
CONTENTS

PREFACE	xix
ACKNOWLEDGMENTS	xxi
PART I FIELD THEORY	1
Chapter 1 Laws of Diffusion	3
1.1 Preliminary Definitions	3
1.2 Diffusion in an Isotropic Medium	4
1.3 Fick's First Law	4
1.4 Units	6
1.5 Vector Form of Fick's First Law	6
1.6 Mass Conservation	7
1.7 Fick's Second Law	10
1.8 Linear Diffusion Equation in Various Coordinate Systems	10
1.9 Important Diffusion Symmetries	11
Exercises	12
Bibliography	15
Chapter 2 Diffusion in Generalized Media	17
2.1 Diffusivity Tensor	17
2.2 Principal Directions	18
2.3 Diffusion in Generalized Media	19

2.4 Influence of Imposed Symmetry	22	5.2 Source Solutions in One, Two, and Three Dimensions	64
2.4.1 Isotropic Materials	24	5.3 Behavior of the Fields Upon Release of a Source	64
2.4.2 Cubic crystals	24	5.3.1 Choice of Concentration, Time, and Length Scales	64
2.4.3 Orthotropic Materials	25	5.3.2 Behavior of Diffusion Responses at Early Times	68
2.4.4 Orthorhombic Crystals	26	5.4 Conservation Integrals for One, Two, and Three Dimensions	68
2.4.5 Monoclinic Crystals	26	5.4.1 Mass Centroids in Higher Dimensions	70
2.4.6 Triclinic Crystals	26	Exercises	72
Exercises	27	Bibliography	73
Bibliography	30		
Chapter 3 Solutions to the Linear Diffusion Equation	31	Chapter 6 Generalized Sources	75
3.1 Linear Diffusion and Transform Methods	31	6.1 Generalizing the Point Source in Three Dimensions	75
3.2 Linear Diffusion into a Semi-Infinite Medium	32	6.1.1 Relationship to Green's Functions	76
3.2.1 Boundary Conditions	33	6.2 Instantaneous Line Source Releasing Diffusant in Three Dimensions	77
3.2.2 Laplace Transforms	33	6.2.1 Hadamard's Method of Descent	78
3.3 Behavior of the Concentration Field	36	6.3 Generalization of the Instantaneous Point Source in Two Dimensions	79
3.4 Instantaneous Planar Diffusion Source in an Infinite Medium	38	6.4 Instantaneous Line Source in Two Dimensions	79
3.5 Conservation of Mass for a Planar Source	41	6.5 Instantaneous Ring Source	81
3.5.1 Estimating the Error Function	42	6.6 Continuous Point Sources	84
3.6 Thin-Film Configuration	43	6.6.1 Steady-State Limit of Continuous Point Sources	87
Exercises	44	6.7 Time-Continuous Line Source in Two Dimensions	87
Bibliography	47	Exercises	88
		Bibliography	94
Chapter 4 Diffusion Couple	49	Chapter 7 Diffusion-Reaction	95
4.1 Superposition of Instantaneous Sources	49	7.1 Linear Diffusion-Reaction	95
4.2 Diffusion Couples	50	7.1.1 One-Dimensional Diffusion-Reaction	96
4.3 Diffusion with a Fixed Boundary Concentration	53	7.1.2 Boundary Conditions for Diffusion-Reaction	97
4.4 Slab Couples	54	7.2 Imposing Steady-State Conditions	97
Exercises	55	7.3 General Kinetic Limits	99
Bibliography	58	7.3.1 Reaction Limit	99
		7.3.2 Diffusion Limit	99
Chapter 5 Diffusion Point Sources in Higher Dimensions	59	7.4 Mixed Diffusion-Reaction Kinetics	100
5.1 Instantaneous Point Source in Three Dimensions	59		
5.1.1 Transform Solution for a Point Source	60		
5.1.2 Mass Constraint in Spherical Symmetry	62		

7.5 Time-Dependent Reaction–Diffusion	101
7.6 Nonlinear Diffusion–Reaction	102
Exercises	103
Bibliography	106
Chapter 8 Linear Flow in Finite Systems	107
8.1 Diffusion in a Single-Phase Composite Slab	107
8.1.1 No-Flow Boundary Condition	108
8.1.2 Fictitious Image Sources	109
8.2 Fourier's Method	113
8.3 Application of Fourier Series	115
8.4 Numerical Approximations	119
8.4.1 Error Function Series Approximation	120
8.4.2 Fourier Series Approximation	121
8.4.3 Numerical Comparison	122
8.5 Codastefano's Method	123
Exercises	126
Bibliography	132
Chapter 9 Spherical Bodies	135
9.1 Diffusion Around Spheres	136
9.1.1 Boundary Conditions	136
9.1.2 Spherical Diffusion Solution	138
9.2 Behavior of the Spherical Concentration Field	140
9.3 Interfacial Fluxes	141
9.4 Quasi-Static Growth and Dissolution	142
9.5 Moving Boundaries	145
9.6 Evolution of a Spherical Particle	145
9.6.1 Conditions on the Phases	145
9.6.2 Conditions at the α – β Interface	146
9.6.3 Moving Boundary Solution	146
9.7 The Characteristic Equation	150

