B. Wayne Bequette

# Process Dynamics

## Modeling, Analysis, and Simulation

Prentice Hall International Series
in the Physical and Chemical
Engineering Sciences

## PRENTICE HALL INTERNATIONAL SERIES IN THE PHYSICAL AND CHEMICAL ENGINEERING SCIENCES

BALZHISER, SAMUELS, AND ELLIASSEN *Chemical Engineering Thermodynamics*
BEQUETTE *Process Dynamics: Modeling, Analysis, and Simulation*
BIEGLER, GROSSMANN, AND WESTERBERG *Systematic Methods of Chemical Process Design*
CROWL and LOUVAR *Chemical Process Safety*
DENN *Process Fluid Mechanics*
FOGLER *Elements of Chemical Reaction Engineering, 2nd Edition*
HANNA AND SANDALL *Computational Methods in Chemical Engineering*
HIMMELBLAU *Basic Principles and Calculations in Chemical Engineering, 6th edition*
HINES AND MADDOX *Mass Transfer*
KYLE *Chemical and Process Thermodynamics, 2nd edition*
NEWMAN *Electrochemical Systems, 2nd edition*
PRAUSNITZ, LICHTENTHALER, and DE AZEVEDO *Molecular Thermodynamics of Fluid-Phase Equilibria, 2nd edition*
PRENTICE *Electrochemical Engineering Principles*
STEPHANOPOULOS *Chemical Process Control*
TESTER AND MODELL *Thermodynamics and Its Applications, 3rd edition*
TURTON *Analysis, Synthesis, and Design of Chemical Processes*

# PROCESS DYNAMICS

## Modeling, Analysis, and Simulation

**B. Wayne Bequette**
*Rensselaer Polytechnic Institute*

Prentice Hall PTR
Upper Saddle River, New Jersey 07458

**Library of Congress Cataloging-in-Publication Data**

Bequette, B. Wayne.
Process dynamics : modeling, analysis, and simulation / B. Wayne Bequette.
p. cm.
Includes bibliographical references and index.
ISBN 0-13-206889-3
1. Chemical processes. I. Title.
TP155.7.B45 1998
660'.284'01185--dc21 97-36053
CIP

Acquisitions editor: Bernard M. Goodwin
Cover design director: Jerry Votta
Manufacturing manager: Alexis R. Heydt
Marketing manager: Miles Williams
Compositor/Production services: Pine Tree Composition, Inc.

Prentice-Hall, Inc.
A Simon & Schuster Company
Upper Saddle River, New Jersey 07458

Prentice Hall books are widely-used by corporations and government agencies for training, marketing, and resale.

The publisher offers discounts on this book when ordered in bulk quantities. For more information contact:

Corporate Sales Department
Phone: 800-382-3419
Fax: 201-236-7141
E-mail: corpsales@prenhall.com

Or write:

Prentice Hall PTR
Corp. Sales Dept.
One Lake Street
Upper Saddle River, New Jersey 07458

Printed in the United States of America
10 9 8 7 6 5 4 3 2 1

ISBN: 0-13-206889-3

Prentice-Hall International (UK) Limited, *London*
Prentice-Hall of Australia Pty. Limited, *Sydney*
Prentice-Hall Canada Inc., *Toronto*
Prentice-Hall Hispanoamericana, S.A., *Mexico*
Prentice-Hall of India Private Limited, *New Delhi*
Prentice-Hall of Japan, Inc., *Tokyo*
Simon & Schuster Asia Pte. Ltd., *Singapore*
Editora Prentice-Hall do Brasil, Ltda., *Rio de Janeiro*

# CONTENTS

Preface xvii

SECTION I PROCESS MODELING 1

1 Introduction 3

- 1.1 Motivation 3
- 1.2 Models 4
  - 1.2.1 How Models Are Used 5
- 1.3 Systems 10
  - 1.3.1 Simulation 10
  - 1.3.2 Linear Systems Analysis 11
  - 1.3.3 A Broader View of Analysis 11
- 1.4 Background of the Reader 12
- 1.5 How To Use This Textbook 12
  - 1.5.1 Sections 12
  - 1.5.2 Numerical Solutions 13
  - 1.5.3 Motivating Examples and Modules 13
- 1.6 Courses Where This Textbook Can Be Used 13
- Summary 14
- Further Reading 14
- Student Exercises 15

2 Process Modeling 16
2.1 Background 17
2.2 Balance Equations 17
2.2.1 Integral Balances 18
2.2.2 Instantaneous Balances 20
2.3 Material Balances 20
2.3.1 Simplifying Assumptions 25
2.4 Constitutive Relationships 27
2.4.1 Gas Law 27
2.4.2 Chemical Reactions 27
2.4.3 Equilibrium Relationships 28
2.4.4 Flow-through Valves 29
2.5 Material and Energy Balances 30
2.5.1 Review of Thermodynamics 31
2.6 Distributes Parameter Systems 34
2.7 Dimensionless Models 35
2.8 Explicit Solutions to Dynamic Models 36
2.9 General Form of Dynamic Models 37
2.9.1 State Variables 37
2.9.2 Input Variables
2.9.3 Parameters 38
2.9.4 Vector Notation 38
Summary 40
Further Reading 40
Student Exercises 41
SECTION II NUMERICAL TECHNIQUES 49
3 Algebraic Equations 51
3.1 Notations 51
3.2 General Form for a Linear System of Equations 51
3.3 Nonlinear Functions of a Single Variable 54
3.3.1 Convergence Tolerance 55
3.3.2 Direct Substitution 55
3.3.3 Interval Halving (Bisection) 58
3.3.4 False Position (Reguli Falsi) 60
3.3.5 Newton's Method (or Newton-Raphson) 60
3.4 MATLAB Routines for Solving Functions of a Single Variable 63
3.4.1 fzero 63
3.4.2 roots 64
3.5 Multivariable Systems 64
3.5.1 Newton's Method for Multivariable Problems 66
3.5.2 Quasi-Newton Methods 69

**3.6 MATLAB Routines for Systems of Nonlinear Algebraic Equations 70**
**Summary 71**
**Further Reading 72**
**Student Exercises 73**
**Appendix 78**

## 4 Numerical Integration 80

**4.1 Background 80**
**4.2 Euler Integration 81**
  4.2.1 Explicit Euler 81
  4.2.2 Implicit Euler 82
  4.2.3 Numerical Stability of Explicit and Implicit Methods 83
**4.3 Runge-Kutta Integration 88**
  4.3.1 Second Order Runge-Kutta 89
  4.3.2 Fourth-Order Runge-Kutta 93
**4.4 MATLAB Integration Routines 94**
  4.4.1 ode23 and ode45 95
**Summary 97**
**Further Reading 97**
**Student Exercises 98**

## SECTION III LINEAR SYSTEMS ANALYSIS 103

## 5 Linearization of Nonlinear Models: The State-Space Formulation 105

**5.1 State Space Models 106**
  5.5.1 General Form of State Space Models 108
**5.2 Linearization of Nonlinear Models 109**
  5.2.1 Single Variable Example 109
  5.5.2 One State Variable and One Input Variable 110
  5.2.3 Linearization of Multistate Models 112
  5.2.4 Generalization 114
**5.3 Interpretation of Linearization 117**
**5.4 Solution of the Zero-Input Form 119**
  5.4.1 Effect of Initial Condition Direction (Use of Similarity Transform) 120
**5.5 Solution of the General State-Space Form 127**
**5.6 MATLAB Routines step and initial 127**
  5.6.1 The MATLAB step Function 129
  5.6.2 The MATLAB initial Function 129
**Summary 130**
**Further Reading 131**
**Student Exercises 131**

6 Solving Linear nth Order ODE Models 142

- 6.1 Background 143
- 6.2 Solving Homogeneous, Linear ODEs with Constant Coefficients 145
  - 6.2.1 Distinct Eigenvalues 146
  - 6.6.2 Repeated Eigenvalues 148
  - 6.2.3 General Result for Complex Roots 152
- 6.3 Solving Nonhomogeneous, Linear ODEs with Constant Coefficients 152
- 6.4 Equations with Time-Varying Parameters 154
- 6.5 Routh Stability Criterion—Determining Stability Without Calculating Eigenvalues 157
  - 6.5.1 Routh Array 157
- Summary 160
- Further Reading 161
- Student Exercises 161

7 An Introduction to Laplace Transforms 168

- 7.1 Motivation 168
- 7.2 Definition of the Laplace Transform 169
- 7.3 Examples of Laplace Transforms 170
  - 7.3.1 Exponential Function 170
  - 7.3.3 Time-Delay (Dead Time) 172
  - 7.3.4 Derivations 173
  - 7.3.5 Integrals 173
  - 7.3.6 Ramp Function 174
  - 7.3.7 Pulse 174
  - 7.3.8 Unit Impulse 176
  - 7.3.9 Review 177
- 7.4 Final and Initial Value Theorems 177
- 7.5 Application Examples 178
  - 7.5.1 Partial Fraction Expansion 179
- 7.6 Table of Laplace Transforms 185
- Summary 187
- Further Reading 187
- Student Exercises 187

8 Transfer Function Analysis of First-Order Systems 190

- 8.1 Perspective 191
- 8.2 Responses of First-Order Systems 191
  - 8.2.1 Step Inputs 193
  - 8.2.2 Impulse Inputs 198
- 8.3 Examples of Self-Regulating Processes 200
- 8.4 Integrating Processes 206

- **8.5 Lead-Lag Models 208**
  - 8.5.1 Simulating Lead-Lag Transfer Functions 209
  - **Summary 211**
  - **Student Exercises 211**

## 9 Transfer Function Analysis of Higher-Order Systems 215

- **9.1 Responses of Second-Order Systems 216**
  - 9.1.1 Step Responses 217
  - 9.1.2 Underdamped Step Response Characteristics 221
  - 9.1.3 Impulse Responses 222
  - 9.1.4 Response to Sine Inputs 224
- **9.2 Second-Order Systems with Numerator Dynamics 226**
- **9.3 The Effect of Pole-Zero Locations on System Step Responses 228**
- **9.4 Padé Approximation for Deadtime 230**
- **9.5 Converting the Transfer Function Model to State-Space Form 232**
- **9.6 MATLAB Routines for Step and Impulse Response 234**
  - 9.6.1 step 234
  - 9.6.2 impulse 236
  - **Summary 236**
  - **Student Exercises 237**

## 10 Matrix Transfer Functions 247

- **10.1 A Second-Order Example 248**
- **10.2 The General Method 251**
- **10.3 MATLAB Routine ss2tf 252**
  - 10.3.1 Discussion of the Results from Example 10.2 255
  - **Summary 257**
  - **Student Exercises 257**

## 11 Block Diagrams 261

- **11.1 Introduction to Block Diagrams 262**
- **11.2 Block Diagrams of Systems in Series 262**
- **11.3 Pole-Zero Cancellation 263**
- **11.4 Systems in Series 267**
  - 11.4.1 Simulating Systems in Series 267
- **11.5 Blocks in Parallel 269**
  - 11.5.1 Conditions for Inverse Response 271
- **11.6 Feedback and Recycle Systems 273**
- **11.7 Routh Stability Criterion Applied to Transfer Functions 276**
  - 11.7.1 Routh Array 277
- **11.8 SIMULINK 278**

**Summary 279**
**Student Exercises 280**

12 Linear Systems Summary 282

- **12.1 Background 283**
- **12.2 Linear Boundary Value Problems 283**
- **12.3 Review of Methods for Linear Initial Value Problems 287**
  - 12.3.1 Linearization 187
  - 12.3.2 Direction Solution Techniques 288
  - 12.3.3 Rewrite the State-Space Model as a Single nth Order Ordinary Differential Equation 289
  - 12.3.4 Use Laplace Transforms Directly on the State-Space Model 290
- **12.4 Introduction to Discrete-Time Models 290**
  - 12.4.1 Discrete Transfer Function Models 291
- **12.5 Parameter Estimation of Discrete Linear Systems 295**
  - **Summary 297**
  - **References 297**
  - **Student Exercises 298**

SECTION IV NONLINEAR SYSTEMS ANALYSIS 301

13 Phase-Plane Analysis 303

- **13.1 Background 304**
- **13.2 Linear System Examples 304**
- **13.3 Generalization of Phase-Plane Behavior 311**
  - 13.3.1 Slope Marks for Vector Fields 313
  - 13.3.2 Additional Discussion 315
- **13.4 Nonlinear Systems 316**
  - 13.4.1 Limit Cycle Behavior 323
  - **Summary 324**
  - **Further Reading 324**
  - **Student Exercises 324**

14 Introduction Nonlinear Dynamics: A Case Study of the Quadratic Map 331

- **14.1 Background 332**
- **14.2 A Simple Population Growth Model 332**
- **14.3 A More Realistic Population Model 334**
  - 14.3.1 Transient Response Results for the Quadratic (Logistic) Map 335
- **14.4 Cobweb Diagrams 339**
- **14.5 Bifurcation and Orbit Diagrams 342**
  - 14.5.1 Observations from the Orbit Diagram (Figure 14.14) 342

**14.6 Stability of Fixed-Point Solutions 344**
  14.6.1 Application of the Stability Theorem to the Quadratic Map 344
  14.6.2 Generalization of the Stability Results for the Quadratic Map 346
  14.6.3 The Stability Theorem and Qualitative Behavior 346
**14.7 Cascade of Period-Doublings 348**
  14.7.1 Period-2 348
  14.7.2 Period-4 351
  14.7.3 Period-n
  14.7.4 Feigenbaum's Number 353
**14.8 Further Comments on Chaotic Behavior 354**
**Summary 354**
**References and Further Reading 355**
**Student Exercises 356**
**Appendix: Matlab M-Files Used in This Module 358**

**15 Bifurcation Behavior of Single ODE Systems 360**

**15.1 Motivation 360**
**15.2 Illustration of Bifurcation Behavior 361**
**15.3 Types of Bifurcations 362**
  15.3.1 Dynamic Responses 365
**Summary 376**
**References and Further Reading 376**
**Student Exercises 377**
**Appendix 379**

**16 Bifurcation Behavior of Two-State Systems 381**

**16.1 Background 381**
**16.2 Single-Dimensional Bifurcations in the Phase-Plane 382**
**16.3 Limit Cycle Behavior 384**
**16.4 The Hopf Bifurcation 388**
  16.4.1 Higher Order Systems ($n > 2$) 391
**Summary 392**
**Further Reading 392**
**Student Exercises 392**

