J. P. STARK
Department of Mechanical Engineering
The University of Texas at Austin

SOLID STATE DIFFUSION

A Wiley-Interscience Publication

JOHN WILEY & SONS

New York · London · Sydney · Toronto

Copyright © 1976 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

No part of this book may be reproduced by any means, nor transmitted, nor translated into a machine language without the written permission of the publisher.

***Library of Congress Cataloging in Publication Data*:**

Stark, John Paul, 1938–
Solid state diffusion.

"A Wiley-Interscience publication."
Includes bibliographical references and index.
1. Dilute alloys. 2. Diffusion. I. Title.

TN690.S75 669'.94 76-16841
ISBN 0-471-82073-3

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

SOLID STATE DIFFUSION

To Susan Anne

试读结束：需要全本请在线购买： www.ertongbook.com

PREFACE

This graduate level book presents the theory of diffusion in solids in as logical a manner as is known to this author. I have included the composite results of many approaches to the problems of diffusion. Much of the understanding is based on varied topics that bear on the subject. Where possible, I have stressed the kinetic theory with examples of dilute alloys. Often, however, I have resorted to the phenomenological developments, because of the complexity associated with the straightforward random walk and kinetic theory approaches.

With the exception of the first chapter, the mathematical background necessary includes only partial differentiation and some matrix algebra. The latter subject is often missed by beginning materials science and metallurgy graduate students; however, the depth herein is not overwhelming since the inverse matrix is the only real complexity used. Chapter 1 includes a fairly complete discussion of the operations surrounding its use and some complex variables, neither of which should present the student with too much difficulty.

Chapters 2, 3, and Appendix A contain some statistical mechanics. The level is comparable to that of *Introduction to Statistical Thermodynamics* by T. Hill, which is highly recommended. The maximum term method is used extensively in the three places where statistical mechanics is necessary. The principle behind the maximum term method is, of course, the minimum free energy of an equilibrium state.

Some readers may feel that the extensive kinetic development in Chapter 2 is presented too early in the text. In my view, it is the most logical way of introducing the phenomenological theory; that is, by showing that the diffusion flux is proportional to the chemical potential gradient, rather than by assuming it to be the case based on some vague thermodynamic presumptions.

The phenomenological theory is of great value in understanding the experiments in concentrated systems. Unfortunately, some authors have not been sufficiently careful in their definitions. Consequently, self-diffusion is carefully defined in Chapter 4, and subsequently related to off-diagonal phenomenological coefficients and vacancy wind terms with specific examples for dilute alloys. The same set of phenomenological coefficients arise when external fields influence mass transfer. This gives the opportunity to compare results from both sets of experiments or theories, as is done in that chapter.

There are problems included for all chapters. The easier problems are found in the earlier chapters; difficult problems and those that require a computer are marked with a dagger. The problems are included to supplement the text in depth and scope.

J. P. STARK

Austin, Texas
February 1976

CONTENTS

CHAPTER 1 INTRODUCTION 1
Flux Equations for a Continuum 1
Diffusion in an Infinite Crystal 5
Diffusion in a Finite Crystal 20
Influence of Neumann's Principle on the Diffusivity Tensor 22

CHAPTER 2 DIFFUSION OF INTERSTITIAL SOLUTES 26
Atomic Vibrations in Crystals 26
Jump Frequency Gradient 30
Jump Frequency Response to an Applied Field 31
Diffusion Mechanisms 33
Diffusion Flux for an Interstitial-Random Walk Calculation 36
Kinetic Theory for a Dilute Ternary fcc Alloy 39
Phenomenological Equations 54
Some Experimental Results 60

CHAPTER 3 SELF-DIFFUSION OF SUBSTITUTIONAL SOLUTES BY A VACANCY MECHANISM IN DILUTE ALLOYS 63
Vacancy Equilibrium in Pure Metals 63
Vacancy-Substitutional Solute Binding in a Dilute Alloy 66
Self-Diffusion by a Vacancy Mechanism 69
Steady-State Calculation of the Solute Jump Frequency 72
Determination of the Correlation Factor 73
Evaluation of P_{11} and P_a for an fcc Crystal 76
Random Walk Calculation of the Jump Frequency and Diffusivity 82
Experimental Results for fcc Crystals 92
Anomalous Diffusion in bcc Crystals 94

