when the remaining ones are known. And we can do this without having to execute the process in the real world. Of course, the better the process model the better is our ability to explain the involved phenomena.

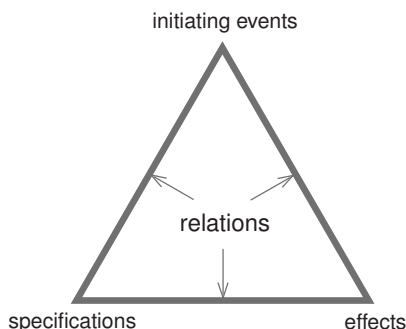


Figure 1.2 Concept of a process model

In particular, we can predict the effects of a process based on its model, and the knowledge of initiating events, and specifications. As a matter of fact, we can predict the effects for different initiating events, and specifications. Doing that enables us to isolate desirable effects, and the related initiating events, and specifications. We can then apply the latter two in the real world to achieve the desirable effects from the process. This exercise basically is process optimization and control.

Referring to Figure 1.1 on p.1, if we know the model of the process taking place in the reaction mixture (system) then we can predict the species concentrations (effects) corresponding to different initial concentrations of A and B (initiating events), and reaction temperatures (specifications). From the predictions over a given time of reactor operation, we can pick out a desirable effect, say, the maximum concentration of C, and the related (optimal) set of initial concentrations, and reaction temperature. Based on this exercise, we can then expect to achieve the maximum concentration of C in the real world by feeding the reactor with A and B such that the mixture has the optimal initial concentrations, and is maintained at the optimal temperature for the given operation time.

In general, using a process model we can predict initiating events, specifications, or effects in the system. The prediction requires the following courses of action:

1. Process modeling – the development of a process model, and
2. Process simulation – the solution or simulation of the model, which mimics the process as it would unfold in the real world.

Types of Process Models

Process models can be categorized based on the process being represented. Thus, a **steady state model** represents a steady state process, and has no time derivatives. An **unsteady state model** represents a unsteady process, and involves one or more time derivatives.

Based on the nature of system properties, a process model may be a **lumped-parameter model**, or **distributed-parameter model**. The former involves uniform properties while the latter has at least one property that varies with space.

Based on the type of equations involved, process models are also classified into algebraic, differential, or differential-algebraic models. Moreover, if all involved equations are linear then the process model is called **linear**. Otherwise, the model is called **non-linear**.

1.3 Process Modeling

Process modeling is essentially an exercise that involves relating together the properties of a system influenced by a process. Represented as mathematical symbols, the properties are associated with each other using relevant relations under one or more assumptions. The outcome is a set of mathematical equations, which is a process model. The system properties – and through them, the initiating events, specifications and effects of the process – are expected to abide by the model thus developed. The model is therefore said to represent or describe the process.

As an example, consider the reaction process in the reactor shown in Figure 1.1 on p. 1. The involved properties are the concentrations of A, B and C, which can be represented as c_A , c_B and c_C , respectively, with initial values $\bar{c}_A$, $\bar{c}_B$ and $\bar{c}_C = 0$. If we assume that during the process the reaction mixture

1. is well-mixed,
2. has constant volume, and
3. is at constant temperature

then based on certain relations, the concentrations can be associated with each other at any time t through the following equations:

$$\frac{dc_i}{dt} = -r, \quad c_i(0) = \bar{c}_i; \quad i = A, B \quad (1.1)$$

$$\frac{dc_C}{dt} = r, \quad c_C(0) = 0 \quad (1.2)$$

$$\text{where} \quad r = k_0 \exp\left(-\frac{E}{RT}\right) c_A^a c_B^b \quad (1.3)$$

where (i) r , k_0 , E and T are, respectively, the rate, frequency factor, activation energy, and temperature of the reaction, (ii) a and b are reaction-specific parameters, and (iii) R is the universal gas constant.

The above set of equations is the model of the reaction process taking place in the reactor. This model relates the initiating events, specifications and effects of the process with each other [see Figure 1.2, p. 5]. The initiating events are represented by the initial concentrations, $\bar{c}_A$, $\bar{c}_B$ and $\bar{c}_C$. The specifications are the values of a , b , k_0 , E , R and T . Finally, the process effects at any time t , are represented by the concentrations $c_A(t)$, $c_B(t)$ and $c_C(t)$. Changes in these properties, or, equivalently, the phenomena they represent, are expected to be in accordance with the model. Thus, for a given set of initiating events, and specifications, we expect to find the process effects from the model.