**17 Introduction to Chaos: The Lorenz Equations 395**

**17.1 Introduction 396**
**17.2 Background 396**
**17.3 The Lorenz Equations 397**
  17.3.1 Steady-State (Equilibrium) Solutions 398

**17.4 Stability Analysis of the Lorenz Equations 399**
  17.4.1 Stability of the Trivial Solution 399
  17.4.2 Stability of the Nontrivial Solutions 400
  17.4.3 Summary of Stability Results 301
**17.5 Numerical Study of the Lorenz Equations 402**
  17.5.1 Conditions for a Stable Trivial (No Flow) Solution 402
  17.5.2 Stable Nontrivial Solutions 403
  17.5.3 Chaotic Conditions 405
**17.6 Chaos in Chemical Systems 407**
**17.7 Other Issues in Chaos 409**
**Summary 410**
**References and Further Reading 410**
**Student Exercises 411**
**Appendix 412**

SECTION IV REVIEW AND LEARNING MODULES 413

Module 1 Introduction to MATLAB 415

**M1.1 Background 416**
**M1.2 Using This Tutorial 416**
**M1.3 Entering Matrices 417**
**M1.4 The MATLAB Workspace 419**
**M1.5 Complex Variables 421**
**M1.6 Some MATLAB Operations 421**
**M1.7 Plotting 422**
**M1.8 More Matrix Stuff 426**
**M1.9 FOR Loops and IF-THEN Statements 427**
**M1.10 m-files 428**
**M1.11 Diary 430**
**M1.12 Toolboxes 430**
**M1.13 Limitations to Student MATLAB 431**
**M1.14 Contacting Mathworks 431**
**Student Exercises 432**

Module 2 Review of Matrix Algebra 435

**M2.1 Motivation and Notation 436**
**M2.2 Common Matrix Operations 436**
**M2.3 Square Matrices 440**
**M2.4 Other Matrix Operations 448**
**Summary 450**
**Student Exercises 450**

Module 3 Linear Regression 452

M3.1 Motivation 452
M3.2 Least Squares Solution for a Line 454
M3.3 Solution for the Equation of a Line Using Matrix-Vector Notation 455
M3.4 Generalization of the Linear Regression Technique 456
M3.5 MATLAB Routines `polyfit` and `polyval` 458

Module 4 Introduction to SIMULINK 464

M4.1 Introduction 464
M4.2 Transfer Function-Based Simulation 466
M4.3 Printing SIMULINK Windows 469

Module 5 Stirred Tank Heaters 471

M5.1 Introduction 471
M5.2 Developing the Dynamic Model 472
M5.3 Steady-State Conditions 475
M5.4 State-Space Model 475
M5.5 Laplace Domain Model 477
M5.6 Step Responses: Linear versus Nonlinear Models 478
M5.7 Unforced System Responses: Perturbations in Initial Conditions 483

Module 6 Absorption 490

M6.1 Background 490
M6.2 The Dynamic Model 491
M6.3 Steady-State Analysis 495
M6.4 Step Responses 496
M6.5 Unforced Behavior 501

Module 7 Isothermal Continuous Stirred Tank Chemical Reactors 506

M7.1 Introduction 506
M7.2 First-Order Irreversible Reaction 507
M7.3 Van de Vusse Reaction 516

Module 8 Biochemical Reactors 529

M8.1 Background 529
M8.2 Modeling Equations 530
M8.3 Steady-State Solution 534
M8.4 Dynamic Behavior 535

M8.5 Linearization 536
M8.6 Phase-Plane Analysis 539
M8.7 Understanding Multiple Steady-States 540
M8.8 Bifurcation Behavior 549

Module 9 Diabatic Continuous Stirred Tank Reactors 559

M9.1 Background 560
M9.2 The Modeling Equations 561
M9.3 Steady-State Solution 563
M9.4 Dynamic Behavior 565
M9.5 Linearization of Dynamic Equations 567
M9.6 Phase-Plane Analysis 571
M9.7 Understanding Multiple Steady-State Behavior 572
M9.8 Further Complexities 580
M9.9 Dimensionless Model 584

Module 10 Ideal Binary Distillation 597

M10.1 Background 597
M10.2 Conceptual Description of Distillation 599
M10.3 Dynamic Material Balances 601
M10.4 Solving the Steady-State Equations 603
M10.5 Solving the Nonlinear Dynamic Equations 605
M10.6 State-Space Linear Distillation Models 606
M10.7 Multiplicity Behavior 608

Index 617

# PREFACE

An understanding of the dynamic behavior of chemical processes is important from both process design and process control perspectives. It is easy to design a chemical process, based on steady-state considerations, which is practically uncontrollable when the process dynamics are considered. The current status of computational hardware and software has made it easy to interactively simulate the dynamic behavior of chemical processes.

It is common for process dynamics to be included as the introductory portion of a process control textbook, however, there are a number of limitations to this approach. Since the emphasis of most of the textbooks is on process control, there is too little space to give adequate depth to modeling, analysis, and simulation of dynamic systems. The focus tends to be on transfer function-based models that are used for control system design. The prime motivation for my textbook is then to provide a more comprehensive treatment of process dynamics, including modeling, analysis, and simulation. This textbook evolved from notes developed for a course on dynamic systems that I have been teaching at Rensselaer since 1991. We have been fortunate to have a two-semester sequence in dynamics and control, allowing more depth to the coverage of each topic.

Topics covered here that are not covered in a traditional text include nonlinear dynamics and the use of MATLAB for numerical analysis and simulation. Also, a significant portion of the text consists of review and learning modules. Each learning module provides model development, steady-state solutions, nonlinear dynamic results, linearization, state space and transfer function analysis and simulation. The motivation for this approach is to allow the student to "tie-together" all of the concepts, rather than treating them independently (and not understanding the connections between the different methods).

An important feature of this text is the use of MATLAB software. A set of m-files used in many of the examples and in the learning modules is available via the world wide web at the following locations:

http:/www/rpi.edu/-bequeb/Process_Dynamics
http:/www.mathworks.com/education/thirdparty.html

Additional learning modules will also be available at the RPI location.

A few acknowledgments are in order. A special thanks to Professor Jim Turpin at the University of Arkansas, who taught me the introductory course in process dynamics and control. His love of teaching should be an inspiration to us all. Many thanks to one of my graduate students, Lou Russo, who not only made a number of suggestions to improve the text, but also sparked an interest in many of the undergraduates that have taken the course. The task of developing a solutions manual has been carried out by Venkatesh Natarajan, Brian Aufderheide, Ramesh Rao, Vinay Prasad, and Kevin Schott.

Preliminary drafts of many chapters were developed over cappuccinos at the Daily Grind in Albany and Troy. Bass Ale served at the El Dorado in Troy promoted discussions about teaching (and other somewhat unrelated topics) with my graduate students; the effect of the many Buffalo wings is still unclear. Final revisions to the textbook were done under the influence of cappuccinos at Cafe Avanti in Chicago (while there is a lot of effort in developing interactive classroom environments at Rensselaer, my ideal study environment looks much like a coffee shop).

Teaching and learning should be dynamic processes. I would appreciate any comments and suggestions that you have on this textbook. I will use the WWW site to provide updated examples, additional problems with solutions, and suggestions for teaching and studying process dynamics.

*B. Wayne Bequette*

# SECTION I

# PROCESS MODELING

# INTRODUCTION

# 1

This chapter provides a motivation for process modeling and the study of dynamic chemical processes. It also provides an overview of the structure of the textbook. After studying this chapter, the student should be able to answer the following questions:

- What is a process model?
- Why develop a process model?
- What is the difference between lumped parameter and distributed parameter systems?
- What numerical package forms the basis for the examples in this text?
- What are the major objectives of this textbook?

The major sections are:

1.1 Motivation
1.2 Models
1.3 Systems
1.4 Background of the Reader
1.5 How to Use This Textbook
1.6 Courses Where This Textbook Can Be Used

## 1.1 MOTIVATION

Robert Reich in *The Work of Nations* has classified three broad categories of employment in the United States. In order of increasing educational requirement these categories are:

routine production services, in-person services, and *symbolic-analytic* services. To directly quote from Reich:

> "Symbolic analysts solve, identify, and broker problems by manipulating *symbols*. They simplify reality into *abstract* images that can be rearranged, juggled, experimented with, communicated to other specialists, and then, eventually, transformed back into reality. The manipulations are done with analytic tools, sharpened by experience. The tools may be *mathematical algorithms*, legal arguments, financial gimmicks, *scientific principles*, psychological insights about how to persuade or to amuse, systems of induction or deduction, or any other set of techniques for doing conceptual puzzles." (italics added for emphasis)

Engineers (and particularly process engineers) are *symbolic analysts*. Process engineers use fundamental scientific principles as a basis for mathematical models that characterize the behavior of a chemical process. Symbols are used to represent physical variables, such as pressure, temperature or concentration. Input information is specified and numerical algorithms are used to solve the models (simulating a physical system). Process engineers analyze the results of these simulations to make decisions or recommendations regarding the design or operation of a process.

Most chemical engineers work with chemical manufacturing processes in one way or another. Often they are process engineers responsible for technical troubleshooting in the day-to-day operations of a particular chemical process. Some are responsible for designing feedback control systems so that process variables (such as temperature or pressure) can be maintained at desired values. Others may be responsible for redesigning a chemical process to provide more profitability. All of these responsibilities require an understanding of the time-dependent (dynamic) behavior of chemical processes.

## 1.2 MODELS

The primary objective of this textbook is to assist you in developing an understanding of the dynamic behavior of chemical processes. A requirement for assessing the dynamic behavior is a time-dependent mathematical model of the chemical process under consideration. Before proceeding, it is worth consulting with two different dictionaries for a definition of *model*.

---

**Dictionary Definitions:** *Model*

*Model* is derived from the Latin *modus*, which means *a measure*. Used as a noun, it means "a small representation of a planned or existing object" (*Webster's New World Dictionary*).

> "A mathematical or physical system, obeying certain specified conditions, whose behavior is used to understand a physical, biological, or social system to which it is analogous in some way" (*McGraw-Hill Dictionary of Scientific and Technical Terms*).

---

Notice that both definitions stress that a model is a representation of a system or object. In this textbook, when we use the term model, we will be referring to a mathematical model. We prefer to use the following definition for model (more specifically, a process model).

**Working Definition:** *Process Model*

A process model is a set of equations (including the necessary input data to solve the equations) that allows us to predict the behavior of a chemical process system.

The emphasis in this text is on the development and use of *fundamental* or first-principles models. By fundamental, we mean models that are based on known physical-chemical relationships. This includes the conservation of mass and conservation of energy,[1] as well as reaction kinetics, transport phenomena, and thermodynamic (phase equilibrium, etc.) relationships.

Another common model is the *empirical* model. An empirical model might be used if the process is too complex for a fundamental model (either in the formulation of the model, or the numerical solution of the model), or if the empirical model has satisfactory predictive capability. An example of an empirical model is a simple least squares fit of an equation to experimental data.

Generally, we would prefer to use models based on fundamental knowledge of chemical-physical relationships. Fundamental models will generally be accurate over a much larger range of conditions than empirical models. Empirical models may be useful for "interpolation" but are generally not useful for "extrapolation"; that is, an empirical model will only be useful over the range of conditions used for the "fit" of the data.

It should be noted that it is rare for a single process model to exist. A model is only an approximate representation of an actual process. The complexity of a process model will depend on the final use of the model. If only an approximate answer is needed, then a simplified model can often be used.

### 1.2.1 How Models Are Used

As we have noted, given a set of input data, a model is used to predict the output "response." A model can be used to solve the following types of problems:

- Marketing: If the price of a product is increased, how much will the demand decrease?
- Allocation: If we have several sources for raw materials, and several manufacturing

---

[1] Of course, the real conservation law is that of mass-energy, but we will neglect the interchange of mass and energy due to nuclear reactions.

plants, how do we distribute the raw materials among the plants, and decide what products each plant produces?

- Synthesis: What process (sequence of reactors, separation devices, etc.) can be used to manufacture a product?
- Design: What type and size of equipment is necessary to produce a product?
- Operation: What operating conditions will maximize the yield of a product?
- Control: How can a process input be manipulated to maintain a measured process output at a desired value?
- Safety: If an equipment failure occurs, what will be the impact on the operating personnel and other process equipment?
- Environmental: How long will it take to "biodegrade" soil contaminated with hazardous waste?

Many of the models cited above are based on a steady-state analysis. This book will extend the steady-state material and energy balance concepts, generally presented in an introductory textbook on chemical engineering principles, to dynamic systems (systems where the variables change with time). As an example of the increasing importance of knowledge of dynamic behavior, consider process design. In the past, chemical process design was based solely on steady-state analysis. A problem with performing only a steady-state design is that it is possible to design a process with desirable steady-state characteristics (minimal energy consumption, etc.) but which is dynamically inoperable. Hence, it is important to consider the dynamic operability characteristics of a process during the design phase. Also, batch processes that are commonly used in the pharmaceutical or specialty chemicals industries are inherently dynamic and cannot be simulated with steady-state models.

In the previous discussion we have characterized models as steady-state or dynamic. Another characterization is in terms of *lumped parameter systems* or *distributed parameter systems*. A lumped parameter system assumes that a variable of interest (temperature, for example) changes only with one independent variable (time, for example, but not space). A typical example of a lumped parameter system is a perfectly mixed (stirred) tank, where the temperature is uniform throughout the tank. A distributed parameter system has more than one independent variable; for example, temperature may vary with both spatial position and time.

### EXAMPLE 1.1 A Lumped Parameter System

Consider a perfectly insulated, well-stirred tank where a hot liquid stream at 60°C is mixed with a cold liquid stream at 10°C (Figure 1.1). The well-mixed assumption means that the fluid temperature in the tank is uniform and equal to the temperature at the exit from the tank. This is an example of a lumped parameter system, since the temperature does not vary with spatial position.