CHAPTER 4 THE INFLUENCE OF INTERNAL AND EXTERNAL FIELDS UPON DIFFUSION BY A VACANCY MECHANISM 98
Phenomenological Equations 98
Definition of Self-Diffusion 101
Intrinsic Diffusion of a Tracer 102
Kirkendall Effect and Mutual Diffusivity 105
Kinetic Theory for Mobility 106
Relation of the Off-Diagonal Phenomenological Coefficients to the Vacancy Wind for a Dilute Solute 119
Phenomenological Development of the Soret Effect in a Binary System 122
Concentration of Vacancies in a Temperature Gradient 125

CHAPTER 5 DIVACANCIES AND CONCENTRATION EFFECTS IN DILUTE ALLOYS 131
The Correlation Factor 131
Calculation of the Fraction of Jumps, C_α, and the Average Jump Frequency 134
Solute Enhancement of Solvent Self-Diffusion 135
Influence of Solute Pairs on Solute Self-Diffusion in a fcc Lattice 140
Influence of Vacancy Pairs on the Solute Diffusivity 156
Random Walk Calculation of $\langle W \rangle$, C_α, and D 162
Thermal Diffusion of Solute Pairs in an fcc Lattice 166

CHAPTER 6 MATRIX EQUATIONS FOR UNEQUAL JUMP DISTANCES 177
The Diffusivity 177
Tracer Drift Velocity 183
Tracer Mobility by a Divacancy Mechanism 188
Influence of a Solute on the Mobility of a Solvent Tracer 191

CHAPTER 7 SLOW AND FAST DIFFUSION OF SUBSTITUTIONAL SOLUTES 195
Diffusion in Dislocations and Grain Boundaries 195
Pure Metal Self-Diffusion—Correlation Factor For Dislocations 202
Interstitial Diffusion of Normally Substitutional Solutes 210
Near-Surface Anomaly 212

APPENDIX A 218
Statistical Mechanics of Vacancy-Divacancy Equilibrium in a Pure fcc Metal 218

APPENDIX B **221**
Quantum Theory for Diffusion Jumps 221

APPENDIX C **224**
Matrix Algebra for A_e 224
APPENDIX D **225**
Outside Reading 225

APPENDIX E **227**
Problems 227

INDEX **235**

CHAPTER 1

INTRODUCTION

FLUX EQUATIONS FOR A CONTINUUM

The motion of atoms in crystals follows various laws that can be written for a macroscopic continuum to follow the dissolution process. The connection between the continuum behavior on which experiments are based and the atomic behavior that can explain the continuum laws is the major purpose of research in diffusion. This is not to imply that the continuum laws are unimportant; they are the basis for nearly all the studies of phase transformations, oxidation rates, and other phenomena related to mass transport in the solid state. However, an understanding of the parameters that are present in the continuum laws and that control the rates with which these processes occur provides part of the basis for the innovative development of new materials behavior.

The manipulation of the continuum laws is usually an exercise in applied mathematics. It may be assumed that such a topic is irrelevant to the presentation of diffusion in solids. This may be true for a large number of cases; however, in research one is attempting to interpret the continuum behavior in terms of the kinetics of atom motion, and such an interpretation can be prejudiced by an incorrect application of the continuum laws. This is particularly true if, for example, two different interpretations would lead to the same results within experimental error. As a consequence, in this book some attention is paid to the manipulation of these laws in the form of differential equations.

