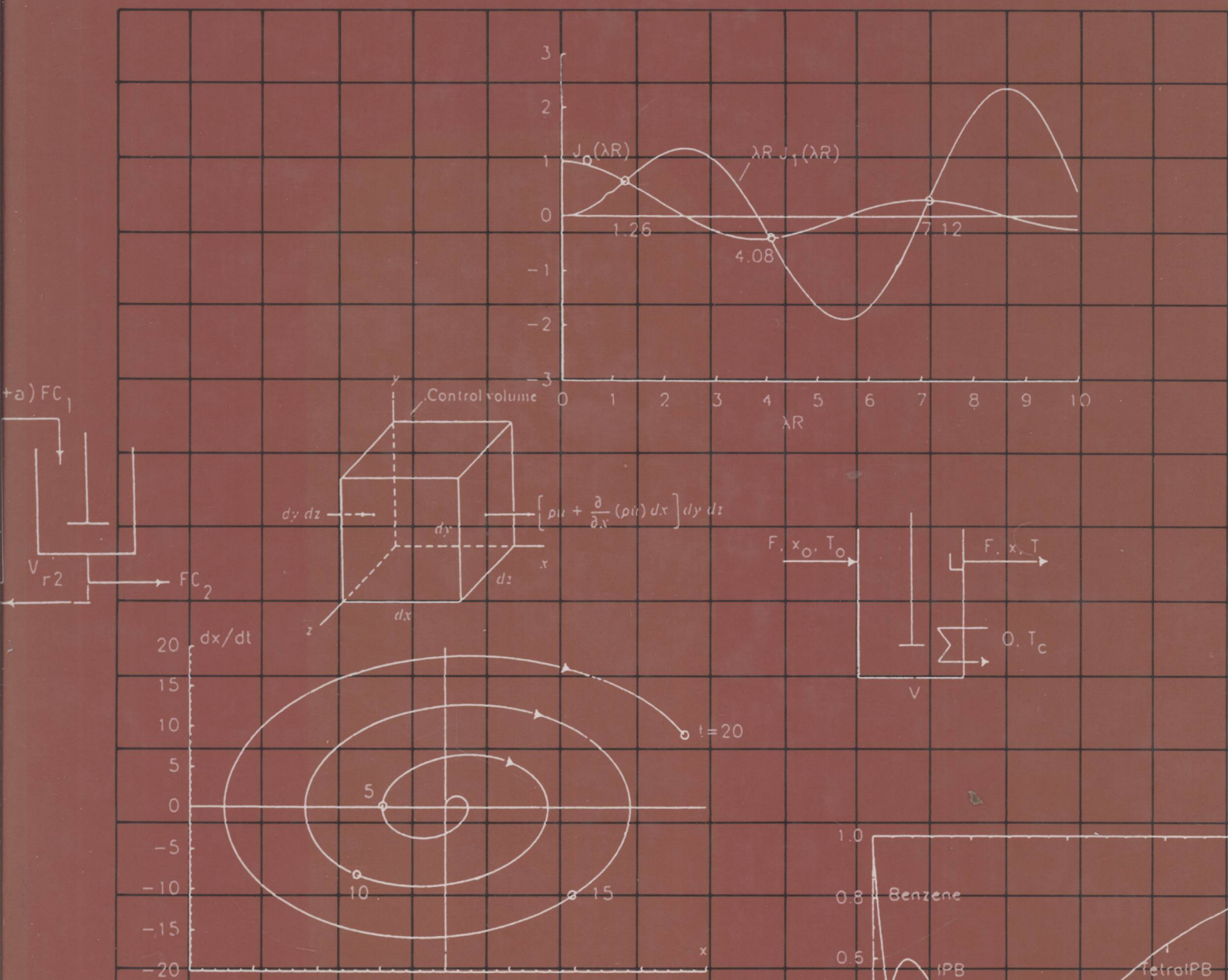


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Modeling with Differential Equations in Chemical Engineering

Stanley M. Walas



Modeling with Differential Equations in Chemical Engineering

Stanley M. Walas

Department of Chemical and Petroleum Engineering
University of Kansas

Butterworth–Heinemann

Boston London Singapore Sydney Toronto Wellington

*To the memory of my parents,
Stanislaus and Apolonia,
and to my wife, Suzy Belle*

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Preface

Two kinds of processes occur in the design and operation of chemical engineering equipment: (a) equilibrium processes, those in which the properties and conditions do not change with time, of which a prominent instance is the equilibrium stage of separating equipment; and (b) dynamic or rate processes, in which properties and conditions may change with time, or in which any property or condition is affected by variations in other properties or conditions. This book deals with major rate processes of interest to chemical engineers, mainly thermodynamics, mass transfer, heat transfer, fluid flow, chemical reactions, and automatic control. Full development of these topics, of course, is neither possible nor desirable here, and attention is restricted primarily to the differential equations that occur there.

Many physical laws are formulated as rate processes, from Newton's second law of motion and the law of mass action on. Mathematically, rates are represented by derivatives. Mathematical relations between derivatives and other functions constitute differential equations. Such equations are solved by eliminating derivatives from them.

To start, this book tells how to solve the main types of differential equations that occur in practice. Emphasis is placed early on numerical and approximate methods of solution, because the bulk of nontrivial problems have to be solved that way. To make way for the many desirable topics, the theoretical basis has had to be skimmed, and preference has been given to detailed applications of methods of solution. For supplementary material on theoretical background and even for additional exercises, the reader is advised to consult conventional textbooks. The problems for the reader include some purely mathematical exercises, but the main emphasis is on problems of an engineering nature. Space and time are always short. The engineer who tries to learn everything that is known about a topic nowadays will have no time to solve his or her own problems.

After the mathematics of differential equations has been pre-

sented, a chapter is devoted to the principles of the mathematical formulation of engineering processes. Then follows the distinctive part of this book, which consists of derivations and solutions of differential equations in some of the major disciplines of chemical engineering. Many of the topics are reinforced by mathematical or numerical examples as well as problems for the reader, mostly with answers.

Little mathematics beyond calculus is expected of the reader. Computer usage by the examples and problems is restricted to readily available user-friendly PC diskettes, and essentially no individual programming is employed. The book should be accessible to third- or fourth-year undergraduates and possibly accessible to graduate students. Also, it should be of interest to professional engineers who have forgotten some of their schoolwork and wish to review or possibly extend some of it.

Although the applications are important to chemical engineers, many of them also should interest other engineers. The purely mathematical aspect of the book likewise should have a wider appeal.

Throughout my long industrial and academic career, I have been concerned with applied mathematics. Now I have found time to assemble this material partly for my own satisfaction, but I would like it to be of interest and perhaps of value to students and other engineers. It has had to be prepared without immediate student participation and thus has missed that baptism by fire. Several reviewers made helpful suggestions on the manuscript. Many of the figures were computer drawn by Said Saim, H.W. Kroeger, Dr. C.S. McCool, and Dr. M.J. Michnik also assisted with computerization. Professor Alkis Constantinides of Rutgers University graciously supplied improvements of his valuable diskette on numerical methods. Appreciation is due particularly to Dr. Reza Shams for his computer expertise and to Dr. Riyaz Kharrat for his mathematical advice, as well as for their faithful monitoring of the progress of the book—when is it going to be finished?