9.8 Diffusion Boundary Layers	154
9.8.1 Massive Transformations	155
Exercise	156
Bibliography	158
Chapter 10 Steady-State Diffusion	161
10.1 Permeation in Linear Flow	161
10.1.1 Molecular Dissociation at Surfaces	162
10.1.2 Steady-State Permeation	162
10.1.3 Permeability Units	163
10.2 Steady Flow with Variable D	163
10.2.1 Boundary Conditions	164
10.3 Steady-State Diffusion in Cylinders: Constant D	168
10.4 Steady-State Diffusion in Spheres	170
Exercise	172
Bibliography	174
Chapter 11 Inverse Methods	175
11.1 Time-Dependent Diffusion with Variable Diffusivity	176
11.2 Boltzmann's Transformation	176
11.3 Matano's Geometry	177
11.3.1 Matano Interface	178
11.4 Application of the Boltzmann–Matano Method	180
11.5 Application of the Method of Sauer, Freise, and den Broeder	182
Exercise	186
Bibliography	187
PART II SOLID-STATE PRINCIPLES	189
Chapter 12 Random Walks and Diffusion	191
12.1 Background	191
12.2 Diffusive Motions	192

12.3 Random Walks	193
12.3.1 Random Numbers	193
12.4 One-Dimensional Random Walks	194
12.5 Combinatoric Formulation	197
12.6 Random Walks in Higher Dimensions	199
12.7 Diffusion Viewed as a Stochastic Process	203
12.8 Diffusivity: A Microscopic Transport Property	205
12.8.1 Time Reversal	206
12.8.2 Einstein's Formula	207
Exercises	208
Bibliography	212
Chapter 13 Structure and Diffusion	213
13.1 Random Walks in Crystals	213
13.1.1 Primitive (Simple) Cubic	214
13.1.2 Body-Centered Cubic	214
13.1.3 Face-Centered Cubic	215
13.2 Constraints Imposed by the Structure	216
13.3 Interpreting Diffusivities in Cubic Crystals	218
13.4 Diffusion Mechanisms	220
13.4.1 Interstitial Diffusion	220
13.4.2 Ring Diffusion	223
13.4.3 Vacancy-Assisted Diffusion	224
13.4.4 Interstitialcy Diffusion	225
13.5 Diffusion in FCC Crystals	227
13.6 Lattice Vacancies	228
13.7 Divacancies	230
Exercises	232
Bibliography	233
Chapter 14 Correlation Effects in Diffusion	235
14.1 Markov Sequences and Correlated Walks	235
14.2 Estimates of the Correlation Factor: Pure Materials	237
14.2.1 Jumping Probability Estimate	238

14.3 Computation of Correlation Factors in Pure Crystals	242
Exercises	243
Bibliography	244
Chapter 15 Vacancy-Assisted Diffusion	245
15.1 Dynamical Theory	245
15.1.1 Flynn's Model	246
15.2 Quasi-Chemical Theory	248
15.2.1 Activated Diffusion Complexes	248
15.2.2 Energy-Momentum Phase Space	248
15.2.3 Self-Diffusion in Crystals	252
15.3 Empirical Relationships	253
15.3.1 Measures of Lattice Stability	253
15.3.2 Activation Energy for Self-Diffusion	253
15.3.3 Corresponding States	255
15.4 Correlation with Diffuser Size	256
15.5 Arrhenius Correlation	256
15.6 Dependence of D on Composition	258
15.7 Le Claire's Correlation	258
15.8 Correlations of D and Q with Composition	259
15.9 Empirical Observations	260
Exercises	261
Bibliography	263
Chapter 16 Diffusion in Dilute Alloys	265
16.1 Five-Frequency Exchange Model	266
16.2 Isotope Effect	271
16.3 Diffusion of H^+ and D^+ with Trapping	273
16.3.1 Fick's Law with Trapping	275
16.4 Saturable Diffusion Traps	277
16.5 Irreversible Traps	278
Exercises	279
Bibliography	281

