Contents

1 History and Bibliography of Diffusion ......................... 1
  1.1 Pioneers and Landmarks of Diffusion ....................... 2
  References .................................................................. 16
  1.2 Bibliography of Solid-State Diffusion ....................... 18

Part I Fundamentals of Diffusion

2 Continuum Theory of Diffusion ..................................... 27
  2.1 Fick’s Laws in Isotropic Media ............................... 27
    2.1.1 Fick’s First Law ........................................ 28
    2.1.2 Equation of Continuity .................................. 29
    2.1.3 Fick’s Second Law – the ‘Diffusion Equation’ ......... 30
  2.2 Diffusion Equation in Various Coordinates ................. 31
  2.3 Fick’s Laws in Anisotropic Media ............................ 33
  References .................................................................. 35

3 Solutions of the Diffusion Equation .............................. 37
  3.1 Steady-State Diffusion .......................................... 37
  3.2 Non-Steady-State Diffusion in one Dimension .............. 39
    3.2.1 Thin-Film Solution ....................................... 39
    3.2.2 Extended Initial Distribution and Constant Surface Concentration ........................................ 41
    3.2.3 Method of Laplace Transformation ...................... 45
    3.2.4 Diffusion in a Plane Sheet – Separation of Variables 47
    3.2.5 Radial Diffusion in a Cylinder .......................... 50
    3.2.6 Radial Diffusion in a Sphere ............................ 51
  3.3 Point Source in one, two, and three Dimensions .......... 52
  References .................................................................. 53

4 Random Walk Theory and Atomic Jump Process .............. 55
  4.1 Random Walk and Diffusion .................................... 56
    4.1.1 A Simplified Model ....................................... 56
    4.1.2 Einstein-Smoluchowski Relation ....................... 58
    4.1.3 Random Walk on a Lattice ............................... 60
4.1.4 Correlation Factor ........................................ 62
4.2 Atomic Jump Process ........................................ 64
References ........................................................ 66

5 Point Defects in Crystals ....................................... 69
5.1 Pure Metals ..................................................... 70
5.1.1 Vacancies .................................................. 70
5.1.2 Divacancies ............................................... 72
5.1.3 Determination of Vacancy Properties ..................... 74
5.1.4 Self-Interstitials .......................................... 79
5.2 Substitutional Binary Alloys .................................. 80
5.2.1 Vacancies in Dilute Alloys ................................. 81
5.2.2 Vacancies in Concentrated Alloys ......................... 82
5.3 Ionic Compounds .............................................. 83
5.3.1 Frenkel Disorder .......................................... 84
5.3.2 Schottky Disorder ......................................... 85
5.4 Intermetallics .................................................. 86
5.5 Semiconductors ................................................. 88
References ........................................................ 91

6 Diffusion Mechanisms ........................................... 95
6.1 Interstitial Mechanism .................................... 95
6.2 Collective Mechanisms .................................... 97
6.3 Vacancy Mechanism ....................................... 98
6.4 Divacancy Mechanism .................................. 100
6.5 Interstitialcy Mechanism ................................ 100
6.6 Interstitial-substitutional Exchange Mechanisms ......... 102
References ........................................................ 103

7 Correlation in Solid-State Diffusion ......................... 105
7.1 Interstitial Mechanism .................................... 107
7.2 Interstitialcy Mechanism .................................. 107
7.3 Vacancy Mechanism of Self-diffusion ..................... 108
7.3.1 A ‘Rule of Thumb’ ..................................... 108
7.3.2 Vacancy-tracer Encounters ............................. 109
7.3.3 Spatial and Temporal Correlation ....................... 112
7.3.4 Calculation of Correlation Factors .................... 112
7.4 Correlation Factors of Self-diffusion ..................... 115
7.5 Vacancy-mediated Solute Diffusion ....................... 116
7.5.1 Face-Centered Cubic Solvents ......................... 117
7.5.2 Body-Centered Cubic Solvents ......................... 120
7.5.3 Diamond Structure Solvents ......................... 121
7.6 Concluding Remarks ......................................... 122
References ........................................................ 124
8 Dependence of Diffusion on Temperature and Pressure ... 127

8.1 Temperature Dependence ........................................ 127
  8.1.1 The Arrhenius Relation .................................. 127
  8.1.2 Activation Parameters – Examples ......................... 130

8.2 Pressure Dependence ............................................. 132
  8.2.1 Activation Volumes of Self-diffusion ...................... 135
  8.2.2 Activation Volumes of Solute Diffusion ................... 139
  8.2.3 Activation Volumes of Ionic Crystals ..................... 140