Contents

LIST OF EXAMPLES ix

PREFACE xiii

CHAPTER 1 DIFFERENTIAL EQUATIONS AND THEIR SOLUTIONS 1

- 1.1. Classification, Definitions, and Concepts 2
- 1.2. Method of Isoclines 4
- 1.3. A Numerical Method 5
- 1.4. Solution of $dy/dx = f(x, y)$ in a Series 6
- 1.5. Solution of $dy/dx = f(x, y)$ as an Integral Equation 6
- 1.6. Analytical Methods of Solution 7
- 1.7. Qualitative Methods 7
 - Further Reading 7
 - Problems 7

CHAPTER 2 EQUATIONS FOR WHICH EXACT SOLUTIONS ARE OBTAINABLE 11

- 2.1. First-Order Ordinary Differential Equations 11
 - 2.1.1. Variables Separable 11
 - 2.1.2. Homogeneous Differential Equations 12
 - 2.1.3. Linear Differential Equations 14
 - 2.1.4. Total or Exact Equations 16
 - 2.1.5. $F(x, y, p) = 0$ Solvable Explicitly for One of the Variables 16
 - 2.1.6. Simultaneous Linear Differential Equations 17
 - 2.1.7. Simultaneous Autonomous Linear Differential Equations 18
 - 2.1.8. Solutions Near Critical Points 20
 - 2.1.9. Autonomous and Nonautonomous Equations 22
- 2.2. Linear Differential Equations with Constant Coefficients 23
 - 2.2.1. Constants of Integration 23
 - 2.2.2. The Homogeneous Differential Equation 23
 - 2.2.3. The Laplace Transform 24
 - 2.2.4. Kinds of Input Functions 29
 - 2.2.5. The Nonhomogeneous Differential Equation 29
 - 2.2.6. Oscillatory Behavior 33
 - 2.2.7. Transfer Functions 36
 - 2.2.8. Systems of Equations 38
 - 2.2.9. Higher Order Equations 40
 - 2.2.10. Matrix Formulation of Large Systems 42
 - Further Reading 44
 - Problems 44

CHAPTER 3 PRIMARILY LINEAR DIFFERENTIAL EQUATIONS WITH VARIABLE COEFFICIENTS 51

- 3.1. Change of Variables 51
 - 3.1.1. Equations of the Form $d^2y/dx^2 = f(x, y, dy/dx)$ 52
 - 3.1.2. The Cauchy–Euler Linear Differential Equation 52
- 3.2. When One Solution Is Known 54
- 3.3. Properties of Infinite Series 54
 - 3.3.1. Convergence Tests 54
 - 3.3.2. Power Series 57
 - 3.3.3. Trigonometric Series 59
 - 3.3.4. Operations with Series 59
- 3.4. Solution of Differential Equations in Power Series 59
- 3.5. Second-Order Linear Differential Equations 65
 - 3.5.1. Arbitrary Constants 65
 - 3.5.2. Recursion Formulas 65

- 3.6. Singular Points 65
 - 3.6.1. Points at Infinity 66
- 3.7. Method of Frobenius for Equations with Regular Singular Points 67
 - 3.7.1. Convergence of Frobenius Solutions 67
- 3.8. Periodic Solutions 67
 - Further Reading 71
 - Problems 71

CHAPTER 4 DIFFERENTIAL EQUATIONS ASSOCIATED WITH ORTHOGONAL FUNCTIONS 75

- 4.1. Trigonometric Functions 75
 - 4.1.1. Complex Form of the Fourier Series 75
- 4.2. Sturm–Liouville Problems 76
- 4.3. Solutions in Series 78
- 4.4. The Legendre Equations and Functions 79
 - 4.4.1. Expansions in Series 82
 - 4.4.2. Related Equations 83
- 4.5. Bessel Equations and Functions 83
 - 4.5.1. Orthogonal Properties 85
 - 4.5.2. Formulas 87
 - 4.5.3. Occurrence of the Equations 88
- 4.6. Other Differential Equations of Boundary Value Problems 90
 - 4.6.1. The Mathieu Equation 90
 - 4.6.2. The Lamé Equation 90
 - 4.6.3. The Laguerre Equation 90
 - 4.6.4. The Hermite Equation 91
 - 4.6.5. The Chebyshev Equation 91
 - Further Reading 94
 - Problems 95

CHAPTER 5. APPROXIMATE ANALYTICAL METHODS OF SOLUTION 97

- 5.1. Linearization 97
 - 5.1.1. Taylor Series 97
 - 5.1.2. Steady States 101
- 5.2. Phase Plane Analysis 101
 - 5.2.1. Stability 104
 - 5.2.2. Nonlinear and Linearized Behaviors 106
 - 5.2.3. Periodic Solutions 106
- 5.3. Other Methods 106
 - 5.3.1. Method of Krylov and Bogoliubov 111
 - 5.3.2. Method of Least Squares 111
 - 5.3.3. The Galerkin Method 111
 - Further Reading 113
 - Problems 114

CHAPTER 6 PARTIAL DIFFERENTIAL EQUATIONS 115

- 6.1. Partial Differentiation 115
 - 6.1.1. Total Differential 115
 - 6.1.2. Change of Variables 115
 - 6.1.3. Implicit Functions 116
 - 6.1.4. Change of Coordinate System for the Laplacian 116
 - 6.1.5. Solutions of Some PDEs 117
- 6.2. First-Order Partial Differential Equations 117
 - 6.2.1. Origins 118
 - 6.2.2. Linear and Quasilinear Types 120
 - 6.2.3. Solutions 120

- 6.2.4. Laplace Transformation 123
- 6.2.5. Particular Solutions 123
- 6.2.6. Nonlinear Equations—Charpit's Method 125
- 6.2.7. Reducible Higher Order Equations 126
- 6.3. Second-Order Linear Partial Differential Equations 126
 - 6.3.1. Second-Order Linear Equations 127
 - 6.3.2. Auxiliary Conditions 127
 - 6.3.3. Classification of Equations 128
 - 6.3.4. Separation of Variables—Fourier Method 130
 - 6.3.5. Orthogonal Functions and Expansions 132
 - 6.3.6. Nonhomogeneous Conditions 132
 - 6.3.7. Nonhomogeneous Equations—The Poisson Equation 139
- 6.4. Laplace Transformation 140
- 6.5. Inversion of Transforms 140
- 6.6. Integral Transforms 140
 - 6.6.1. Finite Sine and Cosine Transforms 146
- 6.7. Nonhomogeneous Systems—Impulse and Step Conditions 147
 - 6.7.1. Impulse Input—Green's Functions 147
 - 6.7.2. Impulse Function 149
 - 6.7.3. Step Input—Superposition with Duhamel's Theorem 149
- 6.8. Integral Equations 151
 - 6.8.1. Origins of Integral Equations 151
 - 6.8.2. Methods of Solution 151
 - 6.8.3. Solution in Series 154
 - 6.8.4. Solution by Iteration 154
 - 6.8.5. Differential Equations 157
- Further Reading 160
- Problems 160

CHAPTER 7 NUMERICAL METHODS 165

- 7.1. Taylor's Series 165
- 7.2. Roots of Algebraic/Transcendental Equations 166
 - 7.2.1. The Newton–Raphson Method 166
 - 7.2.2. Direct Iteration 167
 - 7.2.3. Method with Second Derivatives 167
 - 7.2.4. Roots of Polynomials 167
 - 7.2.5. Simultaneous Nonlinear Equations 167
- 7.3. Systems of Linear Equations 169
 - 7.3.1. Gaussian Elimination 169
 - 7.3.2. Gauss–Jordan Method 170
 - 7.3.3. Gauss–Seidel Method 171
 - 7.3.4. Tridiagonal Systems 171
- 7.4. Eigenvalues and Eigenfunctions 171
- 7.5. Initial Value Ordinary Differential Equations 173
 - 7.5.1. Taylor's Series Method 174
 - 7.5.2. Euler's Methods 174
 - 7.5.3. Runge–Kutta Method 174
 - 7.5.4. Simultaneous Equations 174
 - 7.5.5. Stability and Stiffness 175
 - 7.5.6. Second-Order Equations 175
 - 7.5.7. Multiple Solutions 175
 - 7.5.8. Comparison of Methods 176
- 7.6. Boundary Value Problems 176
 - 7.6.1. The Shooting Method 176
 - 7.6.2. Finite-Difference Method 179
- 7.7. Equations of Higher Order 180
- 7.8. Integral Equations 181
- 7.9. Solution of Partial Differential Equations (PDEs) by Finite Differences 188
 - 7.9.1. Derivatives 188
- 7.10. Parabolic Partial Differential Equations 190
 - 7.10.1. Explicit Method 190
 - 7.10.2. Implicit Method 190
 - 7.10.3. Solution as a Set of ODEs—Method of Lines 192
 - 7.10.4. Value of the Derivative Specified at the Boundary 192