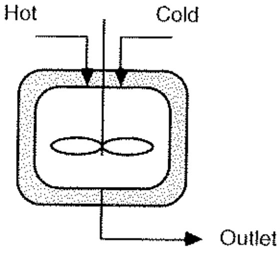


**FIGURE 1.1** Stirred tank.

Consider now the steady-state behavior of this process. If the only stream was the hot fluid, then the outlet temperature would be equal to the hot fluid temperature if the tank were perfectly insulated. Similarly, if the only stream was the cold stream, then the outlet temperature would be equal to the cold fluid temperature. A combination of the two streams yields an outlet temperature that is intermediate between the cold and hot temperatures, as shown in Figure 1.2.

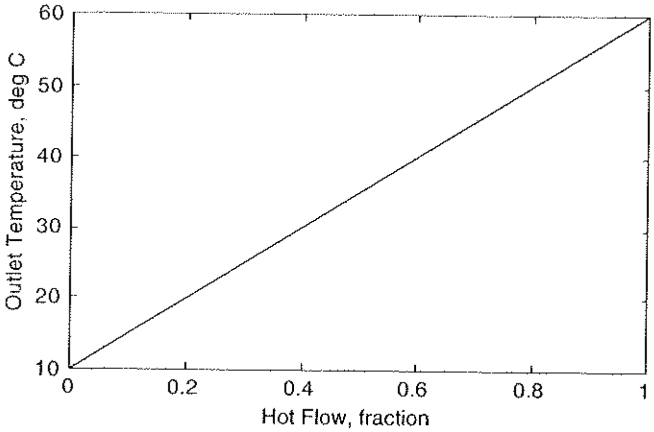


**FIGURE 1.2** Relationship between hot flow and outlet temperature.

We see that there is a linear steady-state relationship between the hot flow (fraction) and the outlet temperature.

Now we consider the dynamic response to a change in the fraction of hot flow. Figure 1.3 compares outlet temperature responses for various step changes in hot flow fraction at $t = 2.5$

minutes. We see that the changes are symmetric, with the same speed of response. We will find later that these responses are indicative of a linear system.

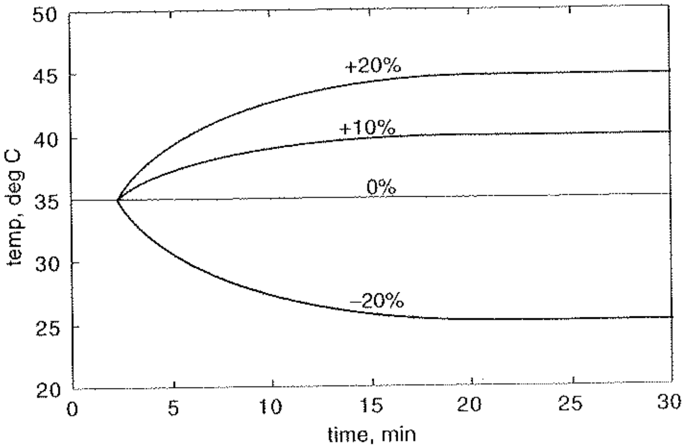


**FIGURE 1.3** Response of temperature to various changes in the hot flow fraction.

## EXAMPLE 1.2 A Distributed Parameter System

A simplified representation of a counterflow heat exchanger is shown in Figure 1.4. A cold water stream flows through one side of the exchanger and is heated by energy transfered from a condensing steam stream. This is a distributed parameter system because the temperature of the water stream can change with time *and* position.

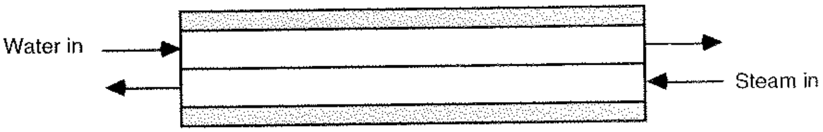


**FIGURE 1.4** Counterflow heat exchanger.

The steady-state temperature profile (water temperature as a function of position) is shown in Figure 1.5. Notice that rate of change of the water temperature with respect to distance decreases as the water temperature approaches the steam temperature (100°C). This is because the temperature gradient for heat transfer decreases as the water temperature increases. The outlet water temperature as a function of inlet water temperature is shown in Figure 1.6.

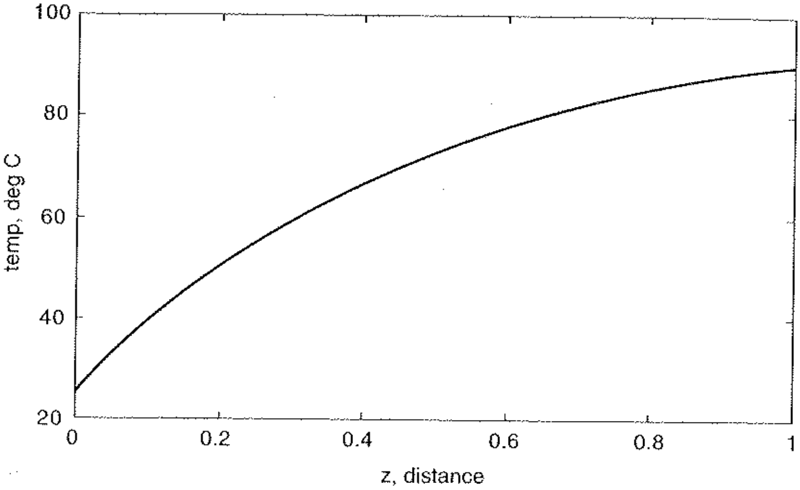


**FIGURE 1.5** Water temperature as a function of position.

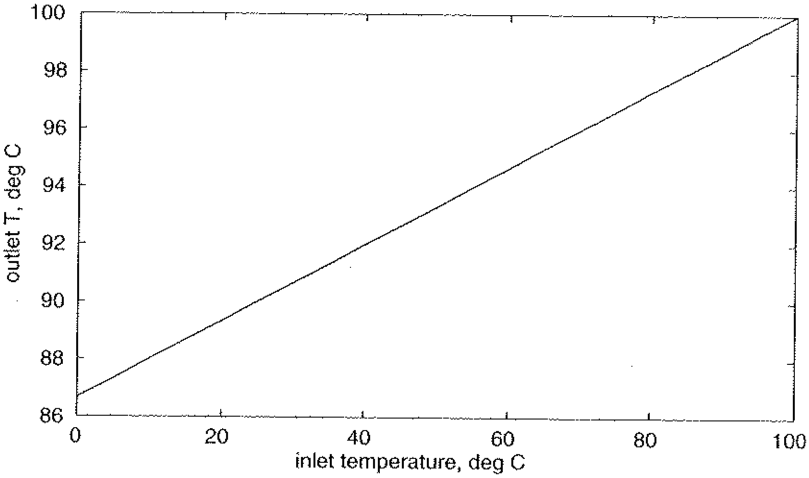


**FIGURE 1.6** Outlet water temperature as a function of inlet water temperature.

Mathematical models consist of the following types of equations (including combinations)

- Algebraic equations
- Ordinary differential equations
- Partial differential equations

The emphasis in this textbook is on developing models that consist of ordinary differential equations. These equations generally result from macroscopic balances around processes, with an assumption of a perfectly mixed system. To find the steady-state solution of a set of ordinary differential equations, we must solve a set of algebraic equations. Partial differential equation models result from microscopic balances and are not covered in this textbook. One of the main techniques for solving partial differential equations is based on converting a partial differential equation to a set of ordinary differential equations. Techniques developed in this textbook can then be used to solve these problems.

## 1.3 SYSTEMS

We have been using the term *system* very loosely. Consider the following definition.

---

**Definition:** *System*

A combination of several pieces of equipment integrated to perform a specific function; thus a fire (artillery) control system may include a tracking radar, computer, and gun (*McGraw-Hill Dictionary of Scientific and Technical Terms*).

---

The example in the definition presented is of interest to electrical, aeronautical, and military engineers. For our purposes, a system will be composed of chemical unit operations, such as chemical reactors, heat exchangers, and separation devices, which are used to produce a chemical product. Indeed, we will often consider a single unit operation to be a system composed of inputs, states (to be defined later) and outputs. A series of modules in Section V of this textbook cover the behavior of a number of specific unit operations.

### 1.3.1 Simulation

One of the goals of this textbook is to develop numerical analysis techniques that allow us to "simulate" the behavior of a chemical process. Typically, steady-state simulation of a lumped parameter system involves the solution of algebraic equations, while dynamic simulation involves the solution of ordinary differential equations. We must be careful when using computer simulation. First of all, we must be able to say, Do the results of this simulation make sense? Common sense and "back of the envelope" calculations will tell us if the numerical results are in the ballpark.

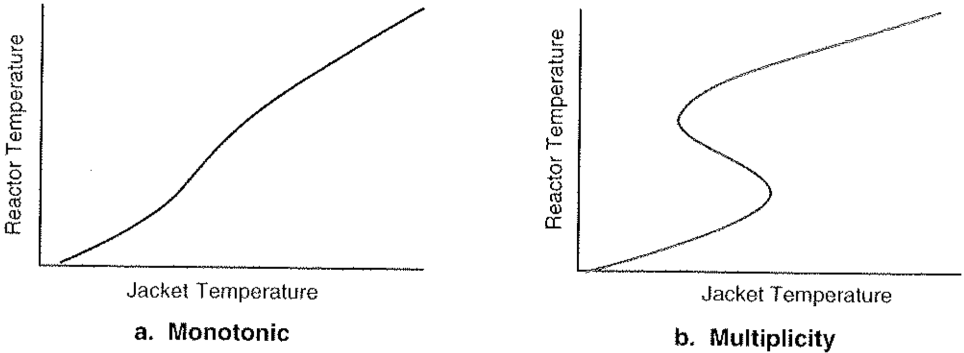
### 1.3.2 Linear Systems Analysis

The mathematical tools that are used to study linear dynamic systems problems are known as *linear systems analysis* techniques. Traditionally, systems analysis techniques have been based on linear systems theory. Two basic approaches are typically used: (i) Laplace transforms are used to analyze the behavior of a single, linear, *n*th order ordinary differential equation, and (ii) state space techniques (based on the linear algebra techniques of eigenvalue and eigenvector analysis) are used to analyze the behavior of multiple first-order linear ordinary differential equations. If a system of ordinary differential equations is nonlinear, they can be linearized at a desired steady-state operating point.

### 1.3.3 A Broader View of Analysis

In this textbook we use *analysis* in a broader context than linear systems analysis that may be applied to a model with a specific value for the parameters. Analysis means seeking a deeper understanding of a process than simply performing a simulation or solving a set of equations for a particular set of parameters and input values. Often we want to understand how the response of system variable (temperature, for example) changes when a parameter (e.g., heat transfer coefficient) or input (flowrate or inlet temperature) changes. Rather than trying to obtain the understanding of the possible types of behavior by merely running many simulations (varying parameters, etc.), we must decide which parameters (or inputs or initial conditions) are likely to vary, and use analysis techniques to determine if a qualitative change of behavior (number of solutions or stability of a solution) can occur.

This qualitative change is illustrated in Figure 1.7 below, which shows possible steady-state behavior for a jacketed chemical reactor. In Figure 1.7a there is a monotonic



**a. Monotonic** **b. Multiplicity**

**FIGURE 1.7** Two qualitatively different types of input/output behavior. Steady-state reactor temperature as a function of steady-state jacket temperature.

relationship between jacket temperature and reactor temperature, that is, as the steady-state jacket temperature increases, the steady-state reactor temperature increases. Figure 1.7b illustrates behavior known as output multiplicity, that is, there is a region of steady-state jacket temperatures where a single jacket temperature can yield three possible reactor temperatures. In Chapter 15 (and module 9) we show how to vary a reactor design parameter to change from one type of behavior to another.

Engineering problem solving can be a combination of art and science. The complexity and accuracy of a solution will depend on the information available or what is desired in the final solution. If you are simply performing a rough (back of the envelope) cost estimate for a process design, perhaps a simple steady-state material and energy balance will suffice. On the other hand, if an optimum design integrating several unit operations is required, then a more complex solution will be involved.

## 1.4 BACKGROUND OF THE READER

It is assumed that the reader of this textbook has a sophomore- or junior-level chemical engineering background. In addition to the standard introductory chemistry, physics, and mathematics (including differential equations) courses, the student has taken an introduction to chemical engineering (material and energy balances, reaction stoichiometry) course.

This textbook can also be used by an engineer in industry who needs to develop dynamic models to perform studies to improve a process or design controllers. Although a few years may have lapsed since the engineer took a differential equations course, the review provided in this text should be sufficient for the development and solution of models based on differential equations. Also, this textbook can serve as review material for first-year graduate student who is interested in process modeling, systems analysis, or numerical methods.

## 1.5 HOW TO USE THIS TEXTBOOK

The ultimate objective of this textbook is to be able to model, simulate, and (more importantly) understand the dynamic behavior of chemical processes.

### 1.5.1 Sections

In Section I (Chapters 1 and 2) we show how to develop dynamic models for simple chemical processes. Numerical techniques for solving algebraic and differential equations are covered in Section II (Chapters 3 and 4). Much of the textbook is based on linear system analysis techniques, which are presented in Section III (Chapters 5 through 12). Nonlinear analysis techniques are presented in Section IV (Chapters 13–17). Section V (Modules 1 through 10) consists of a number of learning modules to reinforce the concepts discussed in Sections I through IV.

### 1.5.2 Numerical Solutions

It is much easier to learn a new topic by "doing" rather than simply reading about it. To understand the dynamic behavior of chemical processes, one needs to be able to solve differential equations and plot response curves. We have used the MATLAB numerical analysis package to solve equations in this text. A MATLAB learning module is in the set of modules in Section V (Module 1) for readers who are not familiar with or need to be reintroduced to MATLAB. MATLAB routines are detailed within the chapter that they are used. Many of the examples have MATLAB m-files associated with them. It is recommended that the reader modify these m-files to understand the effect of parameter changes on the numerical solution.

### 1.5.3 Motivating Examples and Modules

This textbook contains many process examples. Often, new techniques are introduced in the examples. You are encouraged to work through each example to understand how a particular technique can be applied.

There is a limit to the complexity of an example that can be used when introducing a new technique; the examples presented in the chapters tend to be short and illustrate one or two numerical techniques. There is a set of *modules* of models, in Section V, that treats process examples in much more detail. The objective of these modules is to provide a more complete treatment of modeling and simulation of a specific process. In each process modeling module, a number of the techniques introduced in various chapters of the text are applied to the problem at hand.

