

Helmut Mehrer

SPRINGER SERIES IN SOLID STATE SCIENCE 155

Diffusion in Solids

Fundamentals, Methods,
Materials, Diffusion-Controlled Processes

固体中的扩散



Springer

世界图书出版公司
www.wpcbj.com.cn

Helmut Mehrer

Diffusion in Solids

Fundamentals, Methods, Materials,
Diffusion-Controlled Processes

With 267 Figures and 27 Tables

图书在版编目 (CIP) 数据

固体中的扩散 = Diffusion in solids: fundamentals, methods, materials, diffusion - controlled processes: 英文/(德)梅尔(Mehrer,H.)著. —影印本. —北京:世界图书出版公司北京公司, 2013. 10

ISBN 978 - 7 - 5100 - 7020 - 4

I. ①固… II. ①梅… III. ①固体物理学—扩散分析—英文 IV. ①O482

中国版本图书馆 CIP 数据核字 (2013) 第 249218 号

书 名: Diffusion in Solids: Fundamentals, Methods, Materials, Diffusion - Controlled Processes

作 者: Helmut Mehrer

中 译 名: 固体中的扩散

责任编辑: 高蓉 刘慧

出 版 者: 世界图书出版公司北京公司

印 刷 者: 三河市国英印务有限公司

发 行: 世界图书出版公司北京公司 (北京朝内大街 137 号 100010)

联系电话: 010 - 64021602, 010 - 64015659

电子信箱: kjb@wpchj.com.cn

开 本: 24 开

印 张: 28.5

版 次: 2014 年 3 月

版权登记: 图字: 01 - 2013 - 6784

书 号: 978 - 7 - 5100 - 7020 - 4

定 价: 99.00 元

Preface

Diffusion is the transport of matter from one point to another by thermal motion of atoms or molecules. It is relatively fast in gases, slow in liquids, and very slow in solids. Diffusion plays a key rôle in many processes as diverse as intermixing of gases and liquids, permeation of atoms or molecules through membranes, evaporation of liquids, drying of timber, doping silicon wafers to make semiconductor devices, and transport of thermal neutrons in nuclear power reactors. Rates of important chemical reactions are limited by how fast diffusion can bring reactants together or deliver them to reaction sites on enzymes or other catalysts.

Diffusion in solid materials is the subject of this book. Already in ancient times reactions in the solid state such as surface hardening of steels were in use, which according to our present knowledge involves the diffusion of carbon atoms in the crystal lattice of iron. Nevertheless, until the end of the nineteenth century the paradigm '*Corpora non agunt nisi fluida*' was widely accepted by the scientific community. It was mainly due to the pioneering work of William Roberts-Austen and Georg von Hevesy that this paradigm had to be abandoned.

Diffusion in solids is fundamental in the art and science of materials and thus an important topic of solid-state physics, physical chemistry, physical metallurgy, and materials science. Diffusion processes are relevant for the kinetics of many microstructural changes that occur during preparation, processing, and heat treatment of materials. Typical examples are nucleation of new phases, diffusive phase transformations, precipitation and dissolution of a second phase, homogenisation of alloys, recrystallisation, high-temperature creep, and thermal oxidation. Diffusion and electrical conduction in ionic conductors are closely related phenomena. Direct technological applications of diffusion concern, e.g., doping during fabrication of microelectronic devices, solid electrolytes for batteries and fuel cells, surface hardening of steel through carburisation or nitridation, diffusion bonding, and sintering.

Appreciable diffusion in solids mostly takes place at temperatures well above room temperature. Knowledge of diffusion is therefore particularly important for scientists who design materials for elevated temperatures and for engineers who build equipment for operation at such temperatures. However, processes connected with diffusion at room temperature pose problems, too.

Creep, atmospheric corrosion, and embrittlement of solders are among the more prominent of those. With the downscaling of microelectronic circuits to nanometer dimensions, diffusion and electromigration in these circuits must be taken into account.

A deeper knowledge about diffusion requires information on the position of atoms and how they move in solids. The atomic mechanisms of diffusion in crystalline solids are closely connected with defects. Point defects such as vacancies or interstitials are the simplest defects and often mediate diffusion in crystals. Dislocations, grain-boundaries, phase boundaries, and free surfaces are other types of defects. They can act as high-diffusivity paths (diffusion short circuits), because the mobility of atoms along such defects is usually much higher than in the lattice. In solids with structural disorder such as glasses or crystals with highly disordered sublattices the concept of defects is no longer useful. Nevertheless, diffusion is fundamental for transport of matter and for ionic conduction in disordered materials.