- 7.10.5. The Program PARABOL 193
- 7.10.6. Two or More Dimensions 194
- 7.10.7. Simultaneous Partial Differential Equations 194
- 7.11. Elliptic Equations of Poisson and Laplace 195
 - 7.11.1. Rectangular Boundaries 195
 - 7.11.2. The Program ELLIPTIC 199
 - 7.11.3. Other Shapes of Regions 199
- 7.12. Hyperbolic Equations—The Wave Equation 199
 - 7.12.1. The One-Dimensional Form 199
 - 7.12.2. Two Space Dimensions 200
- 7.13. The Finite-Element Method 201
 - Further Reading 204
 - Problems 204

CHAPTER 8 PRINCIPLES OF MODELING 209

- 8.1. Introduction 209
- 8.2. Kinds of Models 209
 - 8.2.1. Dimensionless Variables 209
 - 8.2.2. Range Limitation 209
 - 8.2.3. Basic Types of Models 210
 - 8.2.4. Lumping and Distribution 210
 - 8.2.5. Direct and Indirect Models 210
- 8.3. Coordinate Systems 210
- 8.4. Fields, Potentials, and Fluxes 213
 - 8.4.1. Vector Arithmetic 215
 - 8.4.2. Differentiation and the Operator Del 215
 - 8.4.3. Line Integrals and Circulation 221
 - 8.4.4. Characterization of Fields with Del 223
- 8.5. Dimensional Homogeneity 224
- 8.6. Conservation Principles 227
 - 8.6.1. Mechanics 227
 - 8.6.2. Fluid Mechanics 228
 - 8.6.3. Thermodynamics 229
- 8.7. Physical Laws and Analogies 230
 - Further Reading 233
 - Problems 234

CHAPTER 9 EQUATIONS OF PHYSICS 235

- 9.1. The Wave Equation 235
 - 9.1.1. Transverse Vibrations of a String 235
 - 9.1.2. Longitudinal Vibration of a Rod 237
 - 9.1.3. Vibration of a Membrane 237
 - 9.1.4. Vibration of Beams 238
 - 9.1.5. Sound Waves 241
 - 9.1.6. Electrical Waves in Transmission Lines 242
- 9.2. Conduction of Heat 242
 - 9.2.1. The Heat Equation 242
 - 9.2.2. Reduction to the Simplest Form 243
 - 9.2.3. Multidimensions and Other Coordinates 243
 - 9.2.4. Boundary Conditions 243
- 9.3. Diffusion of Matter 245
 - 9.3.1. Analogy Between Diffusion of Thermal Energy and Diffusion of Matter 245
- 9.4. Laplace and Poisson Equations 246
 - 9.4.1. Gravitational and Other Potentials 246
 - 9.4.2. Solutions of the Equations 247
 - 9.4.3. Relation to Functions of a Complex Variable 247
- 9.5. Equations of Fluid Dynamics 248
 - 9.5.1. Conservation of Mass—The Equation of Continuity 248
 - 9.5.2. Rotation of an Elemental Volume of a Fluid 249
 - 9.5.3. Equation of Motion 249
- 9.6. The Schrödinger Equation of Wave Mechanics 252
- 9.7. Other Disciplines 253
 - 9.7.1. Chemical Reaction Rates 253
 - 9.7.2. Process Control 253
- Further Reading 254
- Problems 254

CHAPTER 10 THERMODYNAMICS 257

- 10.1. The Method of Bridgman 257
- 10.2. The Jacobian Method of Shaw 258
- 10.3. Integration 261
- 10.4. Open Systems 263
- 10.5. Conversion of Heat into Work 267
- 10.6. Chemical Equilibria 269
- 10.7. Phase Equilibria—The Clapeyron Equation 270
- 10.8. Energy of Fluid Flow 271
 - 10.8.1. Mechanical Energy Balance 272
 - 10.8.2. Isothermal Flow of Gases 272
 - 10.8.3. Adiabatic Flow of Gases in Lines 273
- Further Reading 274
- Problems 274

CHAPTER 11 DIFFUSION OF MATTER 277

- 11.1. One-Dimensional Equations 277
- 11.2. Methods of Solution 278
- 11.3. Steady-State Diffusion 278
 - 11.3.1. One-Dimensional Diffusion 278
 - 11.3.2. Steady State in Two Dimensions 279
 - 11.3.3. Diffusion and Chemical Reaction 280
- 11.4. An Infinite Region 280
 - 11.4.1. The Fourier Integral 280
 - 11.4.2. Distribution in an Infinite Region 281
- 11.5. Semi-infinite Regions 284
- 11.6. Finite Regions 286
- 11.7. Spherical Regions 287
- 11.8. Cylindrical Regions 296
- 11.9. Instantaneous Sources 298
- 11.10. Dispersion 299
- 11.11. Dispersion and Chemical Reaction 300
 - 11.11.1. Material Balance 300
 - 11.11.2. Boundary Conditions 301
 - 11.11.3. Solving the Equations 302
- 11.12. Diffusion and Reaction in Catalyst Pores 305
 - 11.12.1. Boundary Conditions for Zero-Order Reactions 306
 - 11.12.2. Solving the Equations 307
- Further Reading 311
- Problems 311

CHAPTER 12 TRANSFER OF HEAT 313

- 12.1. Convection and Radiation at the Boundary 313
- 12.2. Temperatures in Heat Exchangers 314
- 12.3. Heat Conduction Problems in Other Parts of This Book 316
- 12.4. Solutions of Problems 317
- 12.5. Time-Dependent and Periodic Boundary Conditions 319
- 12.6. Numerical Solutions 322
 - 12.6.1. Cartesian Coordinates 322
 - 12.6.2. Polar Coordinates 325
 - 12.6.3. Spherical Coordinates 329
 - 12.6.4. Convection and Radiation at the Boundary 329
- 12.7. Steady States—The Laplace and Poisson Equations 330
 - 12.7.1. Cylindrical Coordinates 330
 - 12.7.2. Cylindrical Regions with Two Space Variables 332
- 12.8. The Laplace Equation in a Spherical Region 336
 - Further Reading 337
 - Problems 337

CHAPTER 13 FLUID DYNAMICS 341

- 13.1. Stream Functions and Potential Functions 341
 - 13.1.1. Irrotational Flow 342
 - 13.1.2. One Function Derived from the Other 344

- 13.1.3. Velocities and Pressures 346
- 13.1.4. Axisymmetric Flow 347
- 13.2. Finding Equations of Streamlines and Potentials 348
- 13.3. Application of Complex Variables 349
 - 13.3.1. Derivatives 350
 - 13.3.2. Superposition of Functions 350
 - 13.3.3. Flow Nets Represented by Common Functions 351
 - 13.3.4. Transformations of Regions 351
- 13.4. Solving the Laplace Equation with the Aid of Conformal Mapping 355
- 13.5. Viscous Incompressible Fluids—The Navier–Stokes Equations 357
 - 13.5.1. One-Dimensional Flows 358
 - 13.5.2. The Unsteady State 359
 - 13.5.3. Two Dimensions 359
 - 13.5.4. Limitations of the Navier–Stokes Theory 362
- 13.6. Flow in Porous and Granular Bodies 362
 - 13.6.1. Higher Dimensions—Steady State 363
 - 13.6.2. Granular and Packed Beds 365
 - 13.6.3. Filtration of Slurries 365
- 13.7. Compressible Fluids 366
 - 13.7.1. Flow Equations 366
 - 13.7.2. Isothermal Flow 367
 - 13.7.3. Adiabatic Flow 367
 - 13.7.4. Isentropic Flow 368
- Further Reading 369
- Problems 369