First, however, the continuum equations are introduced. The continuum results will ultimately be compared to the kinetic behavior of

试读结束：需要全本请在线购买： www.ertongbook.com

individual atoms. These atoms move relative to the crystallographic planes on which the atoms reside, and consequently, the continuum behavior should be written relative to a coordinate system that moves at the same velocity as these atom planes. The flux of matter of a given component in a homogeneous and multicomponent system is a vector quantity reflecting the mass of that component crossing a unit area per unit time. The unit area is normal to the flux vector. An equation for the flux of component K, J_K is

$$J_K = -D_K^* \nabla C_K + C_K V_{FK} \tag{1.1}$$

where D_K^* is the self-diffusion coefficient of a tracer of component K, C_K is the concentration of component K, and V_{FK} is the drift velocity of component K due to a force F. The diffusion coefficient is generally a tensor of rank 2 with typical units of cm^2/sec. The concentration is in some appropriate unit of mass per unit volume, such as moles/cm^3. The product of the diffusion coefficient tensor and the concentration gradient is a tensor contraction.

When the velocity due to an applied force V_{FK} in Eq. 1.1 is zero, this result is known as Fick's first law. The occurrence of the velocity term results from the incidence of atoms experiencing a net drift due to some applied field. Some of the fields that are experimentally known to cause mass transfer are the electric field, gravitational field, temperature gradient, chemical potential gradient, and so forth.

If the lattice planes are moving at some velocity V_L relative to the fixed laboratory frame of reference, then in this fixed coordinate system the flux, $J_K{}^L$, is related to the flux in Eq. 1.1 by the relationship

$$J_K{}^L = J_K + C_K V_L = -D_K^* \nabla C_K + C_K (V_{FK} + V_L) \tag{1.2}$$

Such a situation is often the case because the applied fields causing the motion of component K will also cause the drift of all other components in the system, and if each component moves relative to the lattice at some different rate, the lattice itself may move.

The net rate of change of the mass of component K within a given volume fixed relative to the laboratory coordinates is

$$\frac{d}{dt}\int^V C_K \, dV = \int^V \frac{\partial C_K}{\partial t} \, dV \tag{1.3}$$

The mass of component K inside the volume element V can change in two ways. First, by Eq. 1.2 one can have flow through the surface of the volume element. Second, one can produce an annihilate component K through a chemical reaction, although this is less common in solids. Generally, there may be r chemical reactions of which each contributes to the production of component K. Let the reaction rate per unit volume be $\nu_{Kj}R_j$ for the jth chemical reaction. The rate of production of K per unit volume from the various chemical reactions is

$$\sum_{j=1}^{r} \nu_{Kj}R_j$$

where ν_{Kj} is positive for production and negative for annihilation of component K. The coefficients ν_{Kj} divided by the molecular mass M_K is proportional to the stoichiometric coefficient with which component K is found in the jth chemical reaction, and R_j is the rate that reaction j proceeds in units of mass per volume x time. The surface of the volume element, Ω, yields a vector $d\Omega$ whose normal direction points outward from the volume. The reaction rates and the flux contribute to the rate of change in the concentration of component K through the relation

$$\frac{d}{dt}\int^{V} C_K\, dV = -\int^{\Omega} J_K{}^L \cdot d\Omega + \sum_{j=1}^{r} \int^{V} \nu_{Kj}R_j\, dV \qquad 1.4$$

Gauss' theorem may be applied to the surface integral; this leaves Eq. 1.4 as

$$\frac{d}{dt}\int^{V} C_K\, dV = \int^{V}\left(-\nabla \cdot J_K{}^L + \sum_{j=1}^{r} \nu_{Kj}R_j\right) dV$$

$$= \int^{V} \frac{\partial C_K}{\partial t}\, dV$$

However, the volume element V is completely arbitrary, and this implies that

$$\frac{\partial C_K}{\partial t} = -\nabla \cdot J_K{}^L + \sum_{j=1}^{r} \nu_{Kj}R_j \qquad 1.5$$

Equation 1.5 is a general statement of the law of conservation of mass.

