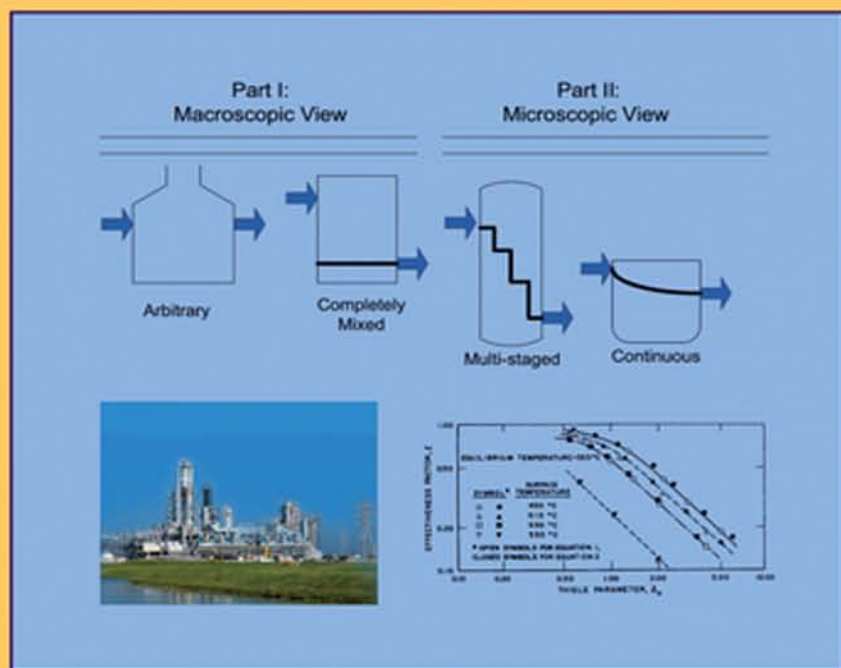


Principles of Chemical Engineering Practice

George DeLancey



WILEY

PRINCIPLES OF CHEMICAL ENGINEERING PRACTICE

PRINCIPLES OF CHEMICAL ENGINEERING PRACTICE

GEORGE DELANCEY

WILEY

Cover image reprinted with permission of BASF: The Chemical Company. All rights reserved. Graph image reprinted with permission of Elsevier, Kovenklioglu and DeLancey, 1979.

Copyright © 2013 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.

Published simultaneously in Canada.

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, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at <http://www.wiley.com/go/permission>.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

Library of Congress Cataloging-in-Publication Data:

DeLancey, George, 1940-

Principles of chemical engineering practice / George DeLancey.

pages cm

Includes index.

ISBN 978-0-470-53674-2 (hardback)

1. Chemical engineering. I. Title.

TP155.D425 2012

660—dc23

2012047056

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

This book is dedicated to my darling wife, Lynn, who nurtured every page and every moment with her generosity, encouragement, and unfaltering support.

CONTENTS

PREFACE	xix
PART I MACROSCOPIC VIEW	1
1 Chemical Process Perspective	3
1.1 Some Basic Concepts in Chemical Processing,	3
1.2 Acrylic Acid Production,	5
1.2.1 Catalysis,	7
1.2.2 Feed Section—Pumps and Compressors,	8
1.2.3 Reactor Section—Reactor, Heat Exchangers, and Gas Absorption,	12
1.2.4 Downstream Processing—Distillation and Extraction,	16
1.2.5 Storage,	19
1.2.6 Safety,	20
1.2.7 Overview of Typical Process,	20
1.3 Biocatalytic Processes—Enzymatic Systems,	21
1.3.1 Biotransformation,	22
1.3.2 Examples of Industrial Processes,	23
1.3.3 Alkyl Glucosides,	23
1.4 Basic Database,	24
Problems,	26
2 Macroscopic Mass Balances	28
2.1 Chemical Processing Systems,	28
Example 2.1-1: Active Units in Acrylic Acid Separation Train,	29
2.1.1 Input and Output Rates of Flow,	29
2.1.1.1 Some Equations of State,	31
Example 2.1.1.1-1: Calculate the Molar Volume of Methane at -250°F ,	32
2.1.1.2 Mass Rate of Production,	36

- 2.2 Steady-State Mass Balances Without Chemical Reactions, 37
 - 2.2.1 Degrees of Freedom, 37
 - Example 2.2.1-1: Manufacture of Sugar, 39
 - Example 2.2.1-2: Air Separation Plant, 40
- 2.3 Steady-State Mass Balances with Single Chemical Reactions, 41
 - 2.3.1 Degrees of Freedom: Reaction Rate and Key Component, 42
 - Example 2.3.1-1: Production of Formaldehyde, 42
 - Example 2.3.1-2: Manufacture of Nitroglycerin, 44
- 2.4 Steady-State Mass Balances with Multiple Chemical Reactions, 46
 - 2.4.1 Degrees of Freedom and Reaction Extents, 46
 - Example 2.4.1-1: Mass Balance on Acrylic Acid Reactor R-301, 46
 - 2.4.2 Test for Independent Reactions, 47
 - Example 2.4.2-1: Independent Reactions in the Acrylic Acid System, 47
 - Example 2.4.2-2: Selection of Independent Reactions, 48
 - 2.4.3 Construction of Independent Reactions, 48
 - Example 2.4.3-1: Independent Reactions in the Acrylic Acid System, 49
- Problems, 50

3 Macroscopic Energy and Entropy Balances 53

- 3.1 Basic Thermodynamic Functions, 53
 - 3.1.1.1 Gibbs–Duhem Equation, 55
- 3.2 Evaluation of H and S for Pure Materials, 55
 - 3.2.1 Gases—Departure Functions, 55
 - Example 3.2.1-1: Departure Functions for H and S Using the Redlich–Kwong–Soave (RKS) Equation of State, 57
 - Example 3.2.1-2: Evaluation of an Enthalpy Change for Ethylene, 57
 - 3.2.2 Liquids and Solids, 58
 - Example 3.2.2-1: Enthalpy Change in the Injection Molding of Polystyrene, 59
- 3.3 Evaluation of H and S Functions for Mixtures, 59
 - 3.3.1 Ideal Gas Mixture, 59
 - 3.3.2 Ideal Solution, 60
 - 3.3.3 Nonideal Gas Mixtures, 60
 - 3.3.4 Nonideal Liquid Solutions: Heat of Solution, 60
 - Example 3.3.4-1: Partial Molar Enthalpies for HCl–Water System, 62
- 3.4 Energy Flows and the First Law, 62
 - 3.4.1 Degrees of Freedom, 63
- 3.5 Energy Balances Without Reaction, 64
 - 3.5.1 Utilization of the Second Law, 64
 - Example 3.5.1-1: Minimum Work Required for Isothermal Pumping of a Liquid, 64
 - 3.5.2 System Definition for Duty and Flow Rate Calculation, 64
 - Example 3.5.2-1: Calculation of Heat Duty and Stream Flow Rate for Exchanger E-309, 65
 - 3.5.3 Arbitrariness of Reference State for Unreactive Systems, 66
 - Example 3.5.3-1: Energy Balance on T-303 Extraction Unit. Feed Reference State, 66
 - Example 3.5.3-2: Calculation of Net Heat Duty for Distillation Tower T-304. Feed Reference State, 67

