MATHEMATICAL MODELING
A Chemical Engineer’s Perspective

Rutherford Aris
Department of Chemical Engineering and Materials Science
University of Minnesota
Minneapolis, Minnesota

ACADEMIC PRESS
San Diego  London  Boston  New York  Sydney  Tokyo  Toronto
CONTENTS

PREFACE xvii

METHOD AND MANNER

I What Is Mathematical Modeling?

A Very Simple Example 3

Example 1. The Well-Stirred Tank 3

Review of the Simplest Example 8

The Simplest Distributed Model 9

Example 2. The Tubular Reactor 9

The General Balance Equations for Distributed Systems 10

Boundary Conditions 13

Example 3. The Danckwerts Boundary Conditions 13

Respecting Uniformity 15

Example 4. Two-Phase Reactor, One-Phase Uniform 15

Extensive and Intensive Quantities 18

Example 5. The Nonisothermal Stirred Tank 18

General Observations on Forming the Model 20

Example 2. The Plug-Flow Tubular Reactor (Reprise) 22
2 Manipulation of Models

Getting Rid of Unnecessary Equations 26

Example 6. Multiple Reactions in a C* 26

The Reduction of the Equations to Dimensionless Form 28

Example 7. The Dissolving Sphere 28

An Alternative Method of Reduction 30

Example 8. The Rising Bubble Problem 31

Scaling 33

Example 7. The Dissolving Sphere (Reprise) 33

Example 9. The Spherical Catalyst Particle 34

Shape Factors 36

Example 10. Diffusion and First-Order Reaction 36

A Priori Estimates 39

Example 11. The Nonisothermal Catalyst Pellet 39

Scaling and Partial Solution in Linear Systems 40

Example 12. The Bubbling Fluidized Bed 40

3 Solving the Equations

Getting a Feel for the Solution 45

Example 13. Two Populations Growing in a Chemostat Competing for a Common Nutrient 45

Special Forms 49

Example 14. Michaelis–Menten Kinetics 50

Example 7. The Dissolving Sphere (Reprise) 50

Example 15. Diffusion and Reaction in a Slab 51

Getting the Most from Calculations 51

Example 11. The Nonisothermal Catalyst Pellet (Reprise) 51

The Use of Parametric Representations 52

Example 8. The Rising Bubble Problem (Reprise) 52

Example 16. The C* with the Gray–Scott Reactions 54

Example 17. Continuous Mixtures and Parallel Gray–Scott Reactions 57

Asymptotics and Perturbations 59

Example 18. Shape Factors for Particles in Packed Bed Exchange 59

Example 15. Diffusion and Reaction in a Slab (Reprise) 60

Example 14. Michaelis–Menten Kinetics (Reprise) 61

Moments and Generating Functions 64

Observing Conditions 67

Example 19. Solvability Conditions 67

Example 20. Conditions Easily Overlooked or Hidden 69
4 Presenting the Model and Its Behavior

The Phase Plane  76
  Example 16. The Gray–Scott Reaction (Reprise)  81
Oscillations in Three Dimensions  87
Forced Oscillations and the Stroboscopic Phase Plane  88
  The Excitation Diagram  90

5 Maxims for Modelers

Text  93

6 Style

Literary Style  96
Genre  98
Plagiarism and Attribution  101
Publish or Perish  102

II Matter

7 Dispersion in Flow

A. On the Dispersion of a Solute in a Fluid Flowing through a Tube  109
  R. Aris

  1. Introduction  109
  2. The General Equations of Diffusion and Flow in a Straight Tube  110
  3. The Tube of Circular Cross-Section  111
  4. Some Special Initial Distributions of Solute  115
  5. The General Case  116
  6. Turbulent Flow in a Tube of Circular Cross-Section  118
  7. Viscous Flow in a Tube of Arbitrary Cross-Section  118
  References  120