8.3 Correlations between Diffusion and Bulk Properties ......... 141
  8.3.1 Melting Properties and Diffusion ......................... 141
  8.3.2 Activation Parameters and Elastic Constants ............. 146
  8.3.3 Use of Correlations ...................................... 147

References .............................................................. 147

9 Isotope Effect of Diffusion ........................................ 151

9.1 Single-jump Mechanisms ......................................... 151

9.2 Collective Mechanisms ........................................... 155

9.3 Isotope Effect Experiments .................................... 155

References .............................................................. 159

10 Interdiffusion and Kirkendall Effect ............................ 161

10.1 Interdiffusion ..................................................... 161
  10.1.1 Boltzmann Transformation ................................ 162
  10.1.2 Boltzmann-Matano Method ................................ 163
  10.1.3 Sauer-Freise Method ...................................... 166

10.2 Intrinsic Diffusion and Kirkendall Effect .................... 168

10.3 Darken Equations ............................................... 170

10.4 Darken-Manning Equations .................................... 172

10.5 Microstructural Stability of the Kirkendall Plane .......... 173

References .............................................................. 176

11 Diffusion and External Driving Forces .......................... 179

11.1 Overview .......................................................... 179

11.2 Fick’s Equations with Drift .................................... 181

11.3 Nernst-Einstein Relation ....................................... 182

11.4 Nernst-Einstein Relation for Ionic Conductors and Haven Ratio ........................................ 184

11.5 Nernst-Planck Equation – Interdiffusion in Ionic Crystals ... 186

11.6 Nernst-Planck Equation versus Darken Equation .............. 188

References .............................................................. 189

12 Irreversible Thermodynamics and Diffusion ...................... 191

12.1 General Remarks ................................................ 191

12.2 Phenomenological Equations of Isothermal Diffusion ....... 193
  12.2.1 Tracer Self-Diffusion in Element Crystals ............... 193
12.2.2 Diffusion in Binary Alloys ......................... 195
12.3 The Phenomenological Coefficients ................... 199
   12.3.1 Phenomenological Coefficients, Tracer Diffusivities, and Jump Models .................. 202
   12.3.2 Sum Rules – Relations between Phenomenological Coefficients ..................... 204
References ............................................... 205

Part II Experimental Methods

13 Direct Diffusion Studies .................................. 209
   13.1 Direct versus Indirect Methods ..................... 209
   13.2 The Various Diffusion Coefficients .................. 212
      13.2.1 Tracer Diffusion Coefficients .................... 212
      13.2.2 Interdiffusion and Intrinsic Diffusion Coefficients 214
   13.3 Tracer Diffusion Experiments ......................... 215
      13.3.1 Profile Analysis by Serial Sectioning .......... 217
      13.3.2 Residual Activity Method ....................... 222
   13.4 Isotopically Controlled Heterostructures ............ 223
   13.5 Secondary Ion Mass Spectrometry (SIMS) ............ 224
   13.6 Electron Microprobe Analysis (EMPA) ................ 227
   13.7 Auger-Electron Spectroscopy (AES) ................... 230
   13.8 Ion-beam Analysis: RBS and NRA ..................... 231
References ............................................... 234

14 Mechanical Spectroscopy .................................. 237
   14.1 General Remarks ..................................... 237
   14.2 Anelasticity and Internal Friction ................. 239
   14.3 Techniques of Mechanical Spectroscopy ............. 242
   14.4 Examples of Diffusion-related Anelasticity ......... 244
      14.4.1 Snoek Effect (Snoek Relaxation) ............... 244
      14.4.2 Zener Effect (Zener Relaxation) ............... 247
      14.4.3 Gorski Effect (Gorski Relaxation) ............. 248
      14.4.4 Mechanical Loss in Ion-conducting Glasses ... 249
   14.5 Magnetic Relaxation .................................. 250
References ............................................... 251

15 Nuclear Methods .......................................... 253
   15.1 General Remarks ..................................... 253
   15.2 Nuclear Magnetic Relaxation (NMR) ................... 253
      15.2.1 Fundamentals of NMR ............................ 254
      15.2.2 Direct Diffusion Measurement by Field-Gradient NMR .......................... 256
      15.2.3 NMR Relaxation Methods ......................... 258
15.3 Mössbauer Spectroscopy (MBS) ........................................ 264
15.4 Quasielastic Neutron Scattering (QENS) ............................ 269
  15.4.1 Examples of QENS studies .................................. 278
  15.4.2 Advantages and Limitations of MBS and QENS ............. 279
References ............................................................................. 281