CHAPTER 14 CHEMICAL REACTIONS 371

- 14.1. Homogeneous Nonflow Reactions 371
 - 14.1.1. Consecutive and Simultaneous Reactions 372
 - 14.1.2. Stoichiometric Balances in Complex Reactions 374
 - 14.1.3. Sets of First-Order Reactions 374
 - 14.1.4. Sets of Higher Order Reactions 376
 - 14.1.5. Variable Temperatures 376
 - 14.1.6. Filling and Emptying Processes 377
- 14.2. Flow Processes 379
 - 14.2.1. Plug Flow Reactors (PFRs) 379
 - 14.2.2. The Unsteady State 380
 - 14.2.3. Steady-State Gas-Phase Reactions—Energy Balance 380
 - 14.2.4. Laminar Flow 380
- 14.3. Continuous Stirred Tank Reactors (CSTRs) 381
 - 14.3.1. Unsteady State 381
 - 14.3.2. Steady State 383
 - 14.3.3. Material and Energy Balances 383
- 14.4. Residence Time Distribution 385
 - 14.4.1. Tracer Response Equations 386
 - 14.4.2. Chemical Conversion with Known RTDs 388
 - 14.4.3. Segregated Flow 388
 - 14.4.4. Maximum Mixed Flow 389
 - 14.4.5. Dispersion in Chemical Reactors 391
- 14.5. Reactors with Axial and Radial Gradients 391
 - 14.5.1. Energy and Material Balances 392
 - 14.5.2. Solving the Equations 393
 - 14.5.3. Numerical Solutions 394
- Further Reading 398
- Problems 398

CHAPTER 15 PROCESS DYNAMICS AND CONTROL 401

- 15.1. Linearization 401
- 15.2. Differential Equations, Signals, and Transfer Functions 401
 - 15.2.1. Signals 401
 - 15.2.2. Transfer Functions 403

viii CONTENTS

15.2.3.	Block Diagrams	404	15.6.	Digital Computer Control	421
15.2.4.	Inversion	405	15.6.1.	Finite-Difference Equations	421
15.2.5.	Time Delay (Dead Time)	405	15.6.2.	z -Transforms	422
15.2.6.	Determination of Transfer Functions	405	15.6.3.	Inversion of z -Transforms	424
15.2.7.	Frequency Response	407	15.6.4.	Closed Control Loops	426
15.3.	Controllers	409	15.6.5.	Other Aspects of Discrete Digital Control	426
15.3.1.	Controller Modes	410	Further Reading	426	
15.3.2.	Stability	410	Problems	427	
15.3.3.	Controller Settings	410			
15.3.4.	Control Operations	413	APPENDIX	429	
15.4.	Shell-and-Tube Heat Exchangers	415	REFERENCES	441	
15.4.1.	Uniform Temperature Distributions	415	INDEX	445	
15.4.2.	Uniform Temperature on One Side Only	415			
15.4.3.	Nonuniform Profiles on Both Sides—The Lumping Approximation	417			
15.5.	Distillation	419			
15.5.1.	Tray Equations	419			
15.5.2.	Feedback Control	420			

List of Examples

- 1.1. Differential Equations Originating in Some Physical Problems 1
- 1.2. Domain of Existence and Uniqueness of Solutions 2
- 1.3. Envelopes as Singular Solutions 3
- 1.4. Numerical Solution by Euler's Method 6
- 1.5. Application of Picard's Method for an Integral Equation 6

- 2.1. Separation of Variables 13
- 2.2. Homogeneous Differentiation Equations 14
- 2.3. Linear Differential Equations 15
- 2.4. Total or Exact Differential Equations 15
- 2.5. $F(x, y, p) = 0$ Solvable for One of the Variables 17
- 2.6. A Pair of Linear Differential Equations 18
- 2.7. Autonomous Equations with Real or Complex Characteristic Roots 19
- 2.8. Two-Point Boundary Conditions Resulting in Various Numbers of Solutions 23
- 2.9. Homogeneous Linear Equations with Constant Coefficients 25
- 2.10. Derivation of Laplace Transforms and Their Inverses 25
- 2.11. Expansion of $F(s)/G(s)$ into Partial Fractions 27
- 2.12. Application of the Method of Undetermined Coefficients 27
- 2.13. Variation of Parameters 28
- 2.14. Application of Laplace Transforms to Solution of Differential Equations 32
- 2.15. Integral Curves with Step Input to the Damped Equation $y'' + 2k\omega y' + \omega^2 y = \omega^2$, with $y_0 = y'_0 = 0$ 34
- 2.16. The Undamped Equation with Sinusoidal Input 34
- 2.17. Response with a Short-Lived Transient 35
- 2.18. The Damped Equation with Sinusoidal Input 35
- 2.19. Reduction and Inversion Complex Transfer Functions 35
- 2.20. A Two-Stage Stirred-Tank Reactor 38
- 2.21. Operator Method for Simultaneous Equations 39
- 2.22. Use of Laplace Transforms for Simultaneous Equations 41
- 2.23. Matrix Solution of Homogeneous First-Order Systems 43

- 3.1. Solutions by Changing Variables 53
- 3.2. Finding Second Independent Solutions 55
- 3.3. Convergence and Divergence 58
- 3.4. Series Expansion of $xe^{-x/2}$ in a Trigonometric Series 61
- 3.5. Operations with Series 61
- 3.6. Series Solutions of Some First- and Second-Order Equations 62
- 3.7. Application of the Frobenius Method 68
- 3.8. A Differential Equation with Three Singular Points—The Hypergeometric Equation 69
- 3.9. Periodic Solutions 71

- 4.1. Expansion of e^{ax} in a Trigonometric Series 76
- 4.2. Finding Eigenvalues 78
- 4.3. Expansions in Series of Legendre Polynomials 82
- 4.4. A Solution in Terms of Legendre Polynomials 83
- 4.5. Applications of the Generalized Forms of the Bessel Equation 86
- 4.6. Expansions in Series of Bessel Functions 87
- 4.7. Radial Diffusion in a Cylinder 88
- 4.8. Formulas of Laguerre, Hermite, and Chebyshev 92
- 4.9. Expansion in Hermite and Chebyshev Polynomials 94

- 5.1. Linearization of Differential Equations 98
- 5.2. A Tank-Filling Process 99
- 5.3. A Continuous Stirred Tank Reactor 100
- 5.4. Finding Steady States 100
- 5.5. Phase Plane Trajectory of a Resonant Oscillation 102
- 5.6. Construction of a Phase Portrait 103
- 5.7. Control of an Exothermic Chemical Reaction 108
- 5.8. A Differential Equation with a Small Parameter 110
- 5.9. Least Squares Solution of a First-Order Equation 112
- 5.10. Dispersion Reactor Model—Galerkin Type Solution 113