B. On the Dispersion of a Solute by Diffusion, Convection, and Exchange between Phases  121
  R. Aris

  1. Introduction  121
  2. Dispersion in Coaxial Cylindrical Annuli  122
  3. Certain Special Cases  128
4. Dispersion in Coaxial Streams of Arbitrary Cross-Section 129
5. Application to the Theory of Chromatography 133
6. Application to a Simplified Theory of Distillation 133
References 135

C. On the Dispersion of Linear Kinematic Waves 136
RUTHERFORD ARIS

1. Introduction 136
2. The Dispersion of a Flood Wave 137
3. General Theorems 140
4. A Kinematic Temperature Wave 140
5. The Ultimate Form of a Kinematic Wave 144
References 146

8 Formal Kinetics

D. Prolegomena to the Rational Analysis of Systems of Chemical Reactions 149
RUTHERFORD ARIS

1. Introduction 149
2. The Representation of Molecular Species and Reactions between Them 150
3. The Representation and Calculus of Composition Changes 154
4. Equilibrium in Systems of Reactions 157
5. Kinetics of Reactions 159
6. Reaction Mechanisms 161
7. Entropy Production 165
8. Discussion 166
Nomenclature 167
References 168

E. Prolegomena to the Rational Analysis of Systems of Chemical Reactions
II. Some Addenda 170
RUTHERFORD ARIS

1. Introduction 170
2. The Uniqueness of Equilibrium under Adiabatic Conditions 171
3. The Consistency of Certain Kinetic and Equilibrium Expressions 172
4. Reaction Mechanisms and Exact Sequences 174
5. Of Chemical Kinetics in General 177
References 179

F. Modelling Cubic Autocatalysis by Successive Bimolecular Steps 180
   R. ARIS, P. GRAY, AND S. K. SCOTT
1. Introduction 180
2. Kinetic Schemes and Mass-Balance Equations 181
3. Behaviour of First-Order Correction to Autocatalator: Stationary-States and Limit Cycles 183
4. Comparison of First-Order Equations with Full, Three-Variable Model 186
Conclusions 187
References 188

G. Reactions in Continuous Mixtures 189
   RUTHERFORD ARIS
Introduction 189
General Formulation for a Single Index 191
Parallel Reaction in a Doubly Distributed Continuum 194
Examples 195
Generalized Background Kinetics 199
Discrete Distributions 201
Distributions of k(x) 202
Asymptotic Behavior 204
Sequential Parallel Reactions 205
Mechanisms 207
Literature Cited 209

H. Reaction of a Continuous Mixture in a Bubbling Fluidized Bed 211
   N. R. AMUNDSON AND R. ARIS
Introduction 211
Gamma Distributions 213
Application of the Gamma Distribution 214
A General Theorem for Simple, Linear Reactor Models 215
Application to a Model of the Bubbling Fluidized Bed 215
The Damköhler Number 218
The Fluid Bed with Astarita's Uniform Kinetics 220
Nomenclature 221
References 223
9 STATICS AND DYNAMICS OF CHEMICAL REACTORS

I. Some Common Features of Periodically Forced Reacting Systems  227
   G. KEVREKIDIS, L. D. SCHMIDT, AND R. ARIS

   Introduction  227
   Numerical Methods  229
      Computation of Periodic Trajectories  229
      The Single Species Forced Reaction  231
      Spontaneously Oscillating Models  233
      Computation of Quasi-periodic Trajectories  234
   Forced Dynamic Phenomena  240
      Small Amplitude Forcing  240
      Stronger Forcing  241
      Other Models and Different Types of Forcing  245
      Comments on the Computational Methods  246
      Control Applications  247
   Conclusions  246
   References  249

J. "Yet Who Would Have Thought the Old Man to Have Had So Much Blood in Him?"—Reflections on the Multiplicity of Steady States of the Stirred Tank Reactor  252
   W. W. FARR AND R. ARIS