## 1.6 COURSES WHERE THIS TEXTBOOK CAN BE USED

This textbook is based on a required course that I have taught to chemical and environmental engineering juniors at Rensselaer since 1991. This *dynamic systems* course (originally titled *lumped parameter systems*) is a prerequisite to a required course on chemical process control, normally taken in the second semester of the junior year. This textbook can be used for the first term of a two-term sequence in dynamics and control. I have not treated process control in this text because I feel that there is a need for more in-depth coverage of process dynamics than is covered in most process control textbooks.

This textbook can also be used in courses such as process modeling or numerical methods for chemical engineers. Although directed towards undergraduates, this text can also be used in a first-year graduate course on process modeling or process dynamics; in this case, much of the focus would be on Section IV (nonlinear analysis) and in-depth studies of the modules.

## SUMMARY

At this point, the reader should be able to define or characterize the following

- Process model
- Lumped or distributed parameter system
- Analysis
- Simulation

## FURTHER READING

The textbooks listed below are nice introductions to material and energy balances. The Russell and Denn book also provides an excellent introduction to models of dynamic systems.

Felder, R.M., & R. Rousseau. (1986). *Elementary Principles of Chemical Processes*, 2nd ed. New York: Wiley.

Himmelblau, D.M. (1996). *Basic Principles and Calculations in Chemical Engineering*, 6th ed. Upper Saddle River, NJ: Prentice-Hall.

Russell, T.R.F., & M.M. Denn. (1971). *Introduction to Chemical Engineering Analysis*, New York: Wiley.

A comprehensive tutorial and reference for MATLAB is provided by Hanselman and Littlefield. The books by Etter provide many excellent examples using MATLAB to solve engineering problems.

Hanselman, D., & B. Littlefield. (1996). *Mastering MATLAB*. Upper Saddle River, NJ: Prentice-Hall.

Etter, D.M. (1993). *Engineering Problem Solving with MATLAB*. Upper Saddle River, NJ: Prentice-Hall.

Etter, D.M. (1996). *Introduction to MATLAB for Engineers and Scientists*. Upper Saddle River, NJ: Prentice-Hall.

The following book by Denn is a graduate-level text that discusses the more philosophical issues involved in process modeling.

Denn, M.M. (1986). *Process Modeling*. New York: Longman.

An undergraduate control textbook with significant modeling and simulation is by Luyben. Numerous FORTRAN examples are presented.

Luyben, W.L. (1990). *Process Modeling, Simulation and Control for Chemical Engineers*, 2nd ed. New York: McGraw-Hill.

A number of control textbooks contain a limited amount of modeling. Examples include:

Seborg, D.E., T.F. Edgar, & D.A. Mellichamp. (1989). *Process Dynamics and Control*. New York: Wiley.

Stephanopoulos, G. (1984). *Chemical Process Control: An Introduction to Theory and Practice*. Englewood Cliffs, NJ: Prentice-Hall.

The following book by Rameriz is more of an advanced undergraduate/first-year graduate student text on numerical methods to solve chemical engineering problems. The emphasis is on FORTRAN subroutines to be used with the IMSL numerical package.

Rameriz, W.F. (1989). *Computational Methods for Process Simulation*. Boston: Butterworths.

Issues in process modeling are discussed by Himmelblau in Chapter 3 of the following book:

Bisio, A., & R.L. Kabel. (1985). *Scaleup of Chemical Processes*. New York: Wiley.

The following book by Reich provides an excellent perspective on the global economy and role played by U.S. workers

Reich, R.B. (1991). *The Work of Nations*. New York: Vintage Books.

## STUDENT EXERCISES

1. Review the matrix operations module (Section V).
2. Work through the MATLAB module (Section V).
3. Consider example 2. If there is a sudden increase in steam pressure (and therefore, temperature) sketch the expected cold-side temperature profiles at 0, 25, 50, 75, and 100% of the distance through the heat exchanger.

# PROCESS MODELING

# 2

In this chapter, a methodology for developing dynamic models of chemical processes is presented. After studying this chapter, the student should be able to:

- Write balance equations using the integral or instantaneous methods.
- Incorporate appropriate constitutive relationships into the equations.
- Determine the state, input and output variables, and parameters for a particular model (set of equations).
- Determine the necessary information to solve a system of dynamic equations.
- Define dimensionless variables and parameters to "scale" equations.

The major sections are:

2.1 Background
2.2 Balance Equations
2.3 Material Balances
2.4 Constitutive Relationships
2.5 Material and Energy Balances
2.6 Distributed Parameter Systems
2.7 Dimensionless Models
2.8 Explicit Solutions to Dynamic Models
2.9 General Form of Dynamic Models

## 2.1 BACKGROUND

Many reasons for developing process models were given in Chapter 1. Improving or understanding chemical process operation is a major overall objective for developing a dynamic process model. These models are often used for (i) operator training, (ii) process design, (iii) safety system analysis or design, or (iv) control system design.

***Operator Training.*** The people responsible for the operation of a chemical manufacturing process are known as *process operators*. A dynamic process model can be used to perform simulations to train process operators, in the same fashion that flight simulators are used to train airplane pilots. Process operators can learn the proper response to upset conditions, before having to experience them on the actual process.

***Process Design.*** A dynamic process model can be used to properly design chemical process equipment for a desired production rate. For example, a model of a batch chemical reactor can be used to determine the appropriate size of the reactor to produce a certain product at a desired rate.

***Safety.*** Dynamic process models can also be used to design safety systems. For example, they can be used to determine how long it will take after a valve fails for a system to reach a certain pressure.

***Control System Design.*** Feedback control systems are used to maintain process variables at desirable values. For example, a control system may measure a product temperature (an output) and adjust the steam flowrate (an input) to maintain that desired temperature. For complex systems, particularly those with many inputs and outputs, it is necessary to base the control system design on a process model. Also, before a complex control system is implemented on a process, it is normally tested by simulating the expected performance using computer simulation.

## 2.2 BALANCE EQUATIONS

The emphasis in an introductory material and energy balances textbook is on *steady-state* balance equations that have the following form:

$$\begin{bmatrix}\text{mass or energy}\\ \text{entering}\\ \text{a system}\end{bmatrix} - \begin{bmatrix}\text{mass or energy}\\ \text{leaving}\\ \text{a system}\end{bmatrix} = 0 \qquad (2.1)$$

Equation (2.1) is deceptively simple because there may be many ins and outs, particularly for component balances. The in and out terms would then include the generation and conversion of species by chemical reaction, respectively. In this text, we are interested in dynamic balances that have the form:

$$\begin{bmatrix} \text{rate of mass or energy} \\ \text{accumulation in} \\ \text{a system} \end{bmatrix} = \begin{bmatrix} \text{rate of mass or} \\ \text{energy entering} \\ \text{a system} \end{bmatrix} - \begin{bmatrix} \text{rate of mass or} \\ \text{energy leaving} \\ \text{a system} \end{bmatrix} \tag{2.2}$$

The rate of mass accumulation in a system has the form $dM/dt$ where $M$ is the total mass in the system. Similarly, the rate of energy accumulation has the form $dE/dt$ where $E$ is the total energy in a system. If $N_i$ is used to represent the moles of component $i$ in a system, then $dN_i/dt$ represents the molar rate of accumulation of component $i$ in the system.

When solving a problem, it is important to specify what is meant by system. In some cases the system may be microscopic in nature (a differential element, for example), while in other cases it may be macroscopic in nature (the liquid content of a mixing tank, for example). Also, when developing a dynamic model, we can take one of two general viewpoints. One viewpoint is based on an *integral* balance, while the other is based on an *instantaneous* balance. Integral balances are particularly useful when developing models for distributed parameter systems, which result in partial differential equations; the focus in this text is on ordinary differential equation-based models. Another viewpoint is the instantaneous balance where the time rate of change is written directly.

### 2.2.1 Integral Balances

An integral balance is developed by viewing a system at two different snapshots in time. Consider a finite time interval, $\Delta t$, and perform material balance over that time interval

$$\begin{bmatrix} \text{mass or energy} \\ \text{inside the system} \\ \text{at } t + \Delta t \end{bmatrix} - \begin{bmatrix} \text{mass or energy} \\ \text{inside the system} \\ \text{at } t \end{bmatrix} = \begin{bmatrix} \text{mass or energy} \\ \text{entering the system} \\ \text{from } t \text{ to } t + \Delta t \end{bmatrix} - \begin{bmatrix} \text{mass or energy} \\ \text{leaving the system} \\ \text{from } t \text{ to } t + \Delta t \end{bmatrix} \tag{2.3}$$

The mean-value theorems of integral and differential calculus are then used to reduce the equations to differential equations.

For example, consider the system shown in Figure 2.1 below, where one boundary represents the mass in the system at time $t$, while the other boundary represents the mass in the system at $t + \Delta t$.

An integral balance on the total mass in the system is written in the form:

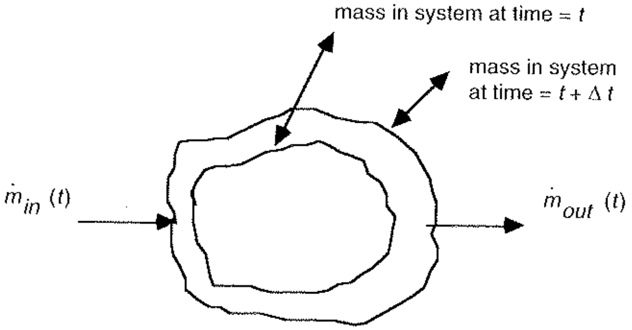


**FIGURE 2.1** Conceptual material balance problem.

$$\begin{bmatrix}\text{mass contained}\\ \text{in the system}\\ \text{at } t+\Delta t\end{bmatrix} - \begin{bmatrix}\text{mass contained}\\ \text{in the system}\\ \text{at } t\end{bmatrix} = \begin{bmatrix}\text{mass entering}\\ \text{the system}\\ \text{from } t \text{ to } t+\Delta t\end{bmatrix} - \begin{bmatrix}\text{mass leaving}\\ \text{the system}\\ \text{from } t \text{ to } t+\Delta t\end{bmatrix}$$

Mathematically, this is written:

$$M\big|_{t+\Delta t} - M\big|_t = \int_t^{t+\Delta t} \dot{m}_{in}\, dt - \int_t^{t+\Delta t} \dot{m}_{out}\, dt$$

or

$$M\big|_{t+\Delta t} - M\big|_t = \int_t^{t+\Delta t} (\dot{m}_{in} - \dot{m}_{out})\, dt \tag{2.4}$$

where $M$ represents the total mass in the system, while $\dot{m}_{in}$ and $\dot{m}_{out}$ represent the mass rates entering and leaving the system, respectively. We can write the righthand side of (2.4), using the mean value theorem of *integral* calculus, as:

$$\int_t^{t+\Delta t} (\dot{m}_{in} - \dot{m}_{out})\, dt = (\dot{m}_{in} - \dot{m}_{out})\big|_{t+\alpha\Delta t}\Delta t$$

where $0 < \alpha < 1$. Equation (2.4) can now be written:

$$M\big|_{t+\Delta t} - M\big|_t = (\dot{m}_{in} - \dot{m}_{out})\big|_{t+\alpha\Delta t}\Delta t$$

dividing by $\Delta t$,

$$\frac{M\big|_{t+\Delta t} - M\big|_t}{\Delta t} = (\dot{m}_{in} - \dot{m}_{out})\big|_{t+\alpha\Delta t}$$

and using the mean value theorem of *differential* calculus ($0 < \beta < 1$) for the lefthand side,

$$\frac{M\big|_{t+\Delta t} - M\big|_t}{\Delta t} = \frac{dM}{dt}\Big|_{t+\beta\Delta t}$$

which yields

$$\left.\frac{dM}{dt}\right|_{t+\beta\Delta t} = (\dot{m}_{in} - \dot{m}_{out})\Big|_{t+\alpha\Delta t}$$

Taking the limit as $\Delta t$ goes to zero, we find

$$\frac{dM}{dt} = \dot{m}_{in} - \dot{m}_{out} \tag{2.5}$$

and representing the total mass as $M = V\rho$, $\dot{m}_{in}$ as $F_{in}\rho_{in}$ and $\dot{m}_{out}$ as $F_{out}\rho$, where $\rho$ is the mass density (mass/volume) and $F$ is a volumetric flowrate (volume/time) we obtain the equation:

$$\frac{dV\rho}{dt} = F_{in}\rho_{in} - F_{out}\rho \tag{2.6}$$

Note that we have assumed that the system is perfectly mixed, so that the density of material leaving the system is equal to the density of material in the system.

### 2.2.2 Instantaneous Balances

Here we write the dynamic balance equations directly, based on an instantaneous rate-of-change:

$$\left[\begin{array}{c}\text{the rate of}\\ \text{accumulation of}\\ \text{mass in the system}\end{array}\right] = \left[\begin{array}{c}\text{rate of}\\ \text{mass entering}\\ \text{the system}\end{array}\right] - \left[\begin{array}{c}\text{rate of}\\ \text{mass leaving}\\ \text{the system}\end{array}\right] \tag{2.7}$$

which can be written directly as,

$$\frac{dM}{dt} = \dot{m}_{in} - \dot{m}_{out} \tag{2.8}$$

or

$$\frac{dV\rho}{dt} = F_{in}\rho_{in} - F_{out}\rho \tag{2.9}$$

which is the same result obtained using an integral balance. Although the integral balance takes longer to arrive at the same result as the instantaneous balance method, the integral balance method is probably clearer when developing distributed parameter (partial differential equation-based) models. An example is shown in Section 2.6.

Section 2.3 covers material balances and Section 2.5 covers material and energy balances. Section 2.4 discusses constitutive relationships.

## 2.3 MATERIAL BALANCES

The simplest modeling problems consist of material balances. In this section we use several process examples to illustrate the modeling techniques used.

**EXAMPLE 2.1 Liquid Surge Tank**

Surge tanks are often used to "smooth" flowrate fluctuations in liquid streams flowing between chemical processes. Consider a liquid surge tank with one inlet (flowing from process I) and one outlet stream (flowing to process II) (Figure 2.2). Assume that the density is constant. Find how the volume of the tank varies as a function of time, if the inlet and outlet flowrates vary. List the *state variables*, *parameters*, as well as the *input* and *output variables*. Give the necessary information to complete the quantitative solution to this problem.