- 6.1. Partial Differentiation 115
- 6.2. Change of Variable 116
- 6.3. Derivations of Some First-Order PDEs 118
- 6.4. Applications of Lagrange's Method to First-Order PDEs 121
- 6.5. Equations of Compressible Fluid Flow—Particular Integrals 123
- 6.6. A Particular Surface Corresponding to a Specified Space Curve 124
- 6.7. An Auxiliary Condition That Does Not Fit 125
- 6.8. Ill-Posed Problems 128
- 6.9. Canonical Transformations 129
- 6.10. Separation of Variables 130
- 6.11. Diffusion into a Vessel 132
- 6.12. Heat Conduction in a Sphere—Legendre Polynomials 134
- 6.13. Nonhomogeneous Conditions for a Vibrating String 135
- 6.14. A Nonhomogeneous Equation—The Heat Equation 136
- 6.15. Reduction of a Nonhomogeneous PDE 137
- 6.16. A Nonhomogeneous Equation—The Poisson Equation 137
- 6.17. Inversion of Laplace Transforms by Residues 141
- 6.18. Laplace Transform Solutions of the Heat Equation 141
- 6.19. Laplace Transform Solutions of the Wave Equation 143
- 6.20. A Transform Involving Bessel Functions 144
- 6.21. Laplace Transform Solution of a Nonhomogeneous Equation 145
- 6.22. Solution of the Heat Equation by Fourier Transformation 145
- 6.23. Finite Sine and Cosine Transforms 146
- 6.24. Items from the Green's Function Handbook of Butkovski (1982) 148
- 6.25. Nonhomogeneous Equations by Duhamel's Method 150
- 6.26. Formulation of Some Integral Equations 152
- 6.27. Kernels of the Convolution or Separable Types 153
- 6.28. Solutions in Series 155
- 6.29. Solution by Iteration 156
- 6.30. Integral Equations from Differential Equations 158

- 7.1. Solution of $f(x) = 0$ by Several Methods 168
- 7.2. A Case of Multiple Solutions 169
- 7.3. Solution of a Linear System by Gaussian Elimination 170
- 7.4. A Tridiagonal System 172
- 7.5. Occurrence of Eigenvalue Problems 172
- 7.6. Characteristic Equation—Its Roots and Eigenvectors the Characteristic System 173
- 7.7. A Nonlinear ODE Solved by the Runge-Kutta Method 177
- 7.8. A Pair of Nonlinear Equations 177
- 7.9. A Large System of First-Order Equations 178
- 7.10. Application of the Shooting Method to Equations with Two-Point Boundary Conditions 178
- 7.11. The Finite Difference Method 180
- 7.12. The Lorentz Equation—A Case of Random Behavior 182
- 7.13. A Chemical Reaction Conforming to a Predator-Prey Model 183
- 7.14. Changing Nature of Equilibrium Points—The Hopf Bifurcation 185
- 7.15. Numerical Evaluation of an Integral Equation 186
- 7.16. Nonlinear Integral Equations 187
- 7.17. The Explicit Method for the Heat Equation 191

x LIST OF EXAMPLES

- 7.18. The Method of Lines 192
- 7.19. Application of the Program PARABOL [Constantinides (1987)] 194
- 7.20. A Pair of PDEs 195
- 7.21. The Laplace Equation with Constant Boundary Conditions 196
- 7.22. The Laplace Equation Solved by Iteration 197
- 7.23. Specification of a Derivative at the Boundary 197
- 7.24. Application of the Program ELLIPTIC 198
- 7.25. The One-Dimensional Wave Equation 201
- 7.26. Finite Elements of One Dimension 203
- 8.1. Separation of Variables in the Laplace Equation 213
- 8.2. Diffusion in Spherical Coordinates 214
- 8.3. The One-Dimensional Heat Equation in Three Coordinate Systems 215
- 8.4. Some Products of Vectors 216
- 8.5. Inseption Method for Dimensional Groups 225
- 8.6. Equation for Isothermal Flow of a Fluid by Rayleigh's Principle 226
- 8.7. Dimensionless Solution of a Partial Differential Equation 226
- 9.1. Vibration of a Long String—D'Alembert's Solutions 236
- 9.2. Longitudinal Vibration of a Rod Fixed at One End 237
- 9.3. Vibrations of Circular and Rectangular Membranes 238
- 9.4. Boundary Conditions for a Conducting Rod 244
- 9.5. Solution by Laplace Transformation 244
- 9.6. Analogy between Diffusion of Thermal Energy and Diffusion of Matter 245
- 9.7. Potential due to a Charged Sphere 247
- 9.8. Integration for the Bernoulli Equation 252
- 10.1. Application of the Bridgman Method 258
- 10.2. Application of the Shaw Jacobian Method 260
- 10.3. Thermodynamic Properties from Data on P , V , T , and C_p^0 261
- 10.4. Enthalpy Change with Pressure and Temperature 262
- 10.5. Work from Expansion of a Gas at Constant Entropy 263
- 10.6. Discharge of a Gas from a Storage Tank 264
- 10.7. Pumping Gas into a Tank with an Isentropic Compressor 264
- 10.8. Pumping Gas into a Cooled Tank 265
- 10.9. Expelling Liquid with Gas Pressure—A Pair of Equations 266
- 10.10. Carnot Efficiency of Work Recovery from a Hot Gas 268
- 10.11. Chemical Equilibrium as a Function of Temperature 270
- 10.12. The Clausius-Clapeyron Equation Applied 271
- 10.13. Pressure Drop in Nonisothermal Liquid Flow 273
- 10.14. Adiabatic and Isothermal Pressure Drops in a Line 274
- 11.1. Steady-State Distribution in a Semicircular Plate 279
- 11.2. Diffusion and Reaction in a Membrane or Interfacial Film 280
- 11.3. Concentration Profiles in an Infinite Region 282
- 11.4. A Semi-infinite Region—Alternate Methods of Solution 284
- 11.5. Diffusion in a Finite Region 287
- 11.6. Measurement of Diffusivity 288
- 11.7. Diffusion from a Saturated Layer of Solution 289
- 11.8. Two Regions Originally with Different Concentrations 289
- 11.9. Diffusion of Gases 290
- 11.10. Variable Diffusion Coefficient 291
- 11.11. Variable Diffusion Coefficients from Measured Concentration Profiles 292
- 11.12. Drying Bodies of Several Shapes 292
- 11.13. Numerical Evaluation of Eq. (11.83) 297
- 11.14. Dispersion in Laminar Flow 299
- 11.15. Dispersion in Turbulent Flow 300
- 11.16. First-Order Reaction with Dispersion 302
- 11.17. Second-Order Reaction with Dispersion 303
- 11.18. The Method of Lines for an Unsteady-State Dispersion-Reaction Equation 304
- 11.19. Steady-State Dispersion-Reaction in Two Dimensions 304
- 11.20. First-Order Reaction in a Slab 307
- 11.21. First-Order Reaction in a Slab with External Diffusional Resistance 308
- 11.22. First-Order Reaction in a Sphere 308
- 11.23. First-Order Reaction in a Cylinder with Sealed Ends 309
- 11.24. Zero-Order Reaction in a Sphere 309
- 11.25. Zero-Order Reaction in a Slab—Analytical and Numerical Solutions, Diffusion from Both Faces 310
- 11.26. Second-Order Reaction in a Sphere—Numerical Solution 310
- 12.1. LMTD in a One-Pass Exchanger 314
- 12.2. Temperature Profile in a Two-Pass Exchanger 315
- 12.3. Moving Boundary in the Thermal Decomposition of Limestone 319
- 12.4. Boundary Condition a Function of Time 320
- 12.5. Transient Response to a Harmonic Input 320
- 12.6. Harmonic Input to a Semi-infinite Region 321
- 12.7. Comparison of Numerical Solutions 323
- 12.8. Analytical Solution of the Problem of Example 12.7. 324
- 12.9. Effect of Step Size with an Explicit Solution 325
- 12.10. Temperatures in a Cylindrical Shell 327
- 12.11. The Method of Lines Applied to a Cylindrical Shell 328
- 12.12. Convection and Radiation at a Boundary 330
- 12.13. Steady Temperature Distribution—Separation of Variables 331
- 12.14. The Poisson Equation in Cylindrical Finite Differences 332
- 12.15. Heat Transfer to a Liquid in Laminar Flow 333
- 12.16. A Hollow Cylinder with Internal Heat Generation 334
- 12.17. A Cylinder with Internal Heat Generation 335
- 12.18. Temperatures in a Sphere at Steady Conditions 336
- 13.1. Flow Past a Cylinder 344
- 13.2. Flow through a Variable Cross Section—Numerical Solution 346
- 13.3. Flow Past a Sphere—Variable Separation Suggested by a Boundary Condition 348
- 13.4. The Doublet and Flow Past a Cylinder 350
- 13.5. The Function $w(z) = e^z$ on the w Plane and the z Plane 355
- 13.6. A Process Occurring in a Quadrantal Region 356
- 13.7. Laplace Solutions in a Semi-infinite Plane and in a Slab 357
- 13.8. Laplace Equation in a Semiannulus 358
- 13.9. Steady Flow between Parallel Planes 359
- 13.10. One Moving Plane 360
- 13.11. Flow through a Circular Pipe 360
- 13.12. Flow between Concentric Rotating Cylinders 361
- 13.13. Unsteady Flow between Parallel Planes 361
- 13.14. Unsteady Flow of a Liquid in a Porous Region 364
- 13.15. Flow of Gas in a Semi-infinite Porous Body 364
- 13.16. Filtration with a Variable Specific Resistance 366
- 14.1. Stoichiometric Balances of Simultaneous Reactions 373
- 14.2. Integration of Simultaneous First-Order Rate Equations 374
- 14.3. Pairs of Nonlinear Equations 376
- 14.4. A Reaction with and without Heat Transfer 378
- 14.5. Filling Periods of Batch Reactors 378
- 14.6. A Complex Gas-Phase Reaction in a PFR 380
- 14.7. An Adiabatic Complex Gas-Phase Reaction in a PFR 382
- 14.8. A Complex Reaction in a Multistage CSTR 383
- 14.9. The Unsteady State of a Complex Reaction in a CSTR 384
- 14.10. Multiple Steady States in an Adiabatic CSTR 384