The content of this book is divided into seven parts. After a historical introduction and a diffusion bibliography, *Part I* introduces basic concepts of diffusion in solid matter such as continuum description, random walk theory, point defects, atomic mechanisms, correlation effects, dependence of diffusion on temperature, pressure and isotope mass, diffusion with driving forces, and some remarks about the relation between diffusion and thermodynamics of irreversible processes. The necessary background is a course in solid-state physics. In *Part II* we describe experimental methods for the determination of diffusion coefficients in solid matter. Direct methods based on Fick's laws and indirect methods such as anelastic relaxation, internal friction, nuclear magnetic relaxation, Mössbauer spectroscopy, quasielastic neutron scattering, impedance spectroscopy, and spreading resistance measurements are treated. In further parts we provide access to information on diffusion in various types of materials such as metals, intermetallics and quasicrystalline alloys (*Part III*), semiconductors (*Part IV*), ionic materials including fast ion conductors (*Part V*), metallic and oxide glasses (*Part VI*). Finally, rapid diffusion paths such as grain-boundary diffusion and diffusion in nanomaterials are considered (*Part VII*). Although these parts cannot replace a comprehensive data collection, typical up-to-date resources available on diffusion for various types of materials are noted.

A thorough understanding of diffusion in materials is crucial for materials development and engineering. Graduate students in solid state physics, physical metallurgy, physical and inorganic chemistry, and geophysical materials will benefit from this book as will physicists, chemists and metallurgists, working in academia and industry.

Acknowledgements

Like any author of a scientific book, I am indebted to previous writers on diffusion and allied subjects. In particular I acknowledge the encouragement of colleagues and friends who provided invaluable assistance during the preparation of the book. Prof. Hartmut Bracht, Prof. Klaus Funke, and Dr. Nikolaas Stolwijk, all from the University of Münster, have read many chapters as they unfolded. Prof. Gabor Erdelyi, Debrecen, Hungary, Prof. Andry Gusak, Cherkassy, Ukraine, Dr. J.N. Mundy, USA, and Prof. Malcom Ingram, University of Aberdeen, Great Britain, stayed in my University as guest scientist for some time and have also reviewed several chapters of the book. Dr. M. Hirscher, Max-Planck-Institut für Metallforschung, Stuttgart, provided comments for the chapter on hydrogen diffusion. Prof. Gerhard Wilde from the University of Münster made useful suggestions for the chapter on nanomaterials. Prof. Graeme Murch, Newcastle, Australia, did a great job in reading the whole book, polishing my English, and providing many helpful suggestions.

To my collaborators Dr. Serguei Divinski, Dr. Arpad Imre, Dr. Halgard Staesche and my PhD students and postdocs Dr. Robert Galler, Dr. Marcel Salamon, Dr. Serguei Peteline, Dr. Eugene Tanguet Nijokep, Dr. Stephan Voss, and to my secretary Sylvia Gurnik I owe many thanks for critically reading parts of the book. Dr. Arpad Imre was a great help in preparing most figures. The contributions and constructive criticisms of all these persons were most helpful.

Professor Dr. Helmut Mehrer
Universität Münster
Institut für Materialphysik
Wilhelm-Klemm-Str. 10
48149 Münster
Germany

Series Editors:

Professor Dr., Dres. h. c. Manuel Cardona
Professor Dr., Dres. h. c. Peter Fulde*
Professor Dr., Dres. h. c. Klaus von Klitzing
Professor Dr., Dres. h. c. Hans-Joachim Queisser

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany

* Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Strasse 38
01187 Dresden, Germany

Professor Dr. Roberto Merlin

Department of Physics, 5000 East University, University of Michigan
Ann Arbor, MI 48109-1120, USA

Professor Dr. Horst Störmer

Dept. Phys. and Dept. Appl. Physics, Columbia University, New York, NY 10027 and
Bell Labs., Lucent Technologies, Murray Hill, NJ 07974, USA

Library of Congress Control Number: 2007923017

ISSN 0171-1873

ISBN 978-3-540-71486-6 Springer Berlin Heidelberg New York

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilm or in any other way, and storage in data banks. Duplication of this publication or parts thereof is permitted only under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer. Violations are liable for prosecution under the German Copyright Law.