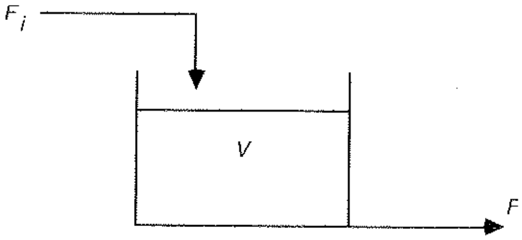


**FIGURE 2.2** Liquid surge tank.

The system is the liquid in the tank, the liquid surface is the top boundary of the system. The following notation is used in the modeling equations:

$F_i$ = inlet volumetric flowrate (volume/time)
$F$ = outlet volumetric flowrate
$V$ = volume of liquid in the tank
$\rho$ = liquid density (mass/volume)

## Integral Method

Consider a finite time interval, $\Delta t$. Performing a material balance over that time interval,

$$\begin{bmatrix}\text{mass of water}\\ \text{inside the tank}\\ \text{at } t+\Delta t\end{bmatrix} - \begin{bmatrix}\text{mass of water}\\ \text{inside the tank}\\ \text{at } t\end{bmatrix} = \begin{bmatrix}\text{mass of water}\\ \text{entering tank}\\ \text{from } t \text{ to } t+\Delta t\end{bmatrix} - \begin{bmatrix}\text{mass of water}\\ \text{leaving tank}\\ \text{from } t \text{ to } t+\Delta t\end{bmatrix}$$

which we can write mathematically as:

$$V\rho\big|_{t+\Delta t} - V\rho\big|_{t} = \int_{t}^{t+\Delta t} F_i\rho\,dt - \int_{t}^{t+\Delta t} F\rho\,dt \qquad (2.10)$$

Bringing the righthand side terms under the same integral

$$V\rho\big|_{t+\Delta t} - V\rho\big|_t = \int_t^{t+\Delta t} (F_i\rho - F\rho)\, dt \tag{2.11}$$

We can use the mean value theorem of integral calculus to write the righthand side of (2.11) (where $0 \le \alpha \le 1$) as:

$$\int_t^{t+\Delta t} (F_i\rho - F\rho)\, dt = (F_i\rho - F\rho)\big|_{t+\alpha\Delta t}\Delta t \tag{2.12}$$

Substituting (2.12) into (2.11)

$$V\rho\big|_{t+\Delta t} - V\rho\big|_t = (F_i\rho - F\rho)\big|_{t+\alpha\Delta t}\Delta t \tag{2.13}$$

Dividing by $\Delta t$, we obtain

$$\frac{V\rho\big|_{t+\Delta t} - V\rho\big|_t}{\Delta t} = (F_i\rho - F\rho)\big|_{t+\alpha\Delta t} \tag{2.14}$$

and using the mean value theorem of differential calculus, as $\Delta t \to 0$

$$\frac{dV\rho}{dt} = F_i\rho - F\rho \tag{2.15}$$

## Instantaneous Method

Here we write the balance equations based on an instantaneous rate-of-change:

$$\begin{bmatrix}\text{the rate of change of}\\ \text{mass of water in tank}\end{bmatrix} = \begin{bmatrix}\text{mass flowrate of}\\ \text{water into tank}\end{bmatrix} - \begin{bmatrix}\text{mass flowrate of}\\ \text{water out of tank}\end{bmatrix}$$

The total mass of water in the tank is $V\rho$, the rate of change is $dV\rho/dt$, and the density of the outlet stream is equal to the tank contents:

$$\frac{dV\rho}{dt} = F_i\rho - F\rho \tag{2.16}$$

which is exactly what we derived using the integral method. Given the same set of assumptions the two methods should yield the same model. You should use the approach (integral or instantaneous) that makes the most sense to you. In this text we generally use the instantaneous approach since it requires the fewest number of steps.

Notice the implicit assumption that the density of water in the tank does not depend upon position (the perfect mixing assumption). This assumption allows an ordinary differential equation (ODE) formulation. We refer to any system that can be modeled by ODEs as *lumped parameter systems*. Also notice that the outlet stream density must be equal to the density of water in the tank. This knowledge also allows us to say that the density terms in (2.16) are equal. This equation is then reduced to[1]

---

[1] It might be tempting to the reader to begin to directly write "volume balance" expressions that look similar to (2.17). We wish to make it clear that there is no such thing as a volume balance and (2.17) is only correct because of the constant density assumption. It is a good idea to always write a mass balance expression, such as (2.16), before making assumptions about the fluid density, which may lead to (2.17).

$$\frac{dV}{dt} = F_i - F \tag{2.17}$$

Equation (2.17) is a linear ordinary differential equation (ODE), which is trivial to solve if we know the inlet and outlet flowrates as a function of time, and if we know an initial condition for the volume in the tank. In equation (2.17) we refer to $V$ as a *state variable*, and $F_i$ and $F$ as *input variables* (even though $F$ is an outlet stream flowrate). If density remained in the equation, we would refer to it as a *parameter*.

In order to solve this problem we must specify the inputs $F_i(t)$ and $F(t)$ and the initial condition $V(0)$.

Example 2.1 provides an introduction to the notion of states, inputs, and parameters. This example illustrates how an overall material balance is used to find how the volume of a liquid phase system changes with time. It may be desirable to have tank height, $h$, rather than tank volume as the state variable. If we assume a constant tank cross-sectional area, $A$, we can express the tank volume as $V = Ah$ and the modeling equation as

$$\frac{dh}{dt} = \frac{F_i}{A} - \frac{F}{A} \tag{2.18}$$

If we also know that the flowrate out of the tank is proportional to the square root of the height of liquid in the tank, we can use the relationship (see student exercise 21)

$$F = \beta\sqrt{h} \tag{2.19}$$

where $\beta$ is a flow coefficient, to find

$$\frac{dh}{dt} = -\frac{\beta\sqrt{h}}{A} + \frac{F_i}{A} \tag{2.20}$$

For this model we refer to $h$ as the *state* variable, inlet flowrate ($F_i$) as the *input* variable and $\beta$ and $A$ as *parameters*.

Notice that a single system (in this case, the liquid surge tank) can have slightly different modeling equations and variables, depending on assumptions and the objectives used when developing the model.

### EXAMPLE 2.2 An Isothermal Chemical Reactor

Assume that two chemical species, $A$ and $B$, are in a solvent feedstream entering a liquid-phase chemical reactor that is maintained at a constant temperature (Figure 2.3). The two species react irreversibly to form a third species, $P$. Find the reactor concentration of each species as a function of time.

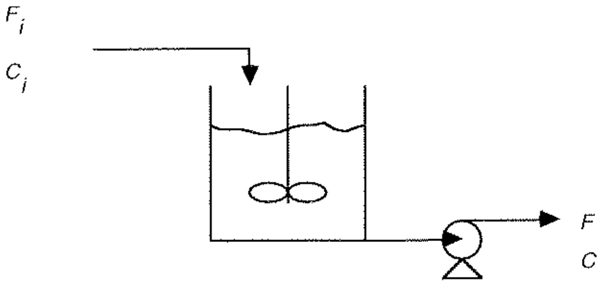


**FIGURE 2.3** Isothermal chemical reactor.

## Overall Material Balance

The overall mass balance is (since the tank is perfectly mixed)

$$\frac{dV\rho}{dt} = F_i\rho_i - F\rho \tag{2.21}$$

*Assumption:* The liquid phase density, $\rho$, is not a function of concentration. The tank (and outlet) density is then equal to the inlet density, so:

$$\rho_i = \rho \tag{2.22}$$

and we can write (2.21) as:

$$\frac{dV}{dt} = F_i - F \tag{2.23}$$

## Component Material Balances

It is convenient to work in molar units when writing component balances, particularly if chemical reactions are involved. Let $C_A$, $C_B$, and $C_P$ represent the molar concentrations of $A$, $B$, and $P$ (moles/volume).

Assume that the stoichiometric equation for this reaction is

$$A + 2B \dashrightarrow P$$

The component material balance equations are (assuming no component $P$ is in the feed to the reactor):

$$\frac{dVC_A}{dt} = F_iC_{Ai} - FC_A + Vr_A \tag{2.24}$$

$$\frac{dVC_B}{dt} = F_iC_{Bi} - FC_B + Vr_B \tag{2.25}$$

$$\frac{dVC_P}{dt} = -FC_P + Vr_P \tag{2.26}$$

Where $r_A$, $r_B$, and $r_P$ represent the rate of *generation* of species $A$, $B$, and $P$ per unit volume, and $C_{Ai}$ and $C_{Bi}$ represent the inlet concentations of species $A$ and $B$. Assume that the rate of reaction of $A$ per unit volume is second-order and a function of the concentration of both A and B. The reaction rate can be written

$$r_A = -kC_AC_B \tag{2.27}$$

where $k$ is the reaction rate constant and the minus sign indicates that $A$ is consumed in the reaction. Each mole of $A$ reacts with two moles of $B$ (from the stoichiometric equation) and produces one mole of $P$, so the rates of generation of $B$ and $P$ (per unit volume) are:

$$r_B = -2\,kC_AC_B \tag{2.28}$$

$$r_P = kC_AC_B \tag{2.29}$$

Expanding the lefthand side of (2.24),

$$\frac{dVC_A}{dt} = V\frac{dC_A}{dt} + C_A\frac{dV}{dt} \tag{2.30}$$

combining (2.23), (2.24), (2.27), and (2.30) we find:

$$\frac{dC_A}{dt} = \frac{F_i}{V}(C_{Ai} - C_A) - kC_AC_B \tag{2.31}$$

Similarly, the concentrations of $B$ and $P$ can be written

$$\frac{dC_B}{dt} = \frac{F_i}{V}(C_{Bi} - C_B) - 2\,kC_AC_B \tag{2.32}$$

$$\frac{dC_P}{dt} = -\frac{F_i}{V}C_P + kC_AC_B \tag{2.33}$$

This model consists of four differential equations (2.23, 2.31, 2.32, 2.33) and, therefore, four state variables ($V$, $C_A$, $C_B$, and $C_P$). To solve these equations, we must specify the initial conditions ($V(0)$, $C_A(0)$, $C_B(0)$, and $C_P(0)$), the inputs ($F_i$, $C_{Ai}$, and $C_{Bi}$) as a function of time, and the parameter ($k$).

### 2.3.1 Simplifying Assumptions

The reactor model presented in Example 2.2 has four differential equations. Often other simplifying assumptions are made to reduce the number of differential equations, to make them easier to analyze and faster to solve. For example, assuming a constant volume ($dV/dt = 0$) reduces the number of equations by one. Also, it is common to feed an excess of one reactant to obtain nearly complete conversion of another reactant. If species B is maintained in a large excess, then $C_B$ is nearly constant. The reaction rate equation can then be expressed:

$$r_A = -k\,C_AC_B \approx -k_1C_A \tag{2.34}$$

where

$$k_1 = kC_B \tag{2.35}$$

The resulting differential equations are (since we assumed $dV/dt$ and $dC_B/dt = 0$)

$$\frac{dC_A}{dt} = \frac{F_i}{V}(C_{Ai} - C_A) - k_1 C_A \tag{2.36}$$

$$\frac{dC_P}{dt} = \frac{F_i}{V}(C_{Pi} - C_P) + k_1 C_A \tag{2.37}$$

Notice that if we only desire to know the concentration of species $A$ we only need to solve one differential equation, since the concentration of $A$ is not dependent on the concentration of $P$.

**EXAMPLE 2.3 Gas Surge Drum**

Surge drums are often used as intermediate storage capacity for gas streams that are transferred between chemical process units. Consider a drum depicted in Figure 2.4, where $q_i$ is the inlet molar flowrate and $q$ is the outlet molar flowrate. Here we develop a model that describes how the pressure in the tank varies with time.

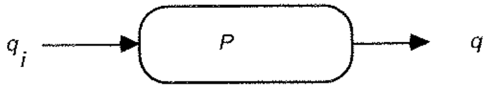


**FIGURE 2.4** Gas surge drum.

Let $V$ = volume of the drum and $\hat{V}$ = molar volume of the gas (volume/mole). The total amount of gas (moles) in the tank is then $V/\hat{V}$.

*Assumption*: The pressure-volume relationship is characterized by the ideal gas law, so

$$P\hat{V} = RT \tag{2.38}$$

where $P$ is pressure, $T$ is temperature (absolute scale), and $R$ is the ideal gas constant. Equation (2.38) can be written

$$\frac{1}{\hat{V}} = \frac{P}{RT} \tag{2.39}$$

and, therefore, the total amount of gas in the tank is

$$\frac{V}{\hat{V}} = \frac{PV}{RT} = \text{total amount (moles) of gas in the tank} \tag{2.40}$$

the rate of accumlation of gas is then $d(PV/RT)/dt$. Assume that $T$ is constant; since $V$ and $R$ are also constant; then the molar rate of accumlation of gas in the tank is:

$$\frac{V}{RT}\frac{dP}{dt} = q_i - q \tag{2.41}$$

where $q_i$ is the molar rate of gas entering the drum and $q$ is the molar rate of gas leaving the drum. Equation (2.41) can be written

$$\frac{dP}{dt} = \frac{RT}{V}(q_i - q) \tag{2.42}$$

To solve this equation for the state variable $P$, we must know the *inputs* $q_i$ and $q$, the parameters $R$, $T$, and $V$, and the initial condition $P(0)$. Once again, although $q$ is the molar rate *out* of the drum, we consider it an input in terms of solving the model.

## 2.4 CONSTITUTIVE RELATIONSHIPS

Examples 2.2 and 2.3 required more than simple material balances to define the modeling equations. These required relationships are known as *constitutive* equations; several examples of constitutive equations are shown in this section.

### 2.4.1 Gas Law

Process systems containing a gas will normally need a gas-law expression in the model. The ideal gas law is commonly used to relate molar volume, pressure, and temperature:

$$P\hat{V} = RT \tag{2.43}$$

The van der Waal's $P\hat{V}T$ relationship contains two parameters ($a$ and $b$) that are system-specific:

$$\left(P + \frac{a}{\hat{V}^2}\right)(\hat{V} - b) = RT \tag{2.44}$$

For other gas laws, see a thermodynamics text such as Smith, Van Ness, and Abbott (1996).