One might argue that it is extraneous to consider chemical reactions occurring within a homogeneous crystal. A simple example can show the importance of such terms in the conservation equation 1.5. Consider, for example, the motion of hydrogen through a steel bar that is about to be embrittled. The hydrogen probably goes into solution in a monatomic form as it resides on interstitial sites within the crystal. If a hydrogen ion meets an oxygen ion and they are close enough together, they may share some of the surrounding electrons forming a pair somewhat of the form H:O. This pair will move through the crystal at a different rate than does an isolated hydrogen ion: hence there may be two important diffusion coefficients to consider, that of the pair and that of the isolated hydrogen ion. It may be convenient in some cases to consider the pair as being less mobile, and such trapping mechanisms may decrease the rate of embrittlement of the steel sample by hydrogen.

A specific example of a problem, in which it was convenient to use chemical reactions in solids, is discussed in Chapter 7. At this point, however, assume that $R_j = 0$ for all j; there are no chemical reactions. Furthermore, in most research problems, Eq. 1.1, 1.2, and 1.5 are used in a one-dimensional form rather than three dimensions as indicated. This is true because the research experimenter attempts to determine a kinetic interpretation of the tracer diffusivity, D_K^*, and the velocity from an applied force, V_{FK}, for each component. This information, as well as a solution to the differential equation 1.5, is most reasonably accomplished with the concentration gradients and applied force collinear in some crystallographic direction. If only the diagonal elements of the diffusion coefficient, written as a matrix, are nonzero (as shown for some systems in this chapter), and assuming the applied field and concentration gradients exist only along the x axis Eq. 1.1 becomes

$$J_K = -D_K^* \frac{\partial C_K}{\partial x} + C_K V_{FK} \qquad 1.6$$

Similarly Eq. 1.5 becomes

$$\frac{\partial C_K}{\partial t} = \frac{-\partial J_K{}^L}{\partial x} \qquad 1.7$$

$$= D_K^* \frac{\partial^2 C_K}{\partial x^2} + \frac{\partial D_K^*}{\partial x} \cdot \frac{\partial C_K}{\partial x} - \frac{\partial C_K}{\partial x}(V_{FK} + V_L)$$

$$-C_K \frac{\partial (V_{FK} + V_L)}{\partial x} \qquad 1.8$$

It will become apparent that if one may write the velocity for an applied force as

$$V_{FK} = V'_K - \frac{\partial D_K^*}{\partial x}$$

then it is possible to write Eq. 1.6 as

$$J_K = -\frac{\partial D_K^* C_K}{\partial x} + C_K V'_K \qquad 1.9$$

If a detailed analysis shows that the tracer diffusion coefficient is position dependent, as would be the case in a temperature gradient, then that analysis would also show that the tracer drift velocity V'_K includes a term $\partial D_K^*/\partial x$. In that instance, Eq. 1.9 must be used in conjunction with Eq.

1.7 because the diffusion coefficient gradient terms do not contribute to the flux; they cancel it. The velocity term V_{FK} in Eqs. 1.1, 1.6, and 1.8 does not contain any contribution from the diffusion coefficient gradient. The contribution of the diffusion coefficient gradient to the flux is discussed in Chapter 2 where a kinetic analysis derives Eq. 1.9 from which Eq. 1.6 may be found by cancelling the appropriate terms.

DIFFUSION IN AN INFINITE CRYSTAL

For an infinitely dilute solute in a binary metal alloy moving through the crystal with an applied electric field, the drift velocity per unit force is nonzero. The net drift velocity is written as $V_{FK} + V_L = Q_K E D_K^* / K_B T$, where Q_K is the effective ionic charge on the solute ion, E is the electric field intensity, K_B is Boltzmann's constant, and T is the absolute temperature. If one assumes that the diffusion coefficient is constant, which will be true if the temperature is uniform, and that E is constant, then Eq. 1.8 becomes

$$\frac{\partial C_K}{\partial t} = D_K^* \left[\frac{\partial^2 C_K}{\partial x^2} - \alpha \frac{\partial C_K}{\partial x} \right] \qquad 1.10$$

where $\alpha = Q_K E / K_B T$. Equation 1.10 is a linear differential equation with constant coefficients. One may solve Eq. 1.10