Reprint from English language edition:

Diffusion in Solids: Fundamentals, Methods, Materials, Diffusion-Controlled Processes
by Helmut Mehrer

Copyright © 2007, Springer-Verlag Berlin Heidelberg

Springer is a part of Springer Science+Business Media

All Rights Reserved

This reprint has been authorized by Springer Science & Business Media for distribution in
China Mainland only and not for export therefrom.

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 <i>versus</i> 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 <i>versus</i> 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 of Interstitial 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	L1 ₂ Intermetallics	355
20.5	D0 ₃ Intermetallics	357
20.6	Uniaxial Intermetallics	360
20.6.1	L1 ₀ Intermetallics	360
20.6.2	Molybdenum Disilicide (C11 _b structure)	362
20.7	Laves Phases	364
20.8	The Cu ₃ Au 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 RbAg ₄ I ₅ and related Compounds	479
27.2 PbF ₂ 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

32.5 Grain-Boundary Diffusion and Segregation.....	576
32.6 Atomic Mechanisms of Grain-Boundary Diffusion.....	579
References	580
33 Dislocation Pipe Diffusion	583
33.1 Dislocation Pipe Model	584
33.2 Solutions for Mean Thin Layer Concentrations	586
References	591
34 Diffusion in Nanocrystalline Materials	593
34.1 General Remarks	593
34.2 Synthesis of Nanocrystalline Materials	594
34.2.1 Powder Processing.....	594
34.2.2 Heavy Plastic Deformation	596
34.2.3 Chemical and Related Synthesis Methods.....	598
34.2.4 Devitrification of Amorphous Precursors	598
34.3 Diffusion in Poly- and Nanocrystals.....	599
34.3.1 Grain Size and Diffusion Regimes	599
34.3.2 Effective Diffusivities in Poly- and Nanocrystals	604
34.4 Diffusion in Nanocrystalline Metals	606
34.4.1 General Remarks	606
34.4.2 Structural Relaxation and Grain Growth	607
34.4.3 Nanomaterials with Bimodal Grain Structure	608
34.4.4 Grain Boundary Triple Junctions	612
34.5 Diffusion and Ionic Conduction in Nanocrystalline Ceramics ..	612
References	618
Index	639

1 History and Bibliography of Diffusion

If a droplet of ink is placed without stirring at the bottom of a bottle filled with water, the colour will slowly spread through the bottle. At first, it will be concentrated near the bottom. After a few days, it will penetrate upwards a few centimeters. After several days, the solution will be coloured homogeneously. The process responsible for the movement of the coloured material is diffusion. Diffusion is caused by the BROWNIAN motion of atoms or molecules that leads to complete mixing. In gases, diffusion progresses at a rate of centimeters per second; in liquids, its rate is typically fractions of millimeters per second; in solids, diffusion is a fairly slow process and the rate of diffusion decreases strongly with decreasing temperature: near the melting temperature of a metal a typical rate is about one micrometer per second; near half of the melting temperature it is only of the order of nanometers per second.

The science of diffusion in solids had its beginnings in the 19th century, although the blacksmiths and metal artisans of antiquity already used the phenomenon to make such objects as swords of steel, gilded copper or bronze wares. Diffusion science is based on several corner stones. The most important ones are: (i) The continuum theory of diffusion originated from work of the German scientist *Adolf Fick*, who was inspired by elegant experiments on diffusion in gases and of salt in water performed by *Thomas Graham* in Scotland. (ii) The BROWNIAN motion was detected by the Scottish botanist *Robert Brown*. He observed small particles suspended in water migrating in an erratic fashion. This phenomenon was interpreted many decades later by *Albert Einstein*. He realised that the ‘dance’ described by *Brown* was a random walk driven by the collisions between particles and the water molecules. His theory provided the statistical cornerstone of diffusion and bridged the gap between mechanics and thermodynamics. It was verified in beautiful experiments by the French Nobel laureate *Jean Baptiste Perrin*. (iii) The atomistics of solid-state diffusion had to wait for the birth date of solid-state physics heralded by the experiments of *Max von Laue*. Equally important was the perception of the Russian and German scientists *Jakov Frenkel* and *Walter Schottky* that point defects play an important rôle for properties of crystalline substances, most notably for those controlling diffusion and the many properties that stem from it.

This chapter is not meant to be a systematic history of diffusion science. It is devoted in its first section to some major landmarks and eminent people