- 3.5.4 Mixing of Nonideal Liquids; Use of Partial Molar Quantities, 68
 - 3.5.4.1 Mixing Two Liquid Streams at Different Temperatures and Concentrations, 68
 - Example 3.5.4.1-1: Dilution of an HCl Mixture, 69
- 3.6 Energy Balances with Reaction-Ideal Solution, 70
 - 3.6.1 Single Reaction-Ideal Solution, 70
 - 3.6.1.1 Reference States for Reactive Systems—Standard Heat of Reaction, 71
 - 3.6.1.2 Heat Duty and Adiabatic Operation, 72
 - Example 3.6.1.2-1 Energy Balances on Methanol Oxidation Reactor, 72
 - 3.6.2 Single Reactions—Neutralization of Acids, 74
 - 3.6.3 Multiple Reactions, 74
 - Example 3.6.3-1: Heat Duty for Acrylic Acid Reactor R-301, 75
 - Example 3.6.3-2: Feed Temperature Required in Methanol Synthesis, 76
- 3.7 Entropy Balances, 77
 - 3.7.1 Macroscopic Entropy Balance, 78
 - 3.7.2 Thermodynamic Models, 78
 - Example 3.7.2-1: Thermodynamic Models for Membrane Outlet Temperature, 78
 - 3.7.3 The Availability and Lost Work, 80
 - 3.7.4 Process Efficiency, 81
 - 3.7.4.1 Heat Exchanger with Saturated Heat Source, 81
 - Example 3.7.4.1-1: Heating Water from 25 to 95°C Using Steam at 0.125 MPa (106°C), 82
 - 3.7.4.2 Distillation, 82
 - Example 3.7.4.2-1: Column Efficiency Evaluation for Acylation Reactor Effluent in Ibuprofen Manufacture, 83

Problems, 83

4 Macroscopic Momentum and Mechanical Energy Balances 86

- 4.1 Momentum Balance, 86
 - Example 4.1-1: Force on a U-Bend, 87
- 4.2 Mechanical Energy Balance, 88
- 4.3 Applications to Incompressible Flow Systems, 89
 - 4.3.1 Flow of Liquids in Piping Systems, 89
 - 4.3.1.1 Flow in Pipes—The Friction Loss Factor, 89
 - 4.3.1.2 Sudden Expansion—Calculation of Friction Loss Factor, 91
 - 4.3.1.3 Fittings and Valves, 91
 - 4.3.1.4 Pump Sizing, 91
 - Example 4.3.1.4-1: Power Required for P-301 A/B: Acrylic Acid Plant, 91
 - Example 4.3.1.4-2: NPSH Consideration in Pumping *o*-Dichlorobenzene from Temporary Storage to Process Storage, 93

Problems, 94

5 Completely Mixed Systems—Equipment Considerations 95

- 5.1 Mixing and Residence Time Distributions—Definitions, 95
 - Example 5.1-1: Production of *n*-Hexyl Glucoside—Residence Time and Reactor Volume, 96

- 5.2 Measurement and Interpretation of Residence Time Distributions, 97
- 5.3 Basic Aspects of Stirred Tank Design, 99
 - 5.3.1 Tank Dimensions and Impeller Specifications, 99
 - Example 5.3.1-1 Mixer Dimensions for T-303 Alternative Solution, 100
 - 5.3.2 Heuristics for Mixing and Agitation, 102
 - 5.3.2.1 Power Requirements, 102
 - 5.3.2.2 Gas–Liquid Systems, 103
 - 5.3.2.3 Liquid–Liquid Systems, 103
 - Example 5.3.2.3-1 Power Required for T-303 Alternative, 104
 - 5.3.2.4 Solid Suspensions, 104
 - Example 5.3.2.4-1 Sizing of Hexyl Glucoside Slurry Adsorber, 105
- Problems, 106

6 Separation and Reaction Processes in Completely Mixed Systems 107

- 6.1 Phase Equilibrium: Single-Stage Separation Operations, 107
- 6.2 Gas–Liquid Operations, 109
 - 6.2.1.1 Gas Absorption and Stripping, 109
 - 6.2.1.2 Flash Vaporization, 110
 - 6.2.2 Vapor–Liquid Equilibrium, 111
 - 6.2.2.1 Equation of State Method, 112
 - 6.2.2.2 Activity Coefficient Method, 115
 - 6.2.2.3 Summary of VLE Expressions and Data, 125
 - Example 6.2.2.3-1: Comparison of Several Methods for Obtaining the K Values for an Equimolar Mixture of Ethane, Propane, and n -Butane at -70°F and 300 psi, 125
 - 6.2.3 Gas Absorption and Stripping, 126
 - 6.2.3.1 Mass Balance—Constant Total Flows, 128
 - 6.2.3.2 Mass Balances—Nondiffusing Components, 130
 - Example 6.2.3.2-1: Acetone Absorption, 130
 - Example 6.2.3.2-2: Determine the Solvent Requirements for Single-Stage Version of Tower 302: Off-Gas Absorber in Acrylic Acid Process, 132
- 6.3 Flash Vaporization, 133
 - 6.3.1 Mass Balances, 133
 - 6.3.2 Energy Balance, 134
 - 6.3.3 Equilibrium, 134
 - 6.3.4 Common Problem Specifications, 134
 - 6.3.5 Distribution Function—Limitations, 135
 - 6.3.6 Bounds on Bubble and Dew Points, 135
 - 6.3.7 Solution for $\mathcal{N}^{(V)}/\mathcal{N}^{(F)} = 0$, P —Bubble-Point Temperature, 135
 - Example 6.3.7-1: Calculate the Bubble Point of the Following Mixture at 2 atm, 136
 - Example 6.3.7-2: Saturation Temperature for IPA–Water System, 136
 - 6.3.8 Solution: for $\mathcal{N}^{(V)}/\mathcal{N}^{(F)} = 1$, P Specified: Dew-Point Temperature, 137
 - Example 6.3.8-1: Calculate the Dew Point of the Mixture in the Preceding Example, 137
 - Example 6.3.8-2: Calculate the Dew Point of an Equimolar Mixture of Propylene and Isobutane at 20 atm Assuming an Ideal Liquid and Application of the Peng–Robinson Equation of State for the Vapor, 137