### 2.4.2 Chemical Reactions

The rate of reaction per unit volume (mol/volume*time) is usually a function of the concentration of the reacting species. For example, consider the reaction $A + 2B \dashrightarrow C + 3D$. If the rate of the reaction of A is first-order in both A and B, we use the following expression:

$$r_A = -k\,C_A C_B \tag{2.45}$$

where

$r_A$ is the rate of reaction of $A$ (mol A/volume*time)
$k$ is the reaction rate constant (constant for a given temperature)
$C_A$ is the concentration of $A$ (mol A/volume)
$C_B$ is the concentration of $B$ (mol B/volume)

Reaction rates are normally expressed in terms of generation of a species. The minus sign indicates that $A$ is consumed in the reaction above. It is good practice to associate the units with all parameters in a model. For consistency in the units for $r_A$, we find that k has units of (vol/mol $B$* time). Notice that 2 mols of $B$ react for each mol of $A$. Then we can write

$$\begin{aligned} r_B &= 2r_A &&= -2k\, C_A C_B \\ r_C &= -r_A &&= k\, C_A C_B \\ r_D &= -3r_A &&= 3\, k\, C_A C_B \end{aligned}$$

Usually, the reaction rate coefficient is a function of temperature. The most commonly used representation is the Arrhenius rate law

$$k(T) = A \exp(-E/RT) \tag{2.46}$$

where

$k(T)$ = reaction rate constant, as a function of temperature
$A$ = frequency factor or preexponential factor (same units as k)
$E$ = activation energy (cal/gmol)
$R$ = ideal gas constant (1.987 cal/gmol K, or another set of consistent units)
$T$ = absolute temperature (deg K or deg R)

The frequency factor and activation energy can be estimated data of the reaction constant as a function of reaction temperature. Taking the natural log of the Arrhenius rate law, we find:

$$\ln k = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \tag{2.47}$$

and we see that $A$ and $E$ can be found from the slope and intercept of a plot of ($\ln k$) versus ($1/T$).

### 2.4.3 Equilibrium Relationships

The relationship between the liquid and vapor phase compositions of component i, when the phases are in equilibrium, can be represented by:

$$y_i = K_i x_i \tag{2.48}$$

where

$x_i$ = liquid phase mole fraction of component i
$y_i$ = vapor phase mole fraction of component i
$K_i$ = vapor/liquid equilibrium constant for component i

The equilibrium constant is a function of composition and temperature. Often, we will see a *constant relative volatility* assumption made to simplify vapor/liquid equilibrium models.

In a binary system, the relationship between the vapor and liquid phases for the light component often used is:

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \tag{2.49}$$

$x$ = liquid phase mole fraction of light component
$y$ = vapor phase mole fraction of light component
$\alpha$ = relative volatility ($\alpha > 1$)

### 2.4.4 Heat Transfer

The rate of heat transfer through a vessel wall separating two fluids (a jacketed reactor, for example) can be described by

$$Q = UA\Delta T \tag{2.50}$$

where

$Q$ = rate of heat transfered from the hot fluid to the cold fluid
$U$ = overall heat transfer coefficient
$A$ = area for heat transfer
$\Delta T$ = difference between hot and cold fluid temperatures

The heat transfer coefficient is often estimated from experimental data. At the design stage it can be estimated from correlations; it is a function of fluid properties and velocities.

### 2.4.5 Flow-through Valves

The flow-through valves are often described by the following relationship:

$$F = C_v f(x) \sqrt{\frac{\Delta P_v}{\text{s.g.}}} \tag{2.51}$$

where

$F$ = volumetric flowrate
$C_v$ = valve coefficient
$x$ = fraction of valve opening
$\Delta P_v$ = pressure drop across the valve
s.g. = specific gravity of the fluid
$f(x)$ = the flow characteristic (varies from 0 to 1, as a function of $x$)

Three common valve characteristics are (i) linear, (ii) equal-percentage, and (iii) quick-opening.

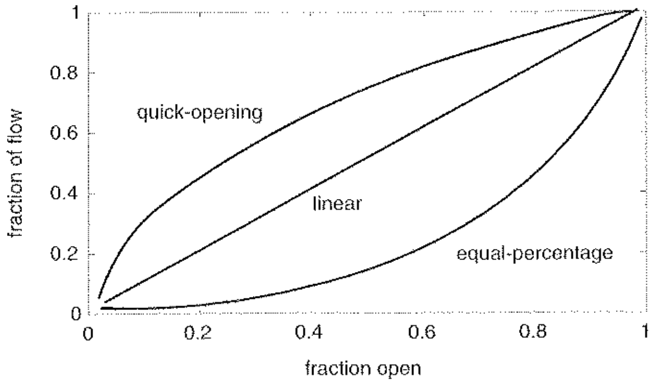


**FIGURE 2.5** Flow characteristics of control valves. $\alpha = 50$ for equal-percentage valve.

For a linear valve

$$f(x) = x$$

For an equal-percentage valve

$$f(x) = \alpha^{x-1}$$

For a quick-opening valve

$$f(x) = \sqrt{x}$$

The three characteristics are compared in Figure 2.5.

Notice that for the quick-opening valve, the sensitivity of flow to valve position (fraction open) is high at low openings and low at high openings; the opposite is true for an equal-percentage valve. The sensitivity of a linear valve does not change as a function of valve position. The equal-percentage valve is commonly used in chemical processes, because of desirable characteristics when installed in piping systems where a significant piping pressure drop occurs at high flowrates. Knowledge of these characteristics will be important when developing feedback control systems.

## 2.5 MATERIAL AND ENERGY BALANCES

Section 2.3 covered models that consist of material balances only. These are useful if thermal effects are not important, where system properties, reaction rates, and so on do not depend on temperature, or if the system is truly isothermal (constant temperature). Many chemical processes have important thermal effects, so it is necessary to develop material and energy balance models. One key is that a basis must always be selected when evaluating an intensive property such as enthalpy.

### 2.5.1 Review of Thermodynamics

Developing correct energy balance equations is not trivial and the chemical engineering literature contains many incorrect derivations. Chapter 5 of the book by Denn (1986) points out numerous examples where incorrect energy balances were used to develop process models.

The total energy (TE) of a system consists of internal (U), kinetic (KE) and potential energy (PE):

$$TE = U + KE + PE$$

where the kinetic and potential energy terms are:

$$KE = \frac{1}{2} mv^2$$

$$PE = mgh$$

Often we will use energy/mole or energy/mass and write the following

$$\hat{TE} = \hat{U} + \hat{KE} + \hat{PE}$$

$$\overline{TE} = \overline{U} + \overline{KE} + \overline{PE}$$

where ^ and ¯ represent per mole and per mass, respectively. The kinetic and potential energy terms, on a mass basis, are

$$\overline{KE} = \frac{1}{2} v^2$$

$$\overline{PE} = gh$$

For most chemical processes where there are thermal effects, we will neglect the kinetic and potential energy terms because their contribution is generally at least two orders of magnitude less than that of the internal energy term.

When dealing with flowing systems, we will usually work with enthalpy. Total enthalpy is defined as:

$$H = U + pV$$

while the enthalpy/mole is

$$\hat{H} = \hat{U} + p\hat{V}$$

and the enthalpy/mass is (since $\rho = 1/(\bar{V})$

$$\overline{H} = \overline{U} + p\overline{V} = \overline{U} + \frac{p}{\rho}$$

we will make use of these relationships in the following example.

**EXAMPLE 2.4 Stirred Tank Heater**

Consider a perfectly mixed stirred-tank heater, with a single feed stream and a single product stream, as shown in Figure 2.6. Assuming that the flowrate and temperature of the inlet stream can vary, that the tank is perfectly insulated, and that the rate of heat added per unit time ($Q$) can vary, develop a model to find the tank temperature as a function of time. State your assumptions.

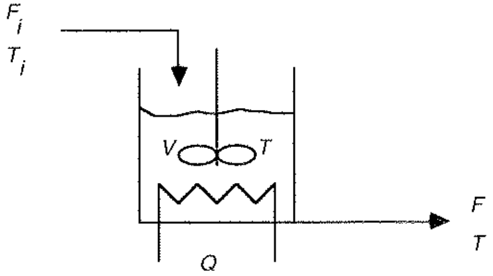


**FIGURE 2.6** Stirred tank heater.

## Material Balance

$$\text{accumulation} = \text{in} - \text{out}$$

$$\frac{dV\rho}{dt} = F_i\rho_i - F\rho \tag{2.52}$$

## Energy Balance

accumulation = in by flow − out by flow + in by heat transfer + work done on system

$$\frac{dTE}{dt} = F_i\rho_i\overline{TE}_i - F\rho\overline{TE} + Q + W_T$$

Here we neglect the kinetic and potential energy:

$$\frac{dU}{dt} = F_i\rho_i\bar{U}_i - F\rho\bar{U} + Q + W_T \tag{2.53}$$

We write the total work done on the system as a combination of the shaft work and the energy added to the system to get the fluid into the tank and the energy that the system performs on the surroundings to force the fluid out.

$$W_T = W_s + F_i P_i - F_p \tag{2.54}$$

This allows us to write (2.53) as:

$$\frac{dU}{dt} = F_i\rho_i\left(\bar{U}_i + \frac{p_i}{\rho_i}\right) - F\rho\left(\bar{U} + \frac{p}{\rho}\right) + Q + W_s \tag{2.55}$$

and since $H = U + pV$, we can rewrite (2.55) as

$$\frac{dH}{dt} - \frac{dpV}{dt} = F_i\rho_i \bar{H}_i - F\rho \bar{H} + Q + W_s \tag{2.56}$$

Since, $dpV/dt = V\,dp/dt + p\,dV/dt$, if the *volume is constant* and the mean pressure change can be neglected (a good assumption for liquids), we can write

$$\boxed{\frac{dH}{dt} = F_i\rho_i\bar{H}_i - F\rho \bar{H} + Q + W_s} \tag{2.57}$$

We must remember the assumptions that went into the development of (2.57):

- The kinetic and potential energy effects were neglected.
- The change in $pV$ term was neglected. This is a good assumption for a liquid system, provided $\Delta p$ is not too large and constant volume is assumed.

The total enthalpy term is:

$$H = V\rho \bar{H}$$

and assuming no phase change, we select an arbitrary reference temperature ($T_{ref}$) for enthalpy:

$$\bar{H}(T) = \int_{T_{ref}}^{T} c_p\, dT$$

Often we assume that the heat capacity is constant, or calcuated at an average temperature, so

$$\bar{H} = c_p(T - T_{ref}) \tag{2.58}$$

$$\bar{H}_i = c_p(T_i - T_{ref}) \tag{2.59}$$

We now write the energy balance (2.57) in the following fashion:

$$\frac{d(V\rho c_p(T - T_{ref}))}{dt} = F_i\rho_i c_p(T_i - T_{ref}) + Q - F\rho c_p(T - T_{ref}) + W_s \tag{2.60}$$

using the *assumptions* of constant density and volume (so $F_i = F$, from (2.52)), we find

$$V\rho c_p \frac{d(T - T_{ref})}{dt} = F\rho c_p[(T_i - T_{ref}) - (T - T_{ref})] + Q + W_s \tag{2.61}$$

or

$$\frac{d(T - T_{ref})}{dt} = \frac{F}{V}(T_i - T) + \frac{Q}{V\rho c_p} + \frac{W_s}{Vec_p} \tag{2.62}$$

but $T_{ref}$ is a constant, so $d\,(T - T_{ref})/dt = dT/dt$. Also, neglecting $W_s$ we can write

$$\frac{dT}{dt} = \frac{F}{V}(T_i - T) + \frac{Q}{V\rho c_p} \tag{2.63}$$

In order to solve this problem, we must specify the parameters $V$, $\rho$, $c_p$, the inputs $F$, $Q$, and $T_i$ (as a function of time), and the initial condition $T(0)$.

## 2.6 DISTRIBUTED PARAMETER SYSTEMS

In this section we show how the balance equations can be used to develop a model for a distributed parameter system, that is, a system where the state variables change with respect to position and time.

Consider a tubular reactor where a chemical reaction changes the concentration of the fluid as it moves down the tube. Here we use a volume element $\Delta V$ and a time element $\Delta t$. The total moles of species A contained in the element $\Delta V$ is written $(\Delta V)C_A$. The amount of species A entering the volume is $FC_A|_V$ and the amount of species leaving the volume is $FC_A|_{V+\Delta V}$. The rate of A leaving by reaction (assuming a first-order reaction) is $(-k\,C_A)\Delta V$.

The balance equation is then:

$$(\Delta V)C_A|_{t+\Delta t} - (\Delta V)C_A|_t = \int_t^{t+\Delta t} [FC_A|_V - FC_A|_{V+\Delta V} - kC_A\Delta V]\,dt$$

Using the mean value theorem of integral calculus and dividing by $\Delta t$, we find:

$$\frac{\Delta V[C_A|_{t+\Delta t} - C_A|_t]}{\Delta t} = FC_A|_V - FC_A|_{V+\Delta V} - kC_A\Delta V \tag{2.64}$$

Dividing by $\Delta V$ and letting $\Delta t$ and $\Delta V$ go to zero, we find:

$$\frac{\partial C_A}{\partial t} = -\frac{\partial FC_A}{\partial V} - kC_A \tag{2.65}$$

Normally, a tube with constant cross-sectional area is used, so $dV = Adz$ and $F = Av_z$, where $v_z$ is the velocity in the $z$-direction. Then the equation can be written:

$$\frac{\partial C_A}{\partial t} = -\frac{\partial v_z C_A}{\partial z} - kC_A \tag{2.66}$$

Similarly, the overall material balance can be found as:

$$\frac{\partial \rho}{\partial t} = -\frac{\partial v_z \rho}{\partial z} \tag{2.67}$$

If the fluid is at a constant density (good assumption for a liquid), then we can write the species balance as

$$\frac{\partial C_A}{\partial t} = -v_z\frac{\partial C_A}{\partial z} - kC_A \tag{2.68}$$

To solve this problem, we must know the initial condition (concentration as a function of distance at the initial time) and one boundary condition. For example, the following boundary and initial conditions

$$\begin{aligned} C_A(z,\ t = 0) &= C_{A0}(z) \\ C_A(0,\ t) &= C_{Ain}(t) \end{aligned} \tag{2.69}$$

indicate that the concentration of A initially is known as a function of distance down the reactor, and that the inlet concentration as a function of time must be specified.