16 Electrical Methods ............................................................. 285
  16.1 Impedance Spectroscopy ............................................. 285
  16.2 Spreading Resistance Profiling ..................................... 290
References ............................................................................. 293

Part III Diffusion in Metallic Materials

17 Self-diffusion in Metals ......................................................... 297
  17.1 General Remarks ...................................................... 297
  17.2 Cubic Metals ............................................................ 299
    17.2.1 FCC Metals – Empirical Facts .............................. 299
    17.2.2 BCC Metals – Empirical Facts ............................ 301
    17.2.3 Monovacancy Interpretation ................................. 302
    17.2.4 Mono- and Divacancy Interpretation ..................... 303
  17.3 Hexagonal Close-Packed and Tetragonal Metals ................. 306
  17.4 Metals with Phase Transitions ..................................... 308
References ............................................................................. 311

18 Diffusion ofInterstitial Solutes in Metals ............................... 313
  18.1 ‘Heavy’ Interstitial Solutes C, N, and O .......................... 313
    18.1.1 General Remarks .............................................. 313
    18.1.2 Experimental Methods ....................................... 314
    18.1.3 Interstitial Diffusion in Dilute Interstitial Alloys ........ 316
  18.2 Hydrogen Diffusion in Metals ......................................... 317
    18.2.1 General Remarks .............................................. 317
    18.2.2 Experimental Methods ....................................... 318
    18.2.3 Examples of Hydrogen Diffusion ........................... 320
    18.2.4 Non-Classical Isotope Effects ............................... 323
References ............................................................................. 324

19 Diffusion in Dilute Substitutional Alloys ................................. 327
  19.1 Diffusion of Impurities ............................................... 327
    19.1.1 ‘Normal’ Impurity Diffusion ................................. 327
    19.1.2 Impurity Diffusion in Al ..................................... 332
  19.2 Impurity Diffusion in ‘Open’ Metals –
    Dissociative Mechanism ............................................. 333
  19.3 Solute Diffusion and Solvent Diffusion in Alloys ................. 336
References ............................................................................. 338
20 Diffusion in Binary Intermetallics ........................................... 341
  20.1 General Remarks ...................................................... 341
  20.2 Influence of Order- Disorder Transitions .......................... 344
  20.3 B2 Intermetallics ..................................................... 346
    20.3.1 Diffusion Mechanisms in B2 Phases .......................... 347
    20.3.2 Example B2 NiAl .............................................. 351
    20.3.3 Example B2 Fe-Al ............................................. 353
  20.4 L12 Intermetallics .................................................. 355
  20.5 D03 Intermetallics .................................................. 357
  20.6 Uniaxial Intermetallics ............................................. 360
    20.6.1 L10 Intermetallics ............................................. 360
    20.6.2 Molybdenum Disilicide (C11b structure) .................... 362
  20.7 Laves Phases ...................................................... 364
  20.8 The Cu3Au Rule .................................................... 366
References ................................................................. 367

21 Diffusion in Quasicrystalline Alloys ...................................... 371
  21.1 General Remarks on Quasicrystals ................................ 371
  21.2 Diffusion Properties of Quasicrystals ............................ 373
    21.2.1 Icosahedral Quasicrystals ................................ 374
    21.2.2 Decagonal Quasicrystals .................................... 379
References ................................................................. 381

Part IV Diffusion in Semiconductors

22 General Remarks on Semiconductors ....................................... 385
  22.1 ‘Semiconductor Age’ and Diffusion ................................ 386
  22.2 Specific Features of Semiconductor Diffusion .................... 389
References ................................................................. 392

23 Self-diffusion in Elemental Semiconductors .............................. 395
  23.1 Intrinsic Point Defects and Diffusion ............................ 396
  23.2 Germanium ........................................................... 398
  23.3 Silicon .................................................................. 402
References ................................................................. 406

24 Foreign-Atom Diffusion in Silicon and Germanium ...................... 409
  24.1 Solubility and Site Occupancy ..................................... 409
  24.2 Diffusivities and Diffusion Modes .................................. 412
    24.2.1 Interstitial Diffusion ......................................... 414
    24.2.2 Dopant Diffusion ............................................... 416
    24.2.3 Diffusion of Hybrid Foreign Elements ...................... 420
  24.3 Self- and Foreign Atom Diffusion – a Summary .................... 421
References ................................................................. 422
25 Interstitial-Substitutional Diffusion ........................................ 425
  25.1 Combined Dissociative and Kick-out Diffusion ..................... 425
    25.1.1 Diffusion Limited by the Flow of Intrinsic Defects ....... 427
    25.1.2 Diffusion Limited by the Flow of Interstitial Solutes .... 429
    25.1.3 Numerical Analysis of an Intermediate Case ............. 430
  25.2 Kick-out Mechanism ................................................... 431
    25.2.1 Basic Equations and two Solutions ......................... 431
    25.2.2 Examples of Kick-Out Diffusion ............................ 434
  25.3 Dissociative Mechanism .............................................. 439
    25.3.1 Basic Equations .............................................. 439
    25.3.2 Examples of Dissociative Diffusion ....................... 440