- Example 6.3.8-3: Repeat Example 6.3.8-2 but Use the DePriester Charts to Formulate the Equilibrium Relations, 139
- 6.3.9 Solution for T, P Specified: Isothermal Flash, 140
 - Example 6.3.9-1: Isothermal Flash Calculation, 141
 - Example 6.3.9-2: Flash of the Extract from the Acid Extractor (Tower 303), Stream 13, 141
- 6.3.10 General Isothermal Flash Iteration, 143
- 6.3.11 Sizing of Flash Drum, 143
 - Example 6.3.11-1: Size the Flash Drum for Example 6.3.9-1, 144
- 6.4 Liquid–Liquid Extraction, 145
 - 6.4.1 Equilibrium in Ternary Systems, 145
 - 6.4.1.1 Solvent Selection, 146
 - 6.4.1.2 Data Collection and Representation, 146
 - 6.4.1.3 Interpolation, 147
 - 6.4.2 Single-Stage Operation, 147
 - 6.4.2.1 Equipment, 147
 - 6.4.2.2 Mixture Rule, 148
 - 6.4.2.3 Mass Balances, 148
 - Example 6.4.2.3-1: Extraction of HAc from Chloroform with Water, 149
 - Example 6.4.2.3-2: T-303 Acid Extractor—Solvent Flow for Single Equilibrium Stage, 150
- 6.5 Adsorption, 151
 - 6.5.1 Adsorbents, 152
 - 6.5.2 Gas Adsorption, 154
 - 6.5.2.1 Equilibrium Relations for a Single Adsorbate, 156
 - 6.5.3 Liquid Adsorption, 157
 - 6.5.3.1 Equilibrium, 157
 - 6.5.3.2 Liquid Adsorption Operations, 157
- 6.6 Single-Phase Stirred Tank Reactors, 159
 - 6.6.1 Continuous Stirred Tank Reactors, 160
 - 6.6.1.1 Liquid Phase Systems—Temperature Specified, 160
 - 6.6.1.2 Gas Phase Systems—Temperature Specified, 161
 - Example 6.6.1.2-1: Multiple Second-Order Reactions and Sizing of R-301, 162
 - 6.6.1.3 Selection of Reactor Temperature, 163
 - Example 6.6.1.3-1: Temperature Selection for Acrylic Acid Reactor, 164
 - 6.6.1.4 CSTR—Energy Balance, 165
 - Example 6.6.1.4-1: *A Priori* Calculation of Heat Load on Acrylic Acid Reactor R-301, 165
 - 6.6.1.5 Autothermal Operation, 166
 - 6.6.1.6 Heuristics, 168
 - 6.6.2 Isothermal Batch Reactor, 168
 - 6.6.2.1 Mass Balance, 168
 - 6.6.2.2 Liquid Phase Reactions at Constant Density, 169
 - 6.6.2.3 Some Background for Example 6.6.2.3-1, 169

- Example 6.6.2.3-1: Production of L-Tyrosine-Feed Stock to L-Dopa Plant, 170
 - 6.6.2.4 Gas Phase Reactions and Equation of State at Constant Volume, 172
 - Example 6.6.2.4-1: Reaction Order for Sulfuryl Chloride Oxidation, 173
- 6.7 Chemical Reaction Equilibrium, 174
 - Example 6.7-1: Equilibrium Constant for the Synthesis of Hexyl Glucoside by Condensation, 176
 - Example 6.7-2: Check on Methanol Conversion to Formaldehyde, 176
 - Example 6.7-3: Phase Equilibrium with Chemical Reaction—Synthesis of Hexyl Glucoside, 178
- Problems, 179

PART II MICROSCOPIC VIEW 181

7 Multistage Separation and Reactor Operations 183

- 7.1 Absorption and Stripping, 183
 - 7.1.1 Isothermal Binary Gas Absorption, 184
 - 7.1.2 Countercurrent Cascade-Tray Tower, 185
 - 7.1.3 Graphical Procedures for Single Components, 186
 - Example 7.1.3-1: Butane Recovery—Fixed Number of Stages, 190
 - 7.1.4 Isothermal Liquid Stripping, 191
 - Example 7.1.4-1: Stripping of Acetone from Water, 193
 - 7.1.5 Dilute Multicomponent Absorption and Stripping, 194
 - Example 7.1.5-1: Methane Purification, 195
 - 7.1.6 Column Efficiency, 196
 - 7.1.7 Column Diameter and Height, 197
 - Example 7.1.7-1: Tower 303: Off-Gas Absorber in Acrylic Acid Process, 197
 - 7.1.8 Heuristics for Absorption, 199
- 7.2 Distillation, 200
 - 7.2.1 Construction of Distillation Operation, 200
 - 7.2.2 Equipment for Distillation, 201
 - 7.2.3 Application of Material and Energy Balances to Feed Tray, 203
 - 7.2.4 Degrees of Freedom, 204
 - 7.2.5 Material Balance for Enriching or Rectifying Section, 205
 - 7.2.6 Material Balance for Stripping Section, 206
 - 7.2.7 Intersection of Operating Lines, 206
 - Example 7.2.7-1: Operating Lines in Acetic Acid–Water Distillation, 207
 - 7.2.8 Number of Stages, 208
 - Example 7.2.8-1: Number of Stages for Acetic Acid–Water Distillation, 210
 - 7.2.9 High Purity Products, 210
 - Example 7.2.9-1: Stages Required for Acetic Acid–Water Distillation Using the Recursion Relations, 211
 - 7.2.10 Energy Requirements, 212
 - 7.2.10.1 Total Condenser, 212
 - 7.2.10.2 Partial Condenser, 212
 - 7.2.10.3 Reboiler, 212

Example 7.2.10.3-1: Energy Loads on the Acetic Acid Distillation Tower, 213	
7.2.11 Efficiency and Column Height, 213	
Example 7.2.11-1: Height of Acetic Acid–Water Column, 214	
7.2.12 Summary of Calculations and Setting Process Operating Conditions, 214	
Example 7.2.12-1: Determine the Minimum Number of Stages for the Acetic Acid–Water Distillation, 215	
Example 7.2.12-2: Determine the Minimum Reflux Ratio for the Acetic Acid–Water Distillation, 215	
7.2.13 Heuristics for Distillation Towers, 217	
Example 7.2.13-1: Tower 305, 218	
7.3 Liquid–Liquid Extraction, 221	
7.3.1 Multistage Cross-Flow Cascade, 221	
7.3.2 Multistage Countercurrent Operation, 222	
Example 7.3.2-1: Extraction of Acetone from MIBK with Water, 224	
Example 7.3.2-2: T-303 Acid Extractor—Number of Equilibrium Stages and Solvent Flow Required, 229	
7.3.3 Extraction Equipment, 232	
7.3.4 Height and Efficiency of Sieve Tray Towers, 233	
Example 7.3.4-1: Height and Number of Trays on Tower 303 with Unagitated Sieve Tray Design, 233	
7.3.5 Mixer–Settler Units, 234	
Example 7.3.5-1: Typical Settler Size for Mixer–Settler Alternative to Tower 303, 234	
7.3.6 Heuristics for Liquid–Liquid Extraction, 234	
7.4 Multiple Reactor Stages, 235	
7.4.1 Comparison with Batch Reactor, 235	
7.4.2 Comparisons with Plug Flow Reactor, 235	
7.4.3 Number of Stages Required for a Given Conversion, 236	
Example 7.4.3-1: Number of Stages for a Diels–Alder Reaction, 236	
7.4.4 Temperature Programs for CSTR Stages, 237	
7.4.4.1 Single Reactions, 237	
7.4.4.2 Multiple Reactions, 238	
7.5 Staged Fixed-Bed Converters for Exothermic Gas Phase Reaction, 238	
Example 7.5-1: Staged Fixed-Bed Converter for SO ₂ Oxidation, 240	
Problems, 241	