- 14.11. RTD of Power Law and Laminar Flow 388
- 14.12. Derivation of the Maximum Mixedness (Zwietering) Equation of a Chemical Reactor 390
- 14.13. Conversion with Several Models 391
- 14.14. Conversion in a Reactor with Dispersion 392
- 14.15. Reaction on a Catalytic Wall—Analytical Solution 394
- 14.16. Reaction on a Catalytic Flow Plate 395
- 14.17. The Method of Lines Applied to a Reactor 395
- 14.18. Dehydrogenation of Ethylbenzene in a Tubular Reactor—Explicit Finite-Difference Solution 396

- 15.1. Linearization with Taylor's Theorem 402
- 15.2. Linearization with the Equations of a CSTR 402
- 15.3. Response of a Process with Feedback 404
- 15.4. Transformation of a Block Signal Diagram 404
- 15.5. Fitting a Second-Order Model with Step Response Data 406

- 15.6. Frequency Response Calculated with Fourier Transform from the Response to a Pulse Input 409
- 15.7. Proportional Control of a Two-Capacity Process 412
- 15.8. Proportional-Integral and PID Control of a Two-Capacity Process 413
- 15.9. Stability Analysis and Controller Settings 414
- 15.10. A Steam-Jacketed Stirred Tank 415
- 15.11. A Uniform Temperature on the Shell Side 416
- 15.12. A Numerical Case of Steam-Water Heat Exchange 417
- 15.13. A Double Pipe Exchanger 418
- 15.14. A Lumped Model of a Multipass Exchanger 418
- 15.15. Derivations of Some z -Transforms 423
- 15.16. Inversion of a z -Transform 424
- 15.17. A Process with Discrete Digital Control 425

DIFFERENTIAL EQUATIONS AND THEIR SOLUTIONS

Differential equations are relations between several variables and their mathematical derivatives, for example,

1. $\frac{dy}{dx} = x + 5$ first-order ordinary
2. $\frac{d^2y}{dx^2} + 3\frac{dy}{dx} + 2y = 0$ second-order
3. $xy' + y = 3$ linear
4. $y''' + 2(y'')^2 + y' = \cos x$ first-degree nonlinear
5. $(y'')^2 + (y')^3 + 3y = x^2$ second-degree nonlinear
6. $\frac{\partial z}{\partial x} = z + x \frac{\partial z}{\partial y}$ first-order partial
7. $\frac{\partial^2 z}{\partial x^2} + \frac{\partial^2 z}{\partial y^2} = x^2 + y$ second-order partial

They may arise out of physical laws that are expressed in terms of rates or as relations between forces, masses, and accelerations. Geometric relations between slopes and curvatures also may lead to differential equations of importance in engineering. For illustration, a number of relatively simple equations are derived in Example 1.1.

The tasks addressed in this book are both the formulation and the solution of differential equations that simulate engineering problems. For practical reasons, a mathematical simulation is sought from which meaningful conclusions can be drawn yet one that is not so complex that numerical results cannot be drawn in the available time with the available equipment.

Example 1.1

Differential Equations Originating in Some Physical Problems

(a) Dibromosuccinic acid decomposes in hot water at a rate that is proportional to its concentration, that is, $-dC/dt = kC$.

(b) A tank of volume V contains brine of concentration C_0 . Fresh water is pumped in at a rate F , and solution overflows at the same rate. The solution is well stirred, so the effluent concentration is the same as that in the tank. Therefore, $-V dC/dt = FC$, with $C = C_0$ when $t = 0$.

(c) The motion of an object sliding on a horizontal surface is retarded by friction that is proportional to the velocity, $F_f = k dx/dt$. A constant force F_0 is impressed. By Newton's second law, the force balance is

$$F_0 - k \frac{dx}{dt} = m \frac{d^2x}{dt^2}$$

(d) Water evaporates from the surface of a porous material at a rate dW/dt that is proportional to the difference between the saturation humidity H_s and existing humidity H of the air. The humidity is the weight of moisture per unit volume. The room has a volume V . The material balance is

$$H = H_0 + \frac{W_0 - W}{V}$$

Accordingly, the rate of drying is

$$-\frac{dW}{dt} = k(H_s - H) = k\left(H_s - H_0 - \frac{W_0 - W}{V}\right)$$

(e) The bottom of a tank is covered with a layer of solid salt that dissolves at a rate that is proportional to the difference $C_s - C$ between the saturation and existing concentrations. The tank is stirred, and fresh water is pumped into the tank as in

part (b). The material balance is

$$V \frac{dC}{dt} = k(C_s - C) - FC$$

(f) A crystal of $K_2Cr_2O_7$ falls through a column of pure water. Its velocity is given by Stokes's law as $dx/dt = k_1 R^2$, where R is its radius. The rate of solution is proportional to the velocity. Putting it all together,

$$-\frac{d(4\pi R^3/3)}{dt} = k_2 \frac{dx}{dt} = k_1 k_2 R^2$$

(g) By Newton's law, a body cools in air at a rate proportional to the difference in temperature, $T - T_{air}$, but the proportionality factor in still air varies as the 0.25 power of the temperature difference. Thus the relation becomes

$$-\frac{dT}{dt} = k(T - T_{air})^{1.25}$$

(h) A reacting system has the stoichiometric form $2A \rightarrow B \rightarrow C$. Substance A changes into B at a rate that is proportional to the square of its concentration. The balances on substances A and B are as follows, where the first equation is solved and substituted into the second to make it directly integrable.

$$-\frac{dA}{dt} = k_1 A^2, \quad A = \frac{A_0}{1 + k_1 A_0 t}$$

$$\frac{dB}{dt} = k_1 A^2 - k_2 B = k_1 \left(\frac{A_0}{1 + k_1 A_0 t} \right)^2 - k_2 B$$

(i) At each point (x, y) of a curve, the slope of the tangent equals the product of the abscissa and ordinate, that is,

2 DIFFERENTIAL EQUATIONS AND THEIR SOLUTIONS

$$\frac{dy}{dx} = xy$$

which has the solution $y = Ce^{x^2/2}$.

