

DIFFUSION AND MASS TRANSFER

JAMES S. VRENTAS
CHRISTINE M. VRENTAS



CRC Press
Taylor & Francis Group

DIFFUSION AND MASS TRANSFER

JAMES S. VRENTAS
CHRISTINE M. VRENTAS



CRC Press

Taylor & Francis Group

Boca Raton London New York

CRC Press is an imprint of the www.tandf.co.uk
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2013 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works

Printed in the United States of America on acid-free paper
Version Date: 20120820

International Standard Book Number: 978-1-4665-1568-0 (Hardback)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (<http://www.copyright.com/>) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Library of Congress Cataloging-in-Publication Data

Vrentas, James S.
Diffusion and mass transfer / James S. Vrentas and Christine M. Vrentas.
pages cm
Includes bibliographical references and index.
ISBN 978-1-4665-1568-0 (hardcover : alk. paper)
1. Diffusion. 2. Mass transfer. I. Vrentas, Christine Mary Jarzebski, 1953- II. Title.

QD543.V735 2013
530.4'75--dc23

2012024819

Visit the Taylor & Francis Web site at
<http://www.taylorandfrancis.com>

and the CRC Press Web site at
<http://www.crcpress.com>

Contents

List of Figures	xi
List of Tables	xvii
Preface.....	xix
Authors	xxi
1. Introduction	1
1.1 Generalized Transport Phenomena Approach to Problem Analysis	1
1.2 General Content.....	3
2. Conservation Laws and Field Equations	5
2.1 Concentrations, Velocities, and Fluxes.....	5
2.2 Thermodynamics of Purely Viscous Fluid Mixtures	9
2.3 Conservation of Mass for a One-Component System.....	13
2.4 Conservation of Mass for a Mixture	14
2.5 Modification of Field Equations for Mass Transfer.....	16
2.6 Conservation of Linear Momentum for One-Component Systems	21
2.7 Conservation of Linear Momentum for a Mixture	25
2.8 Conservation of Moment of Momentum for One-Component Systems.....	27
2.9 Conservation of Moment of Momentum for a Mixture	29
2.10 Strategies for the Solution of Mass Transfer Problems.....	30
3. Boundary Conditions	33
3.1 Definitions.....	33
3.2 Jump Balances for Mass Conservation	34
3.3 Jump Balances for Linear Momentum Conservation	36
3.4 Postulated Boundary Conditions at Phase Interfaces	37
3.5 Boundary Conditions in the Absence of Mass Transfer	38
3.6 Utilization of Jump Balances	41
3.7 Additional Comments on Boundary Conditions	45
3.8 Boundary Conditions and Uniqueness of Solutions.....	50
4. Constitutive Equations	55
4.1 Constitutive Principles	55
4.1.1 Principle of Determinism	56
4.1.2 Principle of Equipresence	56
4.1.3 Principle of Local Action	56
4.1.4 Principle of Material Frame Indifference	58
4.1.5 Principle of Material Invariance	64
4.1.6 Principle of Dissipation (Entropy Inequality).....	65
4.2 First-Order Theory for Binary Systems	68
4.3 Combined Field and Constitutive Equations for First-Order Binary Theory	73
4.4 First-Order Theory for Ternary Systems	77
4.5 Special Second-Order Theory for Binary Systems.....	80
4.6 Viscoelastic Effects in Flow and Diffusion.....	85

4.6.1	Deborah Number	86
4.6.2	Constitutive Expression for the Extra Stress for a First-Order Fluid	88
4.6.3	Viscoelastic Diffusion Flux	91
4.7	Validity of Constitutive Equations	93
5.	Parameters in Constitutive Equations.....	99
5.1	General Approach in Parameter Determination	99
5.2	Diffusion in Polymer–Solvent Mixtures.....	100
5.3	Diffusion in Infinitely Dilute Polymer Solutions	104
5.4	Diffusion in Dilute Polymer Solutions.....	107
5.5	Diffusion in Concentrated Polymer Solutions – Free-Volume Theory for Self-Diffusion.....	111
5.5.1	Volumetric Behavior for Rubbery Polymer–Solvent Systems	112
5.5.2	Volumetric Behavior for Glassy Polymer–Solvent Systems.....	116
5.5.3	Formulation of Equations for Self-Diffusion Coefficients	119
5.5.4	Formulation of Predictive Method for D_1	121
5.5.5	Predictions of D_1	123
5.5.6	Self-Diffusion for Ternary Systems	127
5.6	Diffusion in Concentrated Polymer Solutions – Mutual Diffusion Process.....	128
5.7	Diffusion in Crosslinked Polymers	137
5.8	Additional Properties of Diffusion Coefficients.....	140
6.	Special Behaviors of Polymer–Penetrant Systems	149
6.1	Volumetric Behavior of Polymer–Penetrant Systems	149
6.2	Sorption Behavior of Polymer–Penetrant Systems.....	154
6.3	Antiplasticization	166
6.4	Nonequilibrium at Polymer–Penetrant Interfaces	169
7.	Mathematical Apparatus.....	175
7.1	Basic Definitions.....	175
7.2	Classification of Second-Order Partial Differential Equations	179
7.3	Specification of Boundary Conditions	182
7.4	Sturm–Liouville Theory.....	184
7.5	Series and Integral Representations of Functions.....	189
7.6	Solution Methods for Partial Differential Equations.....	193
7.7	Separation of Variables Method.....	194
7.8	Separation of Variables Solutions	196
7.9	Integral Transforms	204
7.10	Similarity Transformations	212
7.11	Green’s Functions for Ordinary Differential Equations.....	214
7.12	Green’s Functions for Elliptic Equations	222
7.13	Green’s Functions for Parabolic Equations.....	229
7.14	Perturbation Solutions.....	235
7.15	Weighted Residual Method	237
8.	Solution Strategy for Mass Transfer Problems	241
8.1	Proposed Solution Methods	241
8.2	Induced Convection.....	244