8 Microscopic Equations of Change

243

8.1 Mass Flux: Average Velocities and Diffusion, 244
8.1.1 Mass Flow Rates Used in Material Balances, 245
8.1.2 Average Velocities and Diffusion Flows, 246
8.1.3 Superficial Velocities, 248
Example 8.1.3-1 Slip Velocity in Liquid–Liquid and Gas–Liquid Systems, 248
8.2 Momentum Flux: Stress Tensor, 249
8.3 Energy Flux: Conduction, 250
8.4 Balance Equations, 251
8.4.1 Mass Conservation, 251
8.4.2 Linear and Angular Momentum Balance, 252
8.4.3 Conservation of Energy, 252

8.5	Entropy Balance and Flux Expressions, 254
8.5.1	σ_0 : Scalar Processes, 255
8.5.1.1	Volume Flow, 255
8.5.1.2	Homogeneous Reaction Kinetics, 255
8.5.1.3	Heterogeneous Catalytic Kinetics, 256
8.5.2	σ_1 : Vector Processes: Diffusion and Conduction, 260
8.5.3	Viscous Momentum Flux, 261
8.5.4	Estimation of Transport Coefficients, 261
8.5.4.1	Diffusivities, 261
	Example 8.5.4.1-1 Estimation of Methane Diffusivity in Nitrogen for Application to Effective Diffusion in Honeycomb Monolith Reactor, 261
8.5.4.2	Thermal Conductivities, 261
8.5.4.3	Viscosity, 265
8.6	Turbulence, 265
8.6.1	Time-Averaged Mass Balance, 266
8.6.2	Turbulent Flux Expressions, 267
8.6.2.1	Empty Tubes, 267
8.6.2.2	Radial Dispersion in Packed Beds, 268
8.6.2.3	Axial Dispersion, 268
8.7	Application of Balance Equations, 269
8.7.1	Boundary Conditions, 269
8.7.2	Reduction to Scalar Equations: Laminar Flow in Tubes, 270
8.7.3	Introduction to Dimensionless Numbers and Characteristic Times, 272
8.7.4	Dual Geometry and Boundary Conditions for Fixed Beds, 274
	Problems, 275

9 Nonturbulent Isothermal Momentum Transfer 276

9.1	Rectangular Models, 276
9.1.1	Slit Flow: Extrusion of Plastics Through Narrow Dies, 276
	Example 9.1.1-1: Average Velocity and Volumetric Flow Rate, 280
9.2	Cylindrical Systems, 280
9.2.1	Axial Flow—Flow in Pipes and Tubes, 280
	Example 9.2.1-1: Volumetric Flow Rate, 281
	Example 9.2.1-2: Average Velocities, 281
9.2.1.1	Friction Factor, 281
9.2.1.2	Pump Requirements, 281
9.2.1.3	Distribution of Residence Times, 282
9.2.1.4	Laminar Flow Reactor (and Substantial Derivative), 282
	Example 9.2.1.4-1: Application of Microscopic Mass Balance to Laminar Flow Reactor, 282
9.2.1.5	Wetted Wall Towers, 283
	Example 9.2.1.5-1: Error in Film Thickness Approximation, 285
9.2.2	Angular Flow, 286
9.2.2.1	Couette Viscometer, 286
9.3	Spherical Systems, 287
9.3.1	Creeping Flow Around a Solid Sphere, 287

- 9.3.1.1 Application to Decanter Design, 289
 - Example 9.3.1.1-1: Separation of an Oil Water Mixture, 289
- 9.4 Microfluidics—Gas Phase Systems, 289
 - 9.4.1 A Model of Gas Flow in Microchannels, 290
 - 9.4.1.1 Momentum and Mass Balances, 290
 - 9.4.1.2 Mass Balance: Axial Velocity Distribution, 291
 - 9.4.1.3 Pressure Distribution, 292
 - Example 9.4.1.3-1: Helium Flow in a Long Microchannel, 294
- Problems, 294

10 Nonturbulent Isothermal Mass Transfer 296

- 10.1 Membranes, 296
 - 10.1.1 Material Balance for Generic Membrane, 297
 - 10.1.2 Gas Separations, 298
 - Example 10.1.2-1: Greenhouse Gas Removal from Power Station Flue Gas—Completely Mixed Membrane Model with No Sweep, 300
 - 10.1.3 Liquid Separations—Reverse Osmosis, 301
 - Example 10.1.3-1: Regeneration of Pulp Feed Solution in Paper Production, 304
 - 10.1.4 Porous Asymmetric and Composite Membranes—Overall Mass Transfer Coefficient, 305
- 10.2 Diffusion Models for Porous Solids, 307
 - 10.2.1 Effective Diffusivity of Porous Catalysts, 307
 - 10.2.1.1 Pore Diffusion, 307
 - 10.2.1.2 Surface Diffusion, 308
 - 10.2.2 Tortuosity Factor Model, 309
 - 10.2.3 Parallel Pore Model, 309
 - Example 10.2.3-1: Evaluation of Tortuosity in Parallel Pore Model for Honeycomb-Type Monolith Catalyst, 310
- 10.3 Heterogeneous Catalysis, 311
 - 10.3.1 Effectiveness of a Single Closed Pore, 311
 - Example 10.3.1-1: Key Component Kinetics for SO_2 Oxidation, 313
 - 10.3.2 Effectiveness of Catalyst Particle, 314
- 10.4 Transient Adsorption by Porous Solid, 316
 - Example 10.4-1: The Recovery of Hexyl Glucoside, 317
- 10.5 Diffusion with Laminar Flow, 318
 - 10.5.1 Wetted Wall Tower—Short Contact Time, 318
 - 10.5.1.1 Physical Absorption, 318
 - 10.5.1.2 Chemical Absorption, 319
 - 10.5.2 Laminar Flow in a Tube with Catalytic Walls, 320
- Problems, 322

11 Energy Transfer Under Nonturbulent Conditions 324

- 11.1 Conduction in Solids—Composite Walls, 325
 - Example 11.1-1: Insulated Firebox for Steam Reforming, 326
- 11.2 Thermal Effects in Porous Catalysts, 327
 - 11.2.1 Temperature Rise due to Single Chemical Reaction, 327
 - 11.2.2 Effectiveness Factor for Single Irreversible Reaction with Heat Effect, 328

- 11.3 Heat Transfer to Falling Film—Short Contact Times, 330
- 11.4 Moving Boundary Problem, 332
- Example 11.4-1: Onset of Freezing in a Pipe, 333
- Problems, 334