(j) The family of circles of fixed radius r with centers on the x axis has the equation

$$(x - C)^2 + y^2 = r^2$$

where C is an arbitrary constant. Elimination of C by differentiation leads to the differential equation of this family of curves,

$$y^2 \left(\frac{dy}{dx} \right)^2 + y^2 = r^2$$

1.1. CLASSIFICATION, DEFINITIONS, AND CONCEPTS

An *ordinary differential equation* (ODE) involves functions and derivatives of only two variables, one independent and one dependent. Three kinds of symbols are used to designate the derivatives, as in these forms of the same equation:

$$\frac{d^2y}{dx^2} + xy \frac{dy}{dx} + y^2 = f(x, y)$$

$$y'' + xyy' + y^2 = f(x, y)$$

$$D^2y + xyDy + y^2 = f(x, y)$$

A *partial differential equation* (PDE) involves partial derivatives of one or more dependent variables with respect to more than one independent variable and functions of some or all of the variables.

The *order* of a differential equation is the order of the highest derivative. The equation $d^3y/dx^3 + (dy/dx)^2 + xy = 0$ is of the third order.

A *linear differential equation* does not have powers or products of the dependent variables and their derivatives. The general linear ODE of the n th order is $\sum_{n=0}^n f_n(x) d^n y/dx^n = 0$. All other ODEs are nonlinear.

The *degree* of an equation that can be written as a polynomial in the dependent variable and its derivatives is the highest exponent on the highest derivative. The equation $(d^2y/dx^2)^3 + f(x, y)(dy/dx)^4 + g(x, y) = 0$ is of the third degree. Just as algebraic equations of high degree have multiple roots, differential equations of high degree have multiple solutions.

The *solution* of an ODE of the n th order,

$$F\left(x, y, \frac{dy}{dx}, \dots, \frac{d^n y}{dx^n}\right) = 0$$

has n arbitrary constants and can be written

$$f(x, y, C_1, \dots, C_n) = 0$$

or explicitly as

$$y = f(x, C_1, \dots, C_n)$$

In specific cases, the constants C_i can be evaluated by imposing n conditions on the dependent variable or its derivatives. Conditions are of two kinds, initial value or one-point conditions, and boundary value or multiple-point conditions.

In *initial value problems*, values of the dependent variable and $n - 1$ derivatives are specified at a point x_0 . For example, the equation $d^2y/dx^2 + y = 0$ has the solution $y = C_1 \sin x + C_2 \cos x$. The constants C_1 and C_2 can be evaluated when y_0 and y'_0 are specified at x_0 , by solving the two equations

$$y_0 = C_1 \sin x_0 + C_2 \cos x_0 \quad \text{and} \quad y'_0 = C_1 \cos x_0 - C_2 \sin x_0$$

In *boundary value problems*, the n values of the dependent variable or its derivatives are specified at more than one point. Such problems do not always have unique solutions and may, in fact, have no solution. Example 2.8 illustrates this point. In practical problems, care must be taken to make multiple-point conditions compatible with each other.

Uniqueness of Solutions. The solution of a differential equation $y' = f(x, y)$ is unique at a point (x_0, y_0) if the function is continuous and its derivative $\partial f/\partial y$ is bounded (Cauchy's existence theorem). Geometrically this means that only one integral curve passes through (x_0, y_0) . The points of a region at which the uniqueness of a solution is violated are called *singular points*; at such points, zero, one, or multiple solutions may exist. Example 1.2 examines some cases.

Singular solutions are those that cannot be obtained by assigning particular values to the integration constants of a general solution. Usually they are associated with nonlinear differential equations. *Envelopes*, for instance, have every point coincident with a point of each member of a family of curves representing the general solution. Example 1.3 considers a number of such cases.

Example 1.2

Domain of Existence and Uniqueness of Solutions

(a) The equation $dy/dx = x(1 - y^2)^{1/2} = f(x, y)$ has the derivative $\partial f/\partial y = -xy/(1 - y^2)^{1/2}$, which is bounded by $|y| \leq 1$. Moreover, the function f itself is continuous over $|y| \leq 1$. Consequently, the differential equation has a unique solution in any strip $-1 < y < 1$.

(b) For the equation $dy/dx = f(x, y) = x^2 - y^2$, the valid domain is the entire xy plane, because f is continuous everywhere and the derivative $\partial f/\partial x = -2y$ is not bounded.

(c) For the equation $dy/dx = y/(y - x) = f(x, y)$, the derivative is $\partial f/\partial x = -x/(y - x)^2$. At $y = x$, the function f is not continuous, and its derivative is unbounded, so the solution of the differential equation is not necessarily unique at that location.

(d) Table 2.4 gives several examples of the behavior of integral curves in the vicinity of singular points.

(e) In Example 1.3(b), the domain of existence of the solution is between the lines $y = x$ and $y = -x$ on the xy plane.

(f) In Figures 1.1c and 1.1f, the domains of existence are limited to portions of the xy plane.

Example 1.3**Envelopes as Singular Solutions**

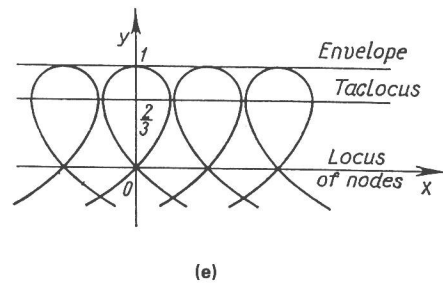
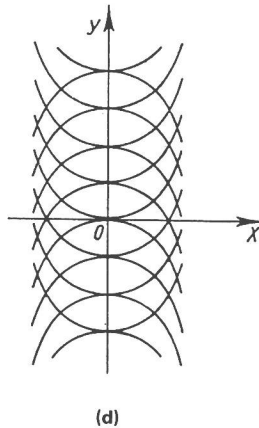
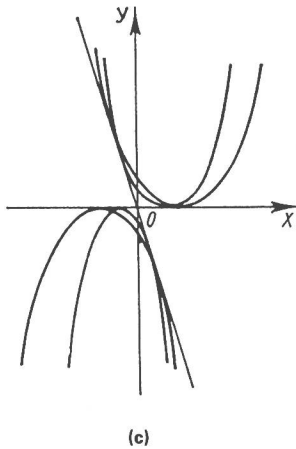
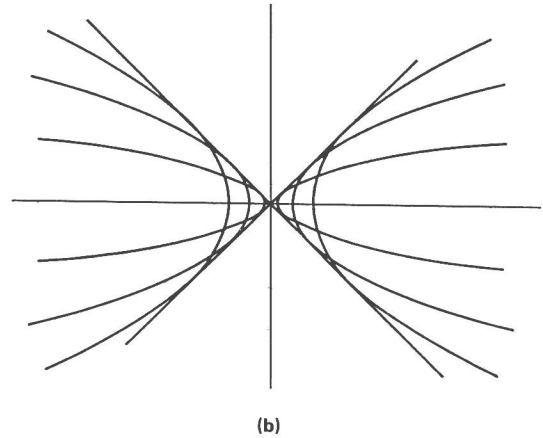
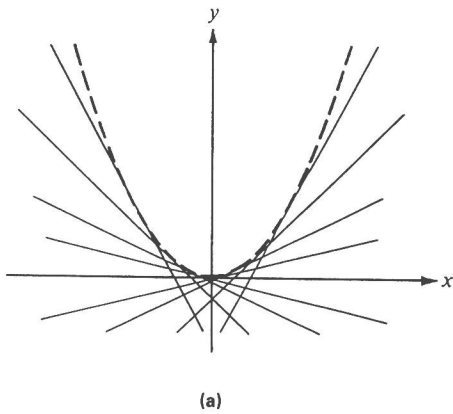
(a) The differential equation is $y = xy' - (y')^2/4$, and its solution is $y = Cx - C^2/4$, a family of straight lines. The envelope $y = x^2$ also is a solution of the differential equation but is not included in the general solution.