9. Solutions of a General Set of Mass Transfer Problems	249
9.1 Mixing of Two Ideal Gases	249
9.2 Steady Evaporation of a Liquid in a Tube.....	255
9.3 Unsteady-State Evaporation.....	258
9.4 Analysis of Free Diffusion Experiments	262
9.5 Dissolution of a Rubbery Polymer.....	265
9.6 Bubble Growth from Zero Initial Size.....	273
9.7 Stability Behavior and Negative Concentrations in Ternary Systems	277
9.8 Analysis of Impurity Migration in Plastic Containers	282
9.9 Efficiency of Green’s Function Solution Method	286
9.10 Mass Transfer in Tube Flow.....	288
9.11 Time-Dependent Interfacial Resistance	294
9.12 Laminar Liquid Jet Diffusion Analysis	299
9.13 Analysis of the Diaphragm Cell	300
9.14 Dissolved Organic Carbon Removal from Marine Aquariums	304
9.15 Unsteady Diffusion in a Block Copolymer.....	308
9.16 Drying of Solvent-Coated Polymer Films.....	314
9.17 Flow and Diffusion Past a Flat Plate with Solid Dissolution.....	318
9.18 Gas Absorption in Vertical Laminar Liquid Jets.....	324
9.19 Utilization of Polymers in Drug Delivery	329
9.20 Gas Absorption and Diffusion into a Falling Liquid Film	336
10. Perturbation Solutions of Mass Transfer Moving Boundary Problems	339
10.1 Dissolution of a Plane Surface of a Pure Gas Phase.....	340
10.2 Bubble Dissolution	347
10.3 Singular Perturbations in Moving Boundary Problems	350
10.4 Dropping Mercury Electrode.....	359
10.5 Sorption in Thin Films	364
10.6 Numerical Analysis of Mass Transfer Moving Boundary Problems	370
11. Diffusion and Reaction	373
11.1 Design of a Tubular Polymerization Reactor	373
11.2 Transport Effects in Low-Pressure CVD Reactors	381
11.3 Solution of Reaction Problems with First-Order Reactions	385
11.4 Plug Flow Reactors with Variable Mass Density	393
11.5 Bubble Dissolution and Chemical Reaction	395
11.6 Danckwerts Boundary Conditions for Chemical Reactors.....	398
12. Transport in Nonporous Membranes	407
12.1 Assumptions Used in the Theory for Membrane Transport.....	407
12.2 Steady Mass Transport in Binary Membranes	412
12.3 Steady Mass Transport in Ternary Membranes	414
12.3.1 Gas Separations.....	416
12.3.2 Solvent Drag	418
12.3.3 Osmotic Effects.....	419
12.4 Unsteady Mass Transport in Binary Membranes	422
12.5 Phase Inversion Process for Forming Asymmetric Membranes.....	427
12.6 Pressure Effects in Membranes.....	431

13. Analysis of Sorption and Desorption	433
13.1 Derivation of a Short-Time Solution Form for Sorption in Thin Films	435
13.2 Sorption to a Film from a Pure Fluid of Finite Volume	437
13.3 A General Analysis of Sorption in Thin Films	442
13.4 Analysis of Step-Change Sorption Experiments	448
13.5 Integral Sorption in Glassy Polymers	450
13.6 Integral Sorption in Rubbery Polymers	461
13.7 Oscillatory Diffusion and Diffusion Waves	466
14. Dispersion and Chromatography	473
14.1 Formulation of Taylor Dispersion Problem	473
14.2 Dispersion in Laminar Tube Flow for Low Peclet Numbers	478
14.3 Dispersion in Laminar Tube Flow for Long Times	483
14.4 Dispersion in Laminar Tube Flow for Short Times	486
14.5 Analysis of an Inverse Gas Chromatography Experiment	490
15. Effects of Pressure Gradients on Diffusion: Wave Behavior and Sedimentation	499
15.1 Wave Propagation in Binary Fluid Mixtures	499
15.2 Hyperbolic Waves	503
15.3 Dispersive Waves	505
15.4 Time Effects for Parabolic and Hyperbolic Equations	507
15.5 Sedimentation Equilibrium	511
16. Viscoelastic Diffusion	515
16.1 Experimental Results for Sorption Experiments	515
16.2 Viscoelastic Effects in Step-Change Sorption Experiments	524
16.3 Slow Bubble Dissolution in a Viscoelastic Fluid	530
17. Transport with Moving Reference Frames	545
17.1 Relationships between Fixed and Moving Reference Frames	545
17.2 Field Equations in Moving Reference Frames	548
17.3 Steady Diffusion in an Ultracentrifuge	552
17.4 Material Time Derivative Operators	554
17.5 Frame Indifference of Material Time Derivatives	557
17.6 Frame Indifference of Velocity Gradient Tensor	560
17.7 Rheological Implications	562
Appendix: Vector and Tensor Notation	565
A.1 General Notation Conventions	565
A.2 Vectors	566
A.3 Tensors	569
A.4 Results for Curvilinear Coordinates	576
A.5 Material and Spatial Representations	578
A.6 Reynolds' Transport Theorem	583
References	587
Index	599