12 Isothermal Mass Transfer Under Turbulent Conditions 335

- 12.1 Intraphase Mass Transfer Coefficients, 335
 - 12.1.1 Film-Penetration Theory, 335
 - 12.1.2 Penetration Theories, 337
 - 12.1.3 Film Theory, 338
- 12.2 Interphase Mass Transfer Coefficients—Controlling Resistances, 338
- 12.3 Measurement and Correlation of Mass Transfer Coefficients, 339
 - 12.3.1 Measurement of Mass Transfer Coefficients, 339
 - 12.3.2 Correlation of Mass Transfer Coefficients, 340
 - Example 12.3.2-1: Determination of Liquid Mass Transfer Coefficients in a Fixed Bed, 341
- 12.4 Fixed Beds, 342
 - 12.4.1 Fixed-Bed Adsorption, 342
 - 12.4.1.1 Ideal Case, 342
 - 12.4.1.2 More General Model, 343
 - 12.4.1.3 Gas Phase, 343
 - 12.4.1.4 Intraparticle Diffusion, 344
 - 12.4.1.5 LDF (Linear Driving Force) Model, 344
- 12.5 Pipes, 345
 - 12.5.1 Turbulent Flow in a Pipe with Catalytic Walls, 345
- 12.6 Particles, Drops, and Bubbles in Agitated Systems, 346
 - 12.6.1 Slurry Adsorption—External Mass Transfer Control, 347
 - Example 12.6.1-1 Adsorption Time and Batch Integration in Continuous Processes, 348
- 12.7 Packed Towers—Gas Absorption, 349
 - 12.7.1.1 Heuristics for Packed Towers, 349
 - 12.7.2 Mass Transfer Correlations, 350
 - 12.7.3 Mass Balances, 351
 - 12.7.3.1 For the Liquid, 352
 - 12.7.3.2 For the Gas, 352
 - 12.7.3.3 Unreactive Case with Henry's Law, 353
 - Example 12.7.3.3-1: Sulfur Dioxide Absorber, 355
- 12.8 Application of Experimental Mass Transfer Coefficients, 357
 - 12.8.1 Free Fluxes, 357
 - 12.8.2 Constrained Fluxes, 358
 - 12.8.2.1 Diffusion Through a Stagnant Film: Absorption with Constant Flows, 358
 - Example 12.8.2.1-1: Height of Packed Bed in SO₂ Absorption Using Method Suitable for Nonlinear Equilibrium Data, 359
 - 12.8.2.2 Equimolar Counter-Diffusion, 360
 - 12.8.2.3 Heterogeneous Chemical Reaction, 360
 - 12.8.2.4 Kinetics Experiments, 361

12.8.2.5	Fixed-Bed Reactor Modeling, 362	
12.8.3	Homogeneous Chemical Reaction, 362	
12.8.3.1	Irreversible First-Order Kinetics, 363	
12.8.3.2	Surface Renewal Theory, 364	
12.8.3.3	Instantaneous Reactions, 364	
12.8.3.4	Linearized Kinetics, 365	
	Problems, 365	
13	Interphase Momentum Transfer Under Turbulent Conditions	367
13.1	Pressure Drop in Conduits and Fixed Beds, 368	
13.1.1	Turbulent Flow of Gases in Pipelines, 369	
13.1.1.1	Isothermal Flow in Pipelines, 370	
	Example 13.1.1.1-1: Pressure Drop and Pipe Size for Gas Supply Line, 370	
13.1.1.2	Compressors, 372	
13.1.2	Pressure Drop in Fixed Beds, 375	
13.2	Flow Over Submerged Spheres, 376	
13.2.1	Momentum Balance for Single Particle, 377	
	Example 13.2.1-1: Diameter of Gas-Liquid Separators, 377	
13.2.2	Terminal Velocities in Newtonian Fluids: Solid Suspensions, 377	
	Example 13.2.2-1: Slurry Adsorption of Hexyl Glucoside, 378	
13.2.3	Fluidization Velocities: Diameter of Fluidized Beds, 379	
	Example 13.2.3-1: Diameter of R-301 Reactor, 380	
13.2.4	Flooding Velocity in Packed Towers: Tower Diameter and Pressure Drop, 381	
	Example 13.2.4-1: Sulfur Dioxide Absorber, 382	
	Problems, 383	
14	Interphase Energy Transfer Under Turbulent Conditions	384
14.1	Heat Transfer Coefficients—Analogy with Mass Transfer, 384	
14.2	Heat Exchangers, 385	
14.2.1	Double Pipe Exchangers, 387	
	Example 14.2.1-1 Cooling of HCl Product from Adiabatic Mixing, 389	
14.2.2	Shell and Tube Heat Exchangers, 390	
14.2.2.1	Constant Wall Temperature, 390	
	Example 14.2.2.1-1: Exchanger 309—Solvent Endings, 392	
14.3	Multi-Tubular Catalytic Reactors, 395	
14.3.1	Fixed-Bed Constant Wall Temperature One-Dimensional Model, 395	
14.3.1.1	Bulk Phase Mass Balance (Molar Units), 396	
14.3.1.2	Particle Phase Mass Balance (Molar Units), 397	
14.3.1.3	Particle Phase Energy Balance, 397	
14.3.1.4	Bulk Phase Energy Balance, 397	
14.3.1.5	Momentum Balance on Interstitial Fluid, 398	
14.3.2	Some Operational Considerations, 398	
	Problems, 399	
15	Microscopic to Macroscopic	400
15.1	Macroscopic Mass Balance, 400	

15.2 Macroscopic Energy Balance,	401
15.3 Macroscopic Mechanical Energy Balance,	402
15.3.1 Unsteady-State Form,	403
15.3.2 Steady-State Systems,	403
Problems,	404

APPENDIX A	PERIODIC TABLE	405
APPENDIX B	CONVERSION FACTORS	406
APPENDIX C	PARTIAL DATABASE FOR ACRYLIC ACID PROCESS	409
APPENDIX D	SOME MATHEMATICAL RESULTS	414
APPENDIX E	MASS BALANCE IN CYLINDRICAL COORDINATES AND LAMINAR FLOW IN Z DIRECTION	418
NOMENCLATURE		419
REFERENCES		423
INDEX		427

PREFACE

This book is about the application of scientific principles and engineering experience to chemical processing. Major chemical engineering operations are organized under the principles of analysis in order to facilitate the consideration of new technologies from a chemical engineering point of view.

New applications have emerged in chemical engineering practice. Microchemical systems, for example, require attention to design parameters not important at larger scales. The shift from commodity chemicals to chemical products by many smaller companies is creating a demand for chemical engineers with a broader view of design than the traditional capstone design experience (Cussler and Moggridge, 2001). Biocatalysis and the chiral technology industry call for the support of undergraduate curricula. Opportunities for the chemical engineering graduate in the development of medical devices and drug manufacture call for more emphasis on the life sciences and physiology.

There is therefore a call to introduce a degree of flexibility into traditional undergraduate chemical engineering curricula for those who wish to serve a broader industrial base. An alternative is to concentrate the basic chemical engineering training in a minimal core designed to secure the distinguishing technical character of the chemical engineer and to provide the ground both for further specialization in traditional chemical engineering and for coherent studies in other areas. The minimization decisions regarding the required topics and the depth of coverage are local decisions that reflect the mission of the program.

This text can support such a local decision process as a consolidation of normally separate courses in material and energy balances, transport phenomena, reactor design, and separations. While not a replacement for these courses, it is

a functional treatment of the underlying skills that characterize them. The selection of major operations reflects the intention of establishing a minimum competency level required to be differentiated as a chemical engineer in an undergraduate engineering curriculum.