(b) The solution of a differential equation is $y^2 = 2Cx + C^2$, a family of parabolas. The derivative is $dy/dC = (x - C)/y = 0$. Eliminating C gives $y = x$ or $y = -x$, which are two straight lines, as the envelopes of the family of parabolas. Figure (b) represents this system.

(c) The differential equation is $2y(y' + 2) = x(y')^2$, whose general solution is $y = (C - x)^2/C$. The straight lines $y = 0$ and $y = -4x$ are the envelopes.

(d) The differential equation is $(y')^2 = 4x^2$, with general solution $y = x^2 + C$ and $y = -x^2 + C$, two families of parabolas. The straight line with equation $x = 0$ is the taclocus of the integral curves.

(e) For the differential equation $(y')^2(2 - 3y)^2 = 4(1 - y)$, the integral is $y^2(1 - y) = (x - C)^2$. The equation of the envelope is $y = 1$, that of the taclocus is $y = \frac{2}{3}$, and that of the locus of nodes is $y = 0$.



Geometrical Interpretation of a Differential Equation. The first-order differential equation represents a *direction field* on the xy plane. A solution is represented by a curve going through point (x_0, y_0) and following the direction field. This concept is illustrated in Figure 1.1a. Other parts of this figure show plots of solutions of

several differential equations. Each curve corresponds to a particular value of an integration constant C . In parts (b), (c), and (e), every point in the plane has some curve passing through it; in part (d), only the region corresponding to the positive y axis is covered; and in part (f) the region covered with curves is a narrow strip.

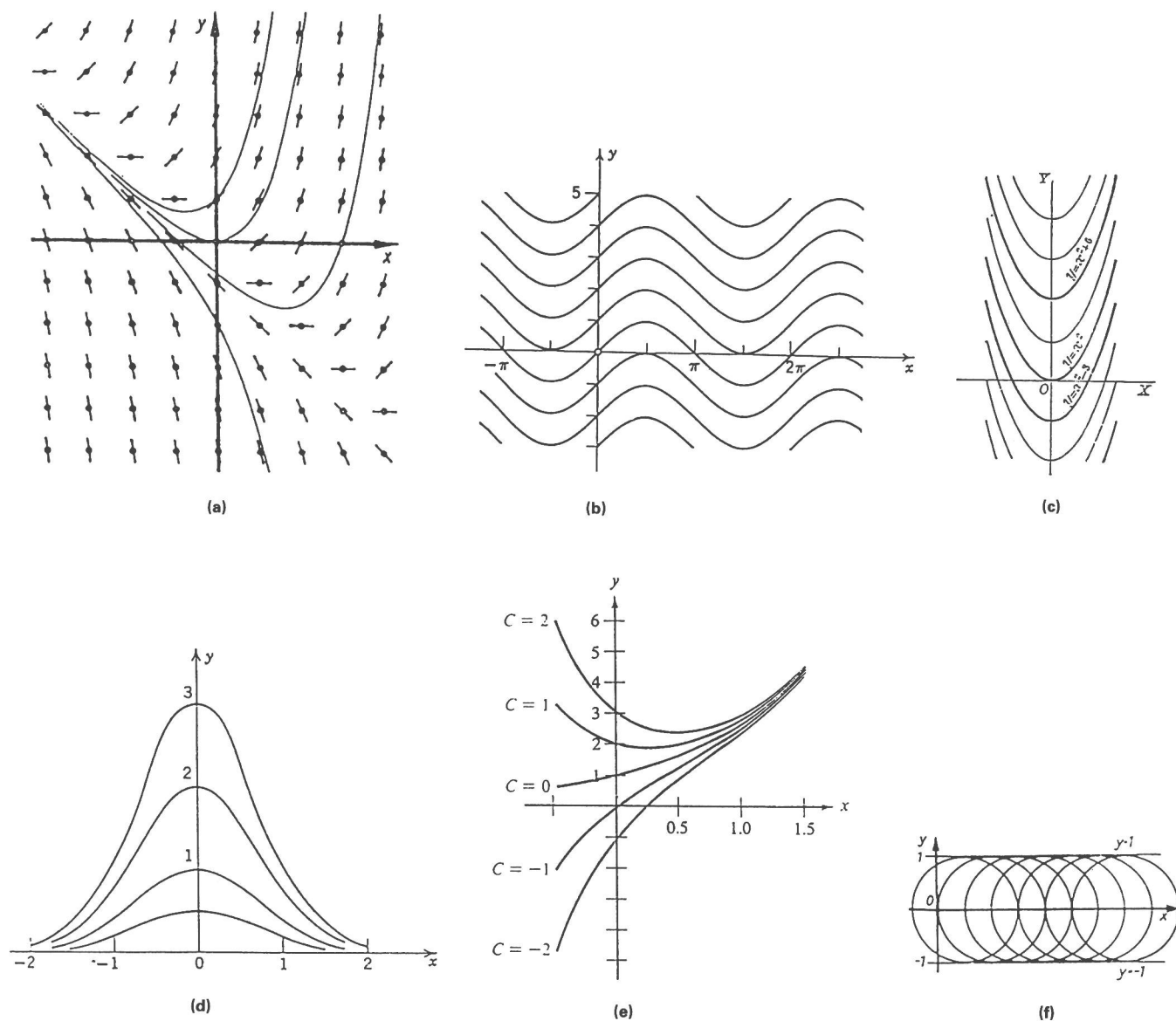


Figure 1.1. Direction fields and families of curves defined by differential equations. (a) Direction field and integral curves defined by $dy/dx = x + y$, with the integral $y = x - 1 + Ce^x$; a curve passes through every point of the plane. (b) Family of curves defined by $dy/dx = \cos x$, with integral $y = \sin x + C$; the whole plane is covered. (c) The equation $dy/dx = 2x$ has the integral $y = x^2 + C$; a curve through any point in the plane is determined by the value of the integration constant C . (d) A family of curves defined by $dy/dx + 2xy = 0$ with the integral $y = C \exp(-x^2)$; only the positive y plane is covered. (e) Family of curves defined by $dy/dx + 2y = 3e^x$, with integral $y = e^x + Ce^{-2x}$; the whole plane is covered. (f) Family of circles defined by $dy/dx = (a^2 - y^2)^{1/2}/y$, with integral $(x - C)^2 + y^2 = a^2$, occupying a band of width $2a = 2$.

1.2. METHOD OF ISOCLINES

An isocline is the locus of a function, $f(x, y, y' = c) = 0$, at a constant value of the derivative $y' = dy/dx$. The equation of the locus can be written $y = f(x, y'_{\text{fixed}})$. A field of closely spaced isoclines can be used in the construction of an integral curve of the equation. Start at a particular point (x_0, y_0) , proceed in the direction corresponding to the isocline through that point to the neighboring isocline, change

direction there, and so on. This is a feasible method of integration of a differential equation only if the isoclines can be constructed easily, such as the straight lines of Figure 1.2a or the circles of Figure 1.2b; the trigonometric isoclines of Figure 1.2c may be considered impractical.

Other graphical methods of drawing integral curves are described in the older literature—for example, by Willers (1948) and by