In deriving the tubular reactor equations we assumed that species A left a volume element only by convection (bulk flow). In addition, the molecules can leave by virtue of a concentration gradient. For example, the amount entering at $V$ is

$$\left(FC_A + AD_{AZ}\frac{dCA}{dz}\right)\Big|_V \tag{2.70}$$

where is the diffusion coefficient. The reader should be able to derive the following reaction-diffusion equation (see exercise 19).

$$\frac{\partial C_A}{\partial t} = -v_z\frac{\partial C_A}{\partial z} + D_{AZ}\frac{\partial^2 C_A}{\partial z^2} - kC_A \tag{2.71}$$

Since this is a second-order PDE, the initial condition ($C_A$ as a function of $z$) and two boundary conditions must be specified.

Partial differential equation (PDEs) models are much more difficult to solve than ordinary differential equations. Generally, PDEs are converted to ODEs by discretizing in the spatial dimension, then techniques for the solution of ODEs can be used. The focus of this text is on ODEs; with a grasp of the solution of ODEs, one can then begin to develop solutions to PDEs.

## 2.7 DIMENSIONLESS MODELS

Models typically contain a large number of parameters and variables that may differ in value by several orders of magnitude. It is often desirable, at least for analysis purposes, to develop models composed of dimensionless parameters and variables. To illustrate the approach, consider a constant volume, isothermal CSTR modeled by a simple first-order reaction:

$$\frac{dC_A}{dt} = \frac{F}{V}(C_{Af} - C_A) - kC_A$$

It seems natural to work with a scaled concentration. Defining

$$x = C/C_{Af0}$$

where $C_{Af0}$ is the nominal (steady-state) feed concentration of A, we find

$$\frac{dx}{dt} = \frac{F}{V}x_f - \left(\frac{F}{V} + k\right)x$$

where $x_f = C_{Af}/C_{Af0}$. It is also natural to choose a scaled time, $\tau = t/t^*$, where $t^*$ is a scaling parameter to be determined. We can use the relationship $dt = t^*d\tau$ to write:

$$\frac{dx}{t^* d\tau} = \frac{F}{V} x_f - \left(\frac{F}{V} + k\right) x$$

A natural choice for $t^*$ appears to be $V/F$ (known as the residence time), so

$$\frac{dx}{d\tau} = x_f - \left(1 + \frac{Vk}{F}\right) x$$

The term $Vk/F$ is dimensionless and known as a Damkholer number in the reaction engineering literature. Assuming that the feed concentration is constant, $x_f = 1$, and letting $\alpha = Vk/F$, we can write:

$$\frac{dx}{d\tau} = 1 - x + \alpha\, x$$

which indicates that a single parameter, $\alpha$, can be used to characterize the behavior of all first-order, isothermal chemical reactions. Similar results are obtained if the dimensionless state is chosen to be conversion

$$x = (C_A - C_{Af0})/C_{Af0}$$

## 2.8 EXPLICIT SOLUTIONS TO DYNAMIC MODELS

Explicit solutions to nonlinear differential equations can rarely be obtained. The most common case where an analytical solution can be obtained is when a single differential equation has variables that are separable. This is a very limited class of problems. A main objective of this textbook is to present a number of techniques (analytical and numerical) to solve more general problems, particularly involving many simultaneous equations. In this section we provide an example of problems where the variables are separable.

### EXAMPLE 2.5 Nonlinear Tank Height

Consider a tank height problem where the outlet flow is a nonlinear function of tank height:

$$\frac{dh}{dt} = \frac{F_i}{A} - \frac{\beta}{A}\sqrt{h}$$

Here there is not an analytical solution because of the nonlinear height relationship and the forcing function. To illustrate a problem with an analytical solution, we will assume that there is no inlet flow to the tank:

$$\frac{dh}{dt} = -\frac{\beta}{A}\sqrt{h}$$

we can see that the variables are separable, so

$$\frac{dh}{\sqrt{h}} = -\frac{\beta}{A}\, dt$$

$$\int_{h_o}^{h} \frac{dh}{\sqrt{h}} = -\int_{t_o}^{t} \frac{\beta}{A}\, dt$$

which has the solution

$$2\sqrt{h} - 2\sqrt{h_o} = -\frac{\beta}{A}(t - t_o)$$

or

$$\sqrt{h} = \sqrt{h_o} - \frac{\beta}{2A}(t - t_o)$$

letting $t_o = 0$, and squaring both sides, we obtain the solution

$$h(t) = \left[\sqrt{h_o} - \frac{\beta}{2A}\, t\right]^2$$

This analytical solution can be used, for example, to determine the time that it will take for the tank height to reach a certain level.

## 2.9 GENERAL FORM OF DYNAMIC MODELS

The dynamic models derived in this chapter consist of a set of first-order (meaning only first derivatives with respect to time), nonlinear, explicit, initial value ordinary differential equations. A representation of a set of first-order differential equations is

$$\begin{aligned}
\dot{x}_1 &= f_1(x_1,\ldots,x_n,u_1,\ldots,u_m, p_1,\ldots,p_r)\\
\dot{x}_2 &= f_2(x_1,\ldots,x_n,u_1,\ldots,u_m, p_1,\ldots,p_r)\\
\cdot &\quad \cdot\\
\cdot &\quad \cdot\\
\dot{x}_n &= f_n(x_1,\ldots,x_n,u_1,\ldots,u_m, p_1,\ldots,p_r)
\end{aligned} \tag{2.72}$$

where $x_i$ is a state variable, $u_i$ is an input variable and $p_i$ is a parameter. The notation $\dot{x}_i$ is used to represent $dx/dt$. Notice that there are $n$ equations, $n$ state variables, $m$ inputs, and $r$ parameters.

### 2.9.1 State Variables

A state variable is a variable that arises naturally in the accumulation term of a dynamic material or energy balance. A state variable is a measurable (at least conceptually) quantity that indicates the state of a system. For example, temperature is the common state variable that arises from a dynamic energy balance. Concentration is a state variable that arises when dynamic component balances are written.

### 2.9.2 Input Variables

An input variable is a variable that normally must be specified before a problem can be solved or a process can be operated. Inputs are normally specified by an engineer based on knowledge of the process being considered. Input variables typically include flowrates of streams entering or leaving a process (notice that the flowrate of an outlet stream might be considered an input variable!). Compositions or temperatures of streams entering a process are also typical input variables. Input variables are often manipulated (by process controllers) in order to achieve desired performance.

### 2.9.3 Parameters

A parameter is typically a physical or chemical property value that must be specified or known to mathematically solve a problem. Parameters are often fixed by nature, that is, the reaction chemistry, molecular structure, existing vessel configuration, or operation. Examples include density, viscosity, thermal conductivity, heat transfer coefficient, and mass-transfer coefficient. When designing a process, a parameter might be "adjusted" to achieve some desired performance. For example, reactor volume may be an important design parameter.

### 2.9.4 Vector Notation

The set of differential equations shown as (2.72) above can be written more compactly in vector form.

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x}, \mathbf{u}, \mathbf{p}) \tag{2.73}$$

where

$\mathbf{x}$ = vector of $n$ state variables
$\mathbf{u}$ = vector of $m$ input variables
$\mathbf{p}$ = vector of $r$ parameters

Notice that the dynamic models (2.73) can also be used to solve steady-state problems, since

$$\dot{\mathbf{x}} = \mathbf{0} \tag{2.74}$$

that is,

$$\mathbf{f}(\mathbf{x},\mathbf{u},\mathbf{p}) = \mathbf{0} \tag{2.75}$$

for steady-state processes. Numerical techniques (such as Newton's method) to solve algebraic equations (2.75) will be presented in Chapter 3.

The steady-state state variables from the solution of (2.75) are often used as the initial conditions for (2.73). Frequently, an input will be changed from its steady-state value, and (2.73) will be solved to understand the transient behavior of the system. The numerical solution of ordinary differential equations will be presented in Chapter 4. In the example below we show Example 2.2 (chemical reactor) in state variable form.

**EXAMPLE 2.6 State Variable Form for Example 2.2**

Consider the modeling equations for Example 2.2 (chemical reactor)

$$\frac{dV}{dt} = F_i - F \tag{2.23}$$

$$\frac{dC_A}{dt} = \frac{F_i}{V}(C_{Ai} - C_A) - kC_A C_B \tag{2.31}$$

$$\frac{dC_B}{dt} = \frac{F_i}{V}(C_{Bi} - C_B) - 2\,kC_A C_B \tag{2.32}$$

$$\frac{dC_P}{dt} = -\frac{F_i}{V}C_P + kC_A C_B \tag{2.33}$$

There are four states ($V$, $C_A$, $C_B$, and $C_P$), four inputs ($F_i$, $F$, $C_{Ai}$, $C_{Bi}$), and a single parameter (k). Notice that although $F$ is the outlet flowrate, it is considered an input to the model, because it must be specified in order to solve the equations.

$$\begin{bmatrix} \dot{V} \\ \dot{C}_A \\ \dot{C}_B \\ \dot{C}_P \end{bmatrix} = \begin{bmatrix} F_i - F \\ \frac{F_i}{V}(C_{Ai} - C_A) - kC_A C_B \\ \frac{F_i}{V}(C_{Bi} - C_B) - 2\,kC_A C_B \\ -\frac{F_i}{V}C_P + kC_A C_B \end{bmatrix}$$

or

$$\begin{bmatrix} \dot{\mathbf{x}}_1 \\ \dot{\mathbf{x}}_2 \\ \dot{\mathbf{x}}_3 \\ \dot{\mathbf{x}}_4 \end{bmatrix} = \begin{bmatrix} \mathbf{u}_1 - \mathbf{u}_2 \\ \frac{\mathbf{u}_1}{\mathbf{x}_1}(\mathbf{u}_3 - \mathbf{x}_2) - \mathbf{p}_1\mathbf{x}_2\mathbf{x}_3 \\ \frac{\mathbf{u}_1}{\mathbf{x}_1}(\mathbf{u}_4 - \mathbf{x}_3) - 2\,\mathbf{p}_1\mathbf{x}_2\mathbf{x}_3 \\ -\frac{\mathbf{u}_1}{\mathbf{x}_1}\mathbf{x}_4 + \mathbf{p}_1\mathbf{x}_2\mathbf{x}_3 \end{bmatrix} = \begin{bmatrix} \mathbf{f}_1(\mathbf{x},\mathbf{u},\mathbf{p}) \\ \mathbf{f}_2(\mathbf{x},\mathbf{u},\mathbf{p}) \\ \mathbf{f}_3(\mathbf{x},\mathbf{u},\mathbf{p}) \\ \mathbf{f}_4(\mathbf{x},\mathbf{u},\mathbf{p}) \end{bmatrix}$$

## SUMMARY

A number of material and energy balance examples have been presented in this chapter. The classic assumption of a perfectly stirred tank was generally used so that all models (except Section 2.6) were lumped-parameter systems. Future chapters develop the analytical and numerical techniques to analyze and simulate these models.

The student should now understand:

- that dynamic models of lumped parameter systems yield ordinary differential equations.
- that steady-state models of lumped parameter systems yield algebraic equations.
- The notion of a state, input, output, parameter.

A plethora of models are presented in modules in the final section of the textbook. More specifically, the following modules are of interest:

| | |
|---|---|
| Module 5. | Heated Mixing Tank |
| Module 6. | Linear Equilibrium Stage Models (Absorption) |
| Module 7. | Isothermal Continuous Stirred Tank Reactors |
| Module 8. | Biochemical Reactor Models |
| Module 9. | Diabatic Reactor Models |
| Module 10. | Nonlinear Equilibrium Stage Models (Distillation) |

Each of these modules covers model development and presents examples for analytical and numerical calculations.

## FURTHER READING

A nice introduction to chemical engineering calculations is provided by:

Felder, R.M., & R. Rousseau. (1986). *Elementary Principles of Chemical Processes*, 2nd ed. New York: Wiley.

Excellent discussions of the issues involved in modeling a mixing tank, incorporating density effects, and energy balances is provided in the following two books:

Denn, M.M. (1986). *Process Modeling*. New York: Longman.

Russell, T.R.F., & M.M. Denn. (1971). *Introduction to Chemical Engineering Analysis*. New York: Wiley.

An introduction to chemical reaction engineering is:

Fogler, H.S. (1992). *Elements of Chemical Reaction Engineering*, 2nd ed. Englewood Cliffs, NJ: Prentice-Hall.

An excellent textbook for an introduction to chemical engineering thermodynamics is:

Smith, J.M. , H.C. Van Ness, & M.M. Abbott. (1996). *Chemical Engineering Thermodynamics*, 5th ed. New York: McGraw-Hill.

The following paper provides an advanced treatment of dimensionless variables and parameters:

Aris, R. (1993). Ends and beginnings in the mathematical modelling of chemical engineering systems. *Chemical Engineering Science*, 48(14), 2507–2517.

The relationships for mass and heat transport are shown in textbooks on transport phenomena. The chemical engineer's bible is

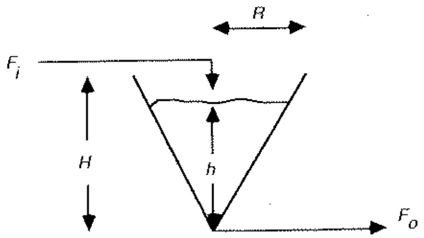
Bird, R.B., W.E. Stewart, & E. Lightfoot. (1960). *Transport Phenomena*. New York: Wiley.

The predator-prey model in student exercise 16 is also known as the Lotka-Volterra equations, after the researchers that developed them in the late 1920s. A presentation of the equations is in the following text:

Bailey, J.E., & D.F. Ollis. (1986). *Biochemical Engineering Fundamentals*, 2nd ed. New York: McGraw-Hill.