Although the book is primarily meant for chemical engineering undergraduates, it may be appropriate for conversion programs designed to prepare graduates of other engineering and science programs for matriculation in chemical engineering master's programs.

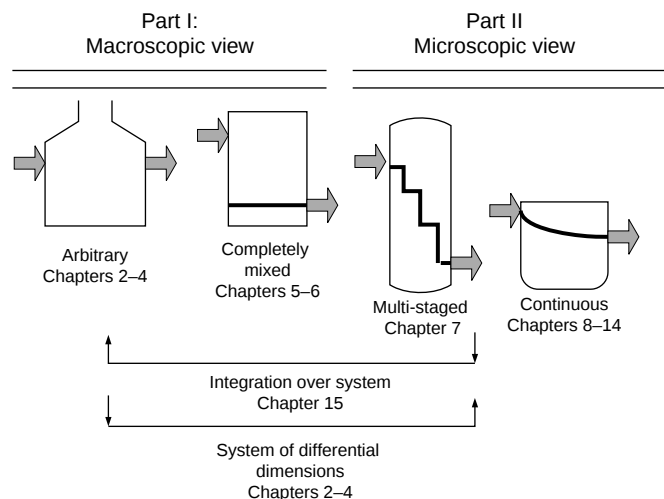
Graduate engineers in both academic and industrial positions may find it convenient to have a single resource with wide coverage.

CONTENT

The principles referred to above consist of the conservation of mass, energy, and momentum at the macroscopic and microscopic levels as well as the principle of the increase of entropy and characterization of equilibrium states by equilibrium thermodynamics. The production of entropy provides an important measure of process efficiency and underpins the conservation laws by providing a theoretical foundation for the nonconvective flows. In addition, the balance equations and equilibrium relations are used to develop models of the chemical process operations from the rate or equilibrium stage point of view, respectively. Efficiency is a link between the two.

The chemical engineering operations that are discussed in the text are as follows:

- Separators
- Heat exchangers.



Organization.

A process flow diagram for the manufacture of acrylic acid is presented at the outset and used for an introduction to chemical processing and equipment. Reference to the acrylic acid process is continued thereafter for presentation of new material in a process context. Example calculations in the text are compared with simulator results pertaining to equipment sizes and operating conditions in the acrylic acid plant.

Heuristics are regarded as fundamental tools and are stated extensively. They are used in calculations and are compared with some independent calculations. Degrees of freedom are employed throughout the earlier sections of the book.

Process control, economics, and safety are not included.

ORGANIZATION

Two major divisions of the subject matter in the text are made on the basis of a macroscopic and a microscopic view: The balance equations for mass, energy, momentum, and entropy are applied at the macroscopic level confined to the equipment ports, through completely mixed and staged systems to the continuous variations within equipment (see Organization).

The “macroscopic view” ensures the conservation of mass, energy, and momentum at the equipment and process levels with consideration only of the conditions at the entrances and exits of the process equipment. The exception is completely mixed systems where the uniform interior conditions appear at the outlet. The macroscopic view is taken at the level of process synthesis where the conditions are consistently set for each processing step to establish the

overall process design and economics. The microscopic view is subsequently adopted to arrive at the detailed design of the processing equipment and the final economics. This viewpoint can provide conditions at every location within the equipment boundaries. For multistaged systems consisting of completely mixed subsystems, the conditions vary stepwise throughout the equipment. The microscopic view ensures the local conservation of mass, energy, and momentum. The macroscopic view is therefore the net effect of this local role, which can be seen by integration over the system volume, thereby “closing the circle.”

CALCULATIONS

Many examples are provided within the chapters throughout the text to elucidate the discussion. Two process-related threads are carried through the examples (see Tables 1.7 and 1.8) in order to provide a broad process perspective for the calculations. Questions for discussion and encouragement to complete the argument or calculation appear periodically. A variety of problems are suggested at the end of chapters in order to initiate the problem-solving activity as a learning tool and to provide experience with scientific and engineering databases. The collection can be augmented to meet specific course objectives or a desired orientation without modifications to the chapters.

Scientific Notebook (MacKichan Software) and Microsoft Excel are primarily used in the example calculations. Scientific Notebook was chosen because the students who used the notes had prior experience with this software in their mathematics courses and they preferred this software over others that were available to them. Moreover, this

software is particularly compatible with the notation used throughout this book.

Excel was used because the ease with which objects could be moved on graphs, the magnification options, and the ability to construct multifunctional plots greatly facilitated stepping off stages and other graphical constructions. The

tabular formulation of recursive calculations is readily accomplished in Excel.

Some experience with the use of this software in an introductory course is available in DeLancey (1999).

GEORGE DELANCEY

PART I

MACROSCOPIC VIEW

CHEMICAL PROCESS PERSPECTIVE

The objective of this chapter is to provide an introduction to chemical processing and chemical processing equipment and to establish a realistic context for much of the more quantitative developments of the same topics appearing in the remaining chapters. A preliminary design of an acrylic acid process (Turton et al., 2003) with a complete flow sheet and stream table provides this context. A connected set of examples and exercises concerned with equipment sizing, material and energy balances, or stream and operating conditions threaded throughout the text are related to the acrylic acid process. The location and nature of these examples are summarized in Table 1.7.

Catalytic aspects of chemical processing are raised in the acrylic acid process and in biocatalytic systems with an introduction to enzyme catalysis. Industrial biotransformations are discussed and the production of hexyl glucoside is selected to provide the context for a second connected thread of examples and exercises throughout the text. In contrast to the acrylic acid thread, this selection is based on a proposed new process with much less information. The examples are therefore in the categories of scale up and process development. The location and nature of the examples in the subsequent chapters are summarized in Table 1.8.

1.1 SOME BASIC CONCEPTS IN CHEMICAL PROCESSING

It will be useful in the following discussion to have in mind what is meant by equilibrium, the steady state, and driving force. These ideas primarily underpin the steps in chemical

processing and fall into the three thermodynamic categories: thermal, chemical, and mechanical. The first two categories are discussed below. The third is left to the reader (see Problem 1.1).

Thermal Refer to Figure 1.1a. Here we imagine that two fluids not necessarily of the same phase are introduced into the two chambers of a rigid insulated container with impermeable walls. The two chambers are separated by a rigid dimensionless barrier (to allow the transfer of heat without mass transfer) and the fluids fill the two mixed chambers. The temperature of the hot fluid (A) will decrease and the temperature of the cold fluid (B) will increase, each approaching the same temperature at the equilibrium state.

If, on the other hand, the fluids are drawn at the same rate they are fed, they will reach a **steady-state** temperature that is constant throughout each phase except for a narrow region near the dimensionless diathermal wall where the temperature decreases continuously from the high to the low value. The same equilibrium temperature is approached from either side of the interface. The two phases are prevented from reaching the intermediate state by the continual replacement and removal of the transferred energy.

If the flows are stopped, the system will equilibrate as in Figure 1.1a. We therefore think of the steady state being subjected to a **driving force** proportional to the distance from equilibrium as in Figure 1.1c where the flux of thermal energy is the response to the force. Since each approaches zero together, we take the linear approximation that the flux is proportional to the force.