1.3.1 Relations

Relations are the ground rules that are used in process modeling to interlink the properties of a system under the influence of a process. These rules comprise **fundamental relations** based on scientific laws, and **constitutive relations**. The rules manifest as equations that constitute process models.

A scientific law is a statement that is generally accepted to be true about one or more phenomena on the basis of repeated experiments and observations. A common example is the law of conservation of mass. This law states that if a system does not exchange mass, or energy (a form of mass) with the surroundings then the mass of the system stays the same, or is conserved. By applying this law to an individual species, and accounting for its generation, or consumption in a system, we derive a fundamental relation called the mass balance of species.

A **constitutive relation** on the other hand is a rule that is true for systems with a specific makeup or constitution. An example is Newton's law of viscosity, which relates shear stress to strain for a system that is a Newtonian fluid.

In the model given by Equations (1.1)–(1.3) on the previous page, the last equation is a constitutive relation. It is valid for the specific reaction mixture of species A, B and C. The two differential equations are the mass balances of the species.

1.3.2 Assumptions

Assumptions of a process model are the necessary conditions that must be satisfied during the execution of the process in order for it to be represented by the model. In equivalent terms, if any assumption of a model is not satisfied during the execution of the process then the latter is not represented by the model.

For example, the assumptions of the model given by Equations (1.1)–(1.3) are perfect mixing, and constant volume as well as temperature. If any of these assumptions is not satisfied during the reaction process then it would become different from the process 'assumed' by the model, and would not be represented by the model. For instance, if mixing is not sufficiently close to perfect then there would be spatial changes in the concentrations of species, and temperature. Consequently, the reaction process would get dominated by diffusion, convection of species, and heat transfer, which are not accounted for by the model.

The above example shows that the assumption of perfect mixing excludes from the model the sub-processes of diffusion, convection and heat transfer in the reaction mixture. In general, an assumption implies the exclusion of one or more sub-processes from the model. Hence, an assumption restricts the model to a specific type of process, and in doing so simplifies the model. Note that the assumption of perfect mixing of the reaction mixture markedly simplifies the model by obviating the need for the diffusive fluxes of the species, and partial differential equations of momentum and heat transfer. Because of this assumption, the concentrations of species, and temperature can be considered uniform throughout the reaction mixture.

Making an assumption is justifiable under one or more of the following circumstances:

1. It is realistic to satisfy the assumption during the execution of the process.
2. Any sub-process excluded by the assumption has negligible influence on the overall process.
3. Without the assumption, any sub-process that should be included in the model can increase its complexity unnecessarily.

Thus, the assumption of perfect mixing can be justified for the reaction process utilizing a good agitator that sufficiently homogenizes the reaction mixture so that the sub-processes of diffusion, convection and heat transfer can be excluded from the model. Dropping the assumption would make the model very complex. Instead it is far more practical to retain the assumption, and satisfy it by having a good agitator for the reaction process.

Remarks

An assumption limits the scope of a model by making it ignore certain sub-processes or details. Therefore, it follows that the fewer the assumptions the more detailed the model. A model with no assumptions would be the most comprehensive, or perfect model with no limitations whatsoever. This of course is not possible.

As a consequence, no model can be derived without an assumption. It may be noted that some assumptions are implied, and not mentioned explicitly. For example, the model for the reaction process given by Equations (1.1)–(1.3) on p. 6 is based on the assumption that there is no intermediate reaction, or product.

1.3.3 Variables and Parameters

A **variable** is any property that could vary with time during the execution of a process in a system. On the other hand, a **parameter** is a property that is fixed or specified. For the reaction process modeled by Equations (1.1)–(1.3), variables are species concentrations, and parameters are the initial concentrations, and process specifications. From the standpoint of a process model, any symbol whose value is not fixed or specified denotes a variable. The remaining symbols represent parameters.

Note that for a system that is not isolated, a variable, or parameter may be a property of mass and (or) energy exchanged with the surroundings.