   Introduction  252
   The System  254
   Discussion I: Butterfly Points  261
   Discussion II: Maximum Multiplicity  270
   Conclusions  278
   Notation  280
   References  280

K. Autonomous Bifurcations of a Simple Biomolecular Surface-Reaction Model  282
   M. A. McKARNIN, R. ARIS, AND L. D. SCHMIDT

   1. Introduction  282
   2. Surface Reaction Model  283
   3. Bifurcation Analysis  286
      (a) Model Symmetry  286
      (b) Steady-State Bifurcations  287
   4. The Stability of the Steady States  294
   5. Hopf Bifurcations  298
L. Forced Oscillations of a Self-Oscillating Bimolecular Surface Reaction Model 307
M. A. McKARNIN, L. D. SCHMIDT, AND R. ARIS

1. Introduction 307
2. Surface Reaction Model 309
3. Mathematical and Numerical Framework 311
4. Excitation Diagram 314
   (a) Small and Large Forcing Amplitudes 316
   (b) Local Codimensional-One Bifurcations 317
   (c) Local Bifurcations of Codimension-Two and Three 321
      (i) Two Floquet Multiplier at −1 321
      (ii) Two Floquet Multipliers at −1 (Bogdanov Points) 321
      (iii) Metacritical Period Doubling 322
      (iv) Saddle-Node Cusp Points 322
      (v) Hopf Bifurcations with Hard Resonances 323
5. Discussion 327
References 331

10 Mass and Heat Transfer

M. An Example of the Relation between Discrete and Continuous Models 337
The Geometry of the Hexaga 337
Heat Transfer 339
The Discrete Model 341
The Continuous Model 342
Two Lemmas 343
Equivalence of the Models in the Limit 344

N. A General Theory of Anisotropic Membranes 345
R. ARIS AND E. L. CUSSLER
Introduction 345
Exponential Dependence 346
Designing for Maximum Anisotropy 350
Application 353
Anisotropy with a General Concentration Dependence 354
Other Configurations 355
Nomenclature 357
References 358
II Modeling in General

O. Of Chemical Engineering and the Liberal Arts: An Inaugural for the Olaf Hougen Visiting Professorship: October 3, 1979 361

P. Two Eyes Are Better Than One: Some Reflections on the Importance of Having More Than One Viewpoint in Mathematical Modelling and Other Disciplines 374

R. ARIS

References 399

Q. Reflections on Keats’ Equation 400

RUTHERFORD ARIS

Keats’ Equation 400

Dirac’s Statements and Dyson’s Analysis 401
Uses of the Word Beautiful 401
Aside on Adventitious Beauty 402
Understanding and Appreciation 402
Birkhoff’s Æsthetic Measure 403
Mathematical Beauty 404
Mathematical Modelling 406
Dimensionless Parameters 407

A Model of Algal Growth 408

Beauty as a Criterion of Truth 410
Craftsmanship and the Enjoyment of Beauty 411

Notation 413
References 414

R. Chemical Engineering Greetings 415

Text 415

III MISCELLANEA

Acknowledgments: An Autobiographical Appendix with Asides

Early Education, 1935–1943 420
Canford, 1943–1946 421
Billingham, 1946–1948 422
Edinburgh, 1948–1950 423
Billingham, 1950–1955 426
Minnesota, 1955–1956 430
Edinburgh, 1956–1958 432
Minneapolis, 1958–1964 433


Minneapolis, 1965–1971 442
Cambridge, 1971–1972 443
Minneapolis, 1972–1974 444

Aside on Neal Amundson and the Department 445

Minneapolis, 1974–1996 447
Minnesota and Sabbaticals, 1978–1996 448

Bibliography

Books 455
Edited Books 456
Chapters in Books Edited by Others 456
Journal Papers 456

INDEX OF GRADUATE STUDENTS AND CO-AUTHORS 467
SUBJECT INDEX TO THE PAPERS IN THE BIBLIOGRAPHY 469
INDEX 473