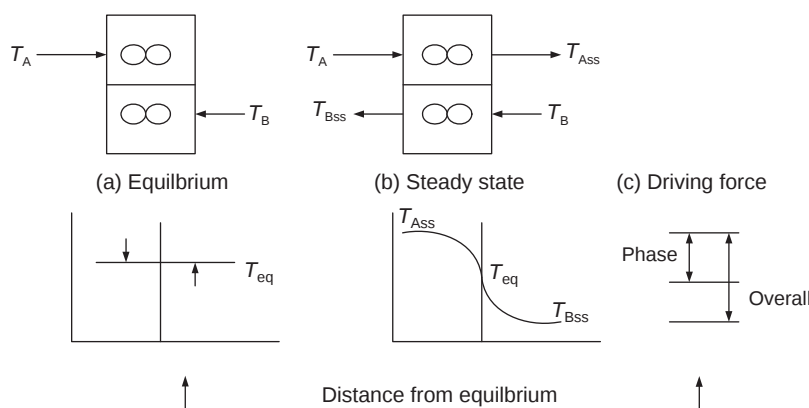


FIGURE 1.1 Rate and equilibrium in thermal processes.

We can focus on one phase and think of the driving force as the distance from the equilibrium value or we can think of the overall driving force as the difference between the phase temperatures. Both driving forces refer to the same flow of energy at steady state and each approaches zero at equilibrium.

Chemical—Unreactive Reaction Refer to Figure 1.2a. We again consider an insulated container with rigid impermeable walls. Here we charge the container with two immiscible liquid phases containing components that are partially soluble in both phases. We will assume for simplicity that the dissolution process of any one of the components in either phase involves no heat effect. Otherwise we would need to repeat the “thermal” discussion. We also assume that no reactions take place. Chemical reactions will be discussed separately.

Similar to the temperature in thermal phenomena, the concentration of each species will increase or decrease until a steady value is reached in each phase. This is a state of **interphase chemical equilibrium**. A fundamental

difference from the thermal case is that the values are not the same in each phase. Whereas the potential for the transfer of thermal energy is the temperature, thermodynamics tells us that the chemical potential is a function of the temperature, pressure, and composition in each phase.

If, as above, the fluids are withdrawn at the same rate they are fed, the concentrations will reach steady-state values that are constant throughout each phase, except for a narrow region near the dimensionless open barrier where the concentrations change stepwise to the values in the companion phase.

If the flows are stopped, the system will equilibrate as in Figure 1.2a. We therefore think of the steady state being subjected to a **driving force** proportional to the distance from equilibrium as in Figure 1.2c where the flux of mass is the response to the force. Since each approaches zero together, we take the linear approximation that the flux of mass is proportional to the driving force.

We can focus on one phase and think of the driving force as the distance from the equilibrium value for that phase or we can think of the overall driving force as the difference

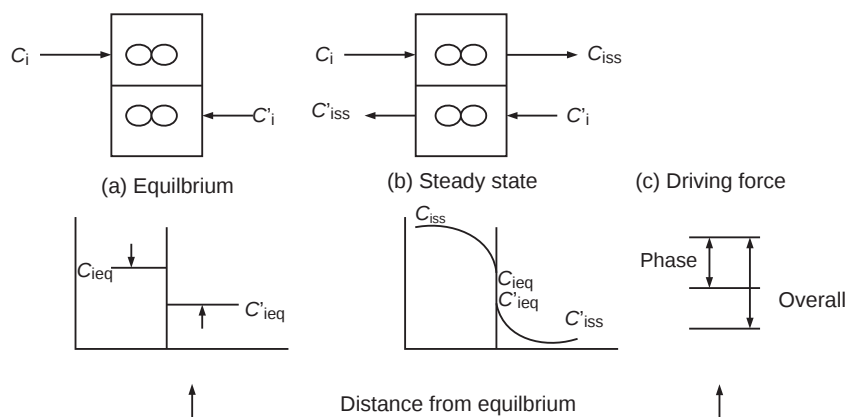


FIGURE 1.2 Rates and equilibrium in chemical processes—interphase phenomena.

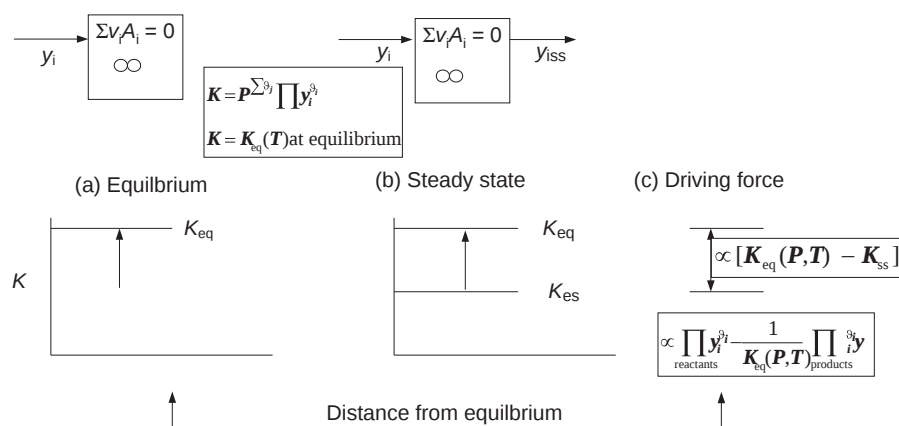


FIGURE 1.3 Reaction rates and equilibrium.

between the phase compositions. Since the interphase equilibrium compositions are not the same, the overall driving force will need to be modified slightly to assure that the rate is the same as that calculated in either phase.

Chemical—Single Ideal Gas-Phase Reaction The case of chemical reaction equilibrium is a bit more complicated in that reaction equilibrium is characterized by the chemical affinity, a linear combination of the chemical potentials mentioned in the preceding paragraph. We can, however, arrive at reaction kinetics, which are at least qualitatively correct and sufficient to understand some basic behavior of chemical reactors. We will consider a single ideal gas-phase reaction for which thermodynamics tells us that the ratio K in Figure 1.3a has a specific value at equilibrium $K_{eq}(T)$.

We again consider a container with rigid impermeable walls. Here we take the walls to be diathermal in order to begin and end the reaction process at the same temperature. We charge the container with a reactive ideal gas mixture. The value of K will increase as shown in Figure 1.3a until the equilibrium value is attained after which no further change will take place. This is the **intrapphase chemical equilibrium** condition. For irreversible reactions, the value of K is extraordinarily large.

If gases are withdrawn at the same rate they are fed as illustrated in Figure 1.3b, the products will be prevented from accumulating and therefore the value of K_{eq} will be prevented from being reached. The concentrations T and P will reach **steady-state** values that are constant throughout. If the flows are stopped, the system will equilibrate as in Figure 1.3a. We therefore think of the steady state being subjected to a **driving force** proportional to the distance from equilibrium as in Figure 1.3c where the rate of reaction is the response to the force. Since each approaches zero together, we take the linear approximation that the flux of mass is proportional to the driving force. The result shown in Figure 1.3c is the law of mass action.