## STUDENT EXERCISES

1. In Example 2.1 it was assumed that the input and output flowrates could be independently varied. Consider a situation in which the outlet flowrate is a function of the height of liquid in the tank. Write the modeling equation for tank height assuming two different constitutive relationships: (i) $F = \beta h$, or (ii) $F = \beta \sqrt{h}$, where $\beta$ is known as a flow coefficient. You will often see these relationships expressed as $F = h/R$ or $F = \sqrt{h}/R$, where $R$ is a flow resistance. List the state variables, parameters, as well as the input and output variables. Give the necessary information to complete the quantitative solution to this problem. If the flowrate has units of liters/min and the tank height has units of meters, find the units of the flow coefficients and flow resistances for (i) and (ii).
2. Consider a conical water tank shown below. Write the dynamic material balance equation if the flowrate out of the tank is a function of the square root of height of water in the tank ($F_o = \beta\sqrt{h}$). List state variables, input variables and parameters. (Hint: Use height as a state variable.)



3. Extend the model developed in Example 2.2 (isothermal reaction) to handle the following stoichiometric equation: $A + B \rightarrow 2P$. Assume that the volume is constant, but the change in concentration of component $B$ cannot be neglected.
4. Extend the model developed in Example 2.2 (isothermal with first-order kinetics) to handle multiple reactions (assume a constant volume reactor).

$$A + B \rightarrow 2P \quad \text{(reaction 1)}$$
$$2A + P \rightarrow Q \quad \text{(reaction 2)}$$

Assume that no $P$ is fed to the reactor. Assume that the reaction rate (generation) of $A$ per unit volume for reaction 1 is characterized by expression

$$r_A = -k_1 C_A C_B$$

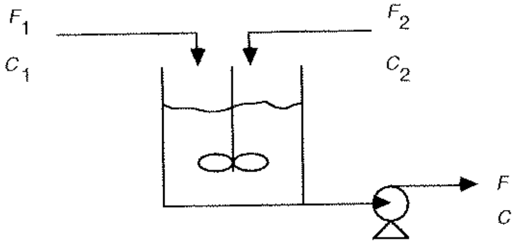
where the minus sign indicates that $A$ is consumed in reaction 1. Assume that the reaction rate (generation) of $A$ per unit volume for reaction 2 is characterized by the expression

$$r_A = -k_2 C_A C_P$$

If the concentrations are expressed in gmol/liter and the volume in liters, what are the units of the reaction rate constants?

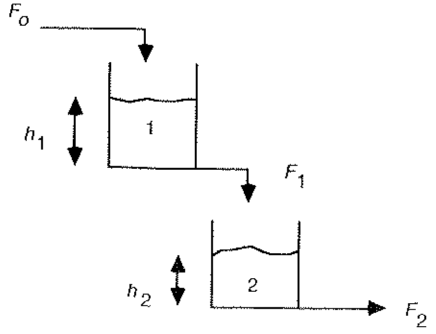
If it is desirable to know the concentration of component $Q$, how many equations must be solved? If our concern is only with $P$, how many equations must be solved? Explain.

5. Model a mixing tank with two feedstreams, as shown below. Assume that there are two components, $A$ and $B$. $C$ represents the concentration of $A$. ($C_1$ is the mass concentration of $A$ in stream 1 and $C_2$ is the mass concentration of $A$ in stream 2). Model the following cases:



**a.** Constant volume, constant density.
**b.** Constant volume, density varies linearly with concentration.
**c.** Variable volume, density varies linearly with concentration.

6. Consider two tanks in series where the flow out of the first tank enters the second tank. Our objective is to develop a model to describe how the height of liquid in tank 2 changes with time, given the input flowrate $F_o(t)$. Assume that the flow out of each tank is a linear function of the height of liquid in the tank ($F_1 = \beta_1 h_1$ and $F_2 = \beta_2 h_2$) and each tank has a constant cross-sectional area.



A material balance around the first tank yields (assuming constant density and $F_1 = \beta_1 h_1$)

7. Two liquid surge tanks (with constant cross-sectional area) are placed in series. Write the modeling equations for the height of liquid in the tanks assuming that the flowrate from the first tank is a function of the difference in levels of the tanks and the flowrate from the second tank is a function of the level in the second tank. Consider two cases: (i) the function is linear and (ii) the function is a square root relationship. State all other assumptions.

8. A gas surge drum has two components (hydrogen and methane) in the feedstream. Let $y_i$ and $y$ represent the mole fraction of methane in the feedstream and drum, respectively. Find $dP/dt$ and $dy/dt$ if the inlet and outlet flowrates can vary. Also assume that the inlet concentration can vary. Assume the ideal gas law for the effect of pressure and composition on density.

9. Consider a liquid surge drum that is a sphere. Develop the modeling equation using liquid height as a state variable, assuming variable inlet and outlet flows.

10. A car tire has a slow leak. The flowrate of air out of the tire is proportional to the pressure of air in the tire (we are using gauge pressure). The initial pressure is 30 psig, and after five days the pressure is down to 20 psig. How long will it take to reach 10 psig?

11. A car tire has a slow leak. The flowrate of air out of the tire is proportional to the square root of the pressure of air in the tire (we are using gauge pressure). The initial pressure is 30 psig, and after 5 days the pressure is down to 20 psig. How long will it take to reach 10 psig? Compare your results with problem 10.

**12.** A small room (10 ft × 10 ft × 10 ft) is perfectly sealed and contains air at 1 atm pressure (absolute). There is a large gas cylinder (100 $\text{ft}^3$) inside the room that contains helium with an initial pressure of 5 atm (absolute). Assume that the cylinder valve is opened (at $t = 0$) and the molar flowrate of gas leaving the cylinder is proportional to the difference in pressure between the cylinder and the room. Assume that room air does not diffuse into the cylinder.

Write the differential equations that (if solved) would allow you to find how the cylinder pressure, the room pressure and the room mole fraction of helium change with time. State all assumptions and show all of your work.

**13.** A balloon expands or contracts in volume so that the pressure inside the balloon is approximately the atmospheric pressure.

- **a.** Develop the mathematical model (write the differential equation) for the volume of a balloon that has a slow leak. Let $V$ represent the volume of the balloon and $q$ represent the molar flowrate of air leaking from the balloon. State all assumptions. List state variables, inputs, and parameters.
- **b.** The following experimental data have been obtained for a leaking balloon.

| $t$ (minutes) | $r$ (cm) |
|---|---|
| 0 | 10 |
| 5 | 7.5 |

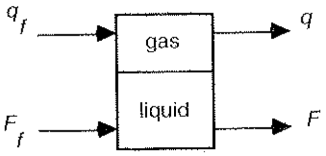
Predict when the radius of the balloon will reach 5 cm using two different assumptions for the molar rate of air leaving the balloon:

(i) The molar rate is constant.

(ii) The molar rate is proportional to the surface area of the balloon.

Reminder: The volume of a sphere is $4/3\ \pi r^3$ and the area of a sphere is $4\pi r^2$.

**14.** Often liquid surge tanks (particularly those containing hydrocarbons) will have a gas "blanket" of nitrogen or carbon dioxide to prevent the accumulation of explosive vapors above the liquid, as depicted below.



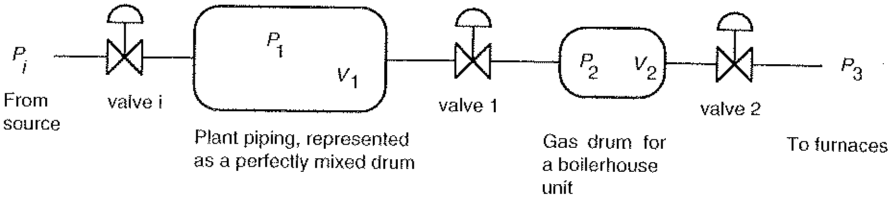
Develop the modeling equations with gas pressure and liquid volume as the state variables. Let $q_f$ and $q$ represent the inlet and outlet gas molar flowrates, $F_f$ and $F$ the liquid volumetric flowrates, $V$ the constant (total) volume, $V_l$ the liquid volume, and $P$ the gas pressure. Assume the ideal gas law. Show that the modeling equations are:

$$\frac{dV_l}{dt} = F_f - F$$

$$\frac{dP}{dt} = \frac{P}{V - V_l}(F_f - F) + \frac{RT}{V - V_l}(q_f - q)$$

and state any other assumptions.

**15.** Most chemical process plants have a natural gas header that circulates through the process plant. A simplified version of such a header is shown below.



Here, the natural gas enters the process plant from a source (the natural gas pipeline) through a control valve. It flows through the plant piping, which we have represented as a perfectly mixed drum for simplicity. Another valve connects the plant piping to the gas drum for a boilerhouse unit. Gas passes through another valve to the boilerhouse furnaces.

Write modeling equations assuming that the pressures in drums 1 and 2 are the state variables. Let the input variables be $h_1$ (valve position 1), $h_2$ (valve position 2), and $P_i$ (source pressure).

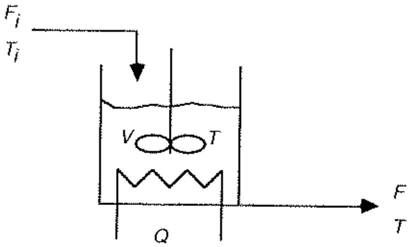
**16.** The Lotka-Volterra equations were developed to model the behavior of predator-prey systems, making certain assumptions about the birth and death rates of each species. Consider a system composed of sheep (prey) and coyotes (predator). In the following Lotka-Volterra equations $x_1$ represents the number of sheep and $x_2$ the number of coyotes in the system.

$$\frac{dx_1}{dt} = \alpha x_1 - \gamma x_1 x_2$$

$$\frac{dx_2}{dt} = \varepsilon\gamma x_1 x_2 - \beta x_2$$

Discuss the meaning of the parameters $\alpha$, $\beta$, $\gamma$, $\varepsilon$ and the assumptions made in the model.

**17.** Consider a perfectly mixed stirred-tank heater, with a single liquid feed stream and a single liquid product stream, as shown below.



Develop the material and energy balance equations that describe this process. $F_i$ is the volumetric flowrate into the tank, $F$ is the volumetric flowrate out of the tank, $T_i$ is the temperature of the fluid entering the tank, $T$ is the temperature of the fluid in the tank, $h$ is the height of liquid in the tank, and $Q$ is the rate of energy added to the tank. State assumptions (such as constant density, etc.).

Assume that the volume can vary with time and that $F$ is proportional to $\sqrt{h}$. How many differential equations does it take to model this system? What are the state variables? What are the parameters? What are the inputs? List the information necessary to solve this problem.

**18.** Consider a gas surge drum with variable inlet and outlet molar flowrates, $q_f$ and $q$, respectively. Assume that heat is being added to the tank at a rate, $Q$. Write the modeling equations that describe how the temperature, $T$, and pressure, $P$, vary with time. Do not neglect the $pV$ term in the energy balance.

**19.** Derive the reaction-diffusion equation

$$\frac{\partial C_A}{\partial t} = -v_z \frac{\partial C_A}{\partial z} + D_{AZ} \frac{\partial^2 C_A}{\partial z^2} - kC_A$$

using the same method to derive the tubular reactor model in Section 2.6. Assume that a chemical species enters a volume element via convection (bulk flow) and a concentration gradient (diffusion):

$$\left.\left(FC_A - AD_{AZ}\frac{dC_A}{dz}\right)\right|_V$$

leaves by convection and a concentration gradient:

$$\left.\left(FC_A - AD_{AZ}\frac{dC_A}{dz}\right)\right|_{V+\Delta V}$$

and also leaves by a first-order reaction.

**20.** Consider the nonlinear tank height model

$$\frac{dh}{dt} = \frac{F_i}{A} - \frac{\beta}{A}\sqrt{h}$$

and define the dimensionless variables $u = F_i/F_s$ and $x = h/h_s$. Where $F_s$ and $h_s$ are the steady-state flowrate and height, respectively ($F_s = \beta\sqrt{h_s}$). Define the dimensionless time, $\tau$, that will yield the following dimensionless equation:

$$\frac{dx}{d\tau} = -\sqrt{x} + u$$

**21.** Derive the constitutive relationship $F = \beta\sqrt{h}$ by considering a steady-state energy balance around a tank with a constant flowrate. Use $P = P_o + \rho g h$ for the pressure at the bottom of the tank, where $P_o$ is the atmospheric pressure (pressure at the top surface), $h$ is the height of liquid in the tank, $\rho$ is the density of fluid. Assume that the cross-sectional area at the surface is much larger than the cross-sectional area of the exit pipe.

**22.** Consider the isothermal CSTR model with first-order kinetics:

$$\frac{dC_A}{dt} = \frac{F}{V}(C_{Af} - C_A) - k\,C_A$$

Use $\tau = kt$ as the dimensionless time. Develop the dimensionless equation for two cases: (i) $x = C_A/C_{Af}$ and (ii) $x = 1 - C_A/C_{Af}$. Compare and contrast the resulting equations with the example in Section 2.7.

**23.** Semibatch reactors are operated as a cross between batch and continuous reactors. A semibatch reactor is initially charged with a volume of material, and a continous feed of reactant is started. There is, however, no outlet stream. Develop the modeling equations for a single first-order reaction. The state variables should be volume and concentration of reactant A.

**24.** Pharmacokinetics is the study of how drugs infused to the body are distributed to other parts of the body. The concept of a compartmental model is often used, where it is assumed that the drug is injected into compartment 1. Some of the drug is eliminated (reacted) in compartment 1, and some of it diffuses into compartment 2 (the rest accumulates in compartment 1). Similarly, some of the drug that diffuses into compartment 2 diffuses back into compartment 1, while some is eliminated by reaction and the rest accumulates in compartment 2. Assume that the rates of diffusion and reaction are directly proportional to the concentration of drug in the compartment of interest. Show that the following balance equations arise, and discuss the meaning of each parameter ($k_{ij}$, units of $\text{min}^{-1}$)

$$\frac{dx_1}{dt} = -(k_{10} + k_{12})x_1 + k_{21}x_2 + u$$

$$\frac{dx_2}{dt} = k_{12}x_1 - (k_{20} + k_{21})\,x_2$$

where $x_1$ and $x_2$ = drug concentrations in compartments 1 and 2 ($\mu$g/ml), and $u$ = rate of drug input to compartment 1 (scaled by the volume of compartment 1, $\mu$g/ml min).