Chapter 17 Kirkendall Effect	283
17.1 Nonreciprocal Diffusion	284
17.2 Kirkendall Effect	285
17.2.1 Kirkendall's Diffusion Couple	285
17.2.2 Kirkendall Experiment	286
17.3 Significance of Kirkendall Marker Motion	288
17.4 Nonreciprocal Atomic Fluxes	289
17.5 Intrinsic Diffusivities: Vacancy Wind	292
17.6 Diffusion–Advection	296
17.6.1 Mass Conservation with Diffusion–Advection	297
17.6.2 Steady-State Diffusion–Advection	299
17.6.3 One-Dimensional Diffusion–Advection	300
17.7 Darken's Analysis of the Kirkendall Effect	300
17.8 Strain Effects	305
Exercise	306
Bibliography	307
Chapter 18 Influence of Solution Ideality	309
18.1 Generalized Forces	309
18.1.1 Analogy of Electrical Resistance	310
18.2 Atom Mobilities	310
18.2.1 Constrained Equilibrium	311
18.2.2 Diffusion Forces	312
18.3 Chemically Inhomogeneous Systems	313
18.4 Limiting Cases	315
18.5 Tracer Diffusion	316
Exercise	319
Bibliography	322
Chapter 19 Diffusional Anelasticity	323
19.1 Background	323
19.2 Standard Linear Solid	324
19.2.1 Cyclic Stress and Strain	325

19.3 Internal Friction	328
19.4 Diffusional Anelasticity	332
19.4.1 Internal Friction in BCC Materials	332
19.4.2 Geometry of Interstitial Sites in BCC	332
19.5 Interstitial Subpopulations in BCC	333
19.6 Reorientation of Atom Pairs in FCC Materials	336
19.7 Internal Friction Methods	338
19.8 Summary of Diffusional Anelastic Effects	339
Exercises	340
Bibliography	342
Chapter 20 Field-Assisted Diffusion	343
20.1 Background	344
20.2 Diffusion Currents in Homogeneous Ionic Solids	345
20.3 Measurement of Ionic Conductivity in Solids	346
20.4 Defects in Ionic Solids	347
20.4.1 Equilibria Among Charged Point Defects	347
20.5 Experiments in Ionic Conductors	349
20.6 Irreversible Thermodynamics and Diffusion	350
20.7 Isothermal Binary Diffusion	352
20.8 Vacancies in Thermal Equilibrium	353
20.9 Net Vacancy Flux	354
Exercise	355
Bibliography	357
Chapter 21 Multiparticle Diffusion: Capillary Effects	359
21.1 Length Scales in Microstructures	360
21.1.1 Interfacial Free Energy	361
21.1.2 Role of Diffusional Transport	361
21.2 Kelvin's Equation	362
21.2.1 Influence of Curvature on the Phase Diagram	365
21.2.2 Influence of Curvature on Solubility	366

21.3 Dimensionless Diffusion Potential	368
21.4 Mean-Field Kinetic Equation	368
21.5 Experimental Observations	371
Exercise	373
Bibliography	375
Chapter 22 Population Dynamics	377
22.1 Continuity Equation	377
22.2 Scale-Factor Population Dynamics	379
22.3 Particle Distribution Function	382
22.4 Volume Fraction Constraint	384
22.5 Coarsening Kinetics	386
22.5.1 Experimental Observations	387
Exercise	388
Bibliography	390
Chapter 23 Multicomponent Diffusion	391
23.1 Fick's First Law for Multicomponent Diffusion	392
23.1.1 Multicomponent Fick's First Law in One Dimension	393
23.1.2 Multicomponent Intrinsic Diffusivities and the Interdiffusion Coefficients	395
23.2 Fick's Second Law for Multicomponent Diffusion	396
23.3 Multicomponent Diffusion Couples	398
23.4 Square-Root Diffusivity Method	399
23.5 Approximation Using Effective Binary Diffusion Coefficients	400
Exercises	400
Bibliography	404
Chapter 24 Multicomponent Diffusion: <i>Profiler</i> Program	405
24.1 Background	406
24.2 <i>Profiler</i>	406
24.3 Application to a Ternary Alloy	408
24.3.1 Extrema in the Composition Profile	409

24.4 Composition Directions, Eigenvalues, and Eigenvectors	410
24.4.1 Zero-Flux Planes	411
24.4.2 Properties of the [r] Matrix	411
24.5 Multicomponent Diffusion Paths	413
24.6 Multicomponent Concentration Profiles	415
Exercise	415
Bibliography	417
Appendix A Ten-Place Error Function Values	419
Table A.1 $\frac{d}{dx}[\text{erf}(x)]$ and $\text{erf}(x)$ for $0 \leq x \leq 2$	419
Table A.2 $\frac{d}{dx}[\text{erf}(x)]$ for $2 \leq x \leq 4$	422
Appendix B Instruction Manual for <i>Profiler</i>	425
INDEX	441