References ............................................................................. 445

Part V Diffusion and Conduction
in Ionic Materials

26 Ionic Crystals ............................................................... 449
  26.1 General Remarks ....................................................... 449
  26.2 Point Defects in Ionic Crystals .................................... 451
    26.2.1 Intrinsic Defects .............................................. 452
    26.2.2 Extrinsic Defects ............................................. 454
  26.3 Methods for the Study of Defect and Transport Properties .... 456
  26.4 Alkali Halides ......................................................... 458
    26.4.1 Defect Motion, Tracer Self-diffusion, and Ionic Conduction 458
    26.4.2 Example NaCl ................................................... 462
    26.4.3 Common Features of Alkali Halides ......................... 467
  26.5 Silver Halides AgCl and AgBr ...................................... 468
    26.5.1 Self-diffusion and Ionic Conduction ....................... 469
    26.5.2 Doping Effects .................................................. 471

References ............................................................................. 473

27 Fast Ion Conductors .......................................................... 475
  27.1 Fast Silver-Ion Conductors .......................................... 477
    27.1.1 AgI and related Simple Anion Structures .................. 477
    27.1.2 RbAg₄I₅ and related Compounds .............................. 479
  27.2 PbF₂ and other Halide Ion Conductors ............................ 480
  27.3 Stabilised Zirconia and related Oxide Ion Conductors ........ 481
  27.4 Perovskite Oxide Ion Conductors .................................. 482
  27.5 Sodium β-Alumina and related Materials ........................ 482
  27.6 Lithium Ion Conductors .............................................. 484
  27.7 Polymer Electrolytes .................................................. 485

References ............................................................................. 488
Part VI Diffusion in Glasses

28 The Glassy State .................................................. 493
  28.1 What is a Glass? ............................................ 493
  28.2 Volume-Temperature Diagram ............................... 494
  28.3 Temperature-Time-Transformation Diagram ................ 496
  28.4 Glass Families .............................................. 498
  References .......................................................... 501

29 Diffusion in Metallic Glasses ................................. 503
  29.1 General Remarks ............................................ 503
  29.2 Structural Relaxation and Diffusion ....................... 506
  29.3 Diffusion Properties of Metallic Glasses ................. 509
  29.4 Diffusion and Viscosity in Glass-forming Alloys ....... 517
  References .......................................................... 518

30 Diffusion and Ionic Conduction in Oxide Glasses ........... 521
  30.1 General Remarks ............................................ 521
  30.2 Experimental Methods ...................................... 526
  30.3 Gas Permeation .............................................. 529
  30.4 Examples of Diffusion and Ionic Conduction .............. 530
  References .......................................................... 542

Part VII Diffusion along High-Diffusivity Paths
and in Nanomaterials

31 High-diffusivity Paths in Metals .............................. 547
  31.1 General Remarks ............................................ 547
  31.2 Diffusion Spectrum ......................................... 548
  31.3 Empirical Rules for Grain-Boundary Diffusion ........... 549
  31.4 Lattice Diffusion and Microstructural Defects .......... 551
  References .......................................................... 552

32 Grain-Boundary Diffusion ....................................... 553
  32.1 General Remarks ............................................ 553
  32.2 Grain Boundaries .......................................... 554
    32.2.1 Low- and High-Angle Grain Boundaries ............... 555
    32.2.2 Special High-Angle Boundaries ......................... 557
  32.3 Diffusion along an Isolated Boundary (Fisher Model) .... 559
  32.4 Diffusion Kinetics in Polycrystals ......................... 568
    32.4.1 Type A Kinetics Regime ................................ 568
    32.4.2 Type B Kinetics Regime ................................ 570
    32.4.3 Type C Kinetics Regime ................................ 574
Diffusion in Solids
Fundamentals, Methods, Materials, Diffusion-Controlled Processes
Mehrer, H.
2007, XIX, 654 p., Hardcover
ISBN: 978-3-540-71486-6