1.2 ACRYLIC ACID PRODUCTION

Figure 1.4 is a process flow diagram of a continuous process for the manufacture of 50,000 metric ton/year of 99.9 mol% acrylic acid from a one-step oxidation of propylene. One reactor is therefore used, which stands in contrast to the commonly used dual reactor system. The process is based upon the 1986 AIChE Student Contest Problem. The process conditions and equipment sizes are reported by Turton et al. (2003).

There are a number of commercial software packages that are known to produce accurate designs of chemical processes in the hands of experienced engineers (Aspen Plus, Aspen Hysys, Chemcad, etc.). Turton et al. (2003) used Chemcad and expected the results to represent a preliminary process design. We will use the calculated results as if they were actual plant data. Actual plant data at this level of detail are neither available nor needed in light of the sophistication of the software to gain a familiarity with process concepts as well as equipment and basic ideas in chemical engineering analysis and design. However, any comparisons of approximate calculations with these calculations are comparisons with more rigorous calculation procedures, not actual data.

Continuous processes are common in the chemical industry where such products as organic chemicals, plastics, and solvents are produced in large quantities to meet market demands. These products are referred to as bulk or commodity chemicals. Batch processes on the other hand are commonly used by the pharmaceutical industry to produce a wide variety, but small amounts, of pharmaceuticals. These products fall under the category of fine chemicals. Semicontinuous process is the combination of batch and continuous processing, in which the chemical state of one or more chemical compounds is altered stepwise toward a well-defined target. A process flow diagram (PFD) is a schematic representation of the process.

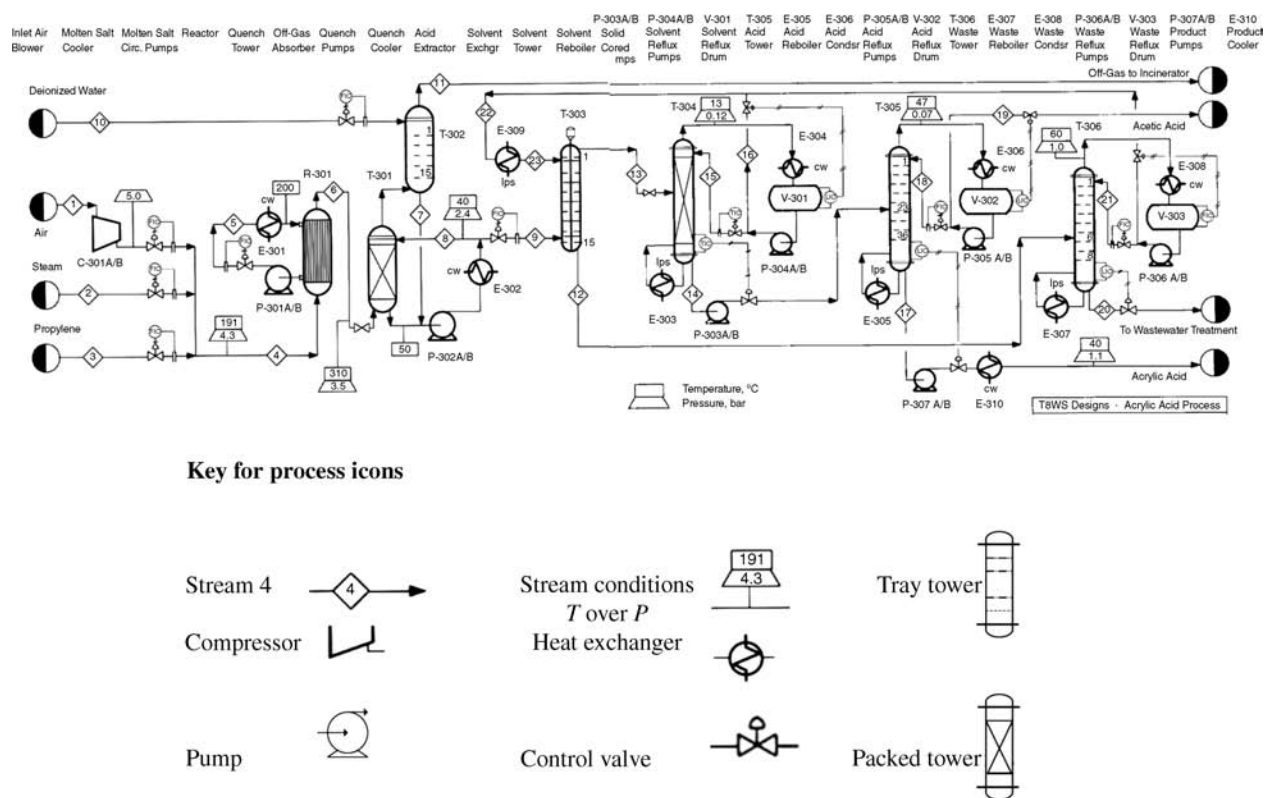


FIGURE 1.4 Process flow diagram for acrylic acid production plant (Turton et al., 2003). Reprinted with permission of Pearson.

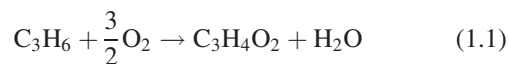
In a chemical process, material is moved in streams by mechanical devices such as pumps and compressors from one process unit to another. A summary of the schematic representations of these items is given in Figure 1.4.

The streams are connected to the process units by pipes and ducts for fluids and by screw or belt conveyors in the case of solids, for example. The process units perform operations on the content of the streams to change their temperature, pressure, phase, and/or composition. These units are often referred to as unit operations and are carefully configured by the chemical engineer to transform raw materials into the desired products, economically and safely. Some units are combinations of unit operations.

All of these processes consist of a sequence of operations in which the process streams begin at raw material storage and end with product storage. There are other streams called utilities, which are employed by the process units as sources or sinks of thermal energy. The supply and regeneration of the utility streams may be part of the process or these services may be supplied by a separate facility. In the latter case, the utility streams arrive and are returned after use to the utility site for regeneration.

We will look more carefully into each of these aspects of chemical processing for the production of 50,000 metric ton/year of acrylic acid via the process given in the flow diagram

(Figure 1.4). Normally, the adopted chemical route is the result of an intensive search involving technical, economic, and safety considerations. More than one route may be simulated to better evaluate the economics of the final competitors. A two-step process comprised of the oxidation of propylene to acrolein followed by the oxidation of acrolein to acrylic acid (Speight, 2002) is the common industrial choice. In the present case, the partial oxidation of propylene has been selected from other alternative routes to acrylic acid, which may be viewed as an alternative proposition for a single-step process over a new catalyst.



An economic view can be initiated at the outset of process development by considering only the raw material costs and product sales price. The net change for the chemical reaction must, of course, be positive or “economically endothermic” before the reaction is even considered to be a possibility for adoption. Some chemical prices are available in the *Chemical Market Reporter*, available online by subscription. Professional publications such as *Chemical and Engineering News* and *Chemical Engineering Progress* publish limited pricing information. In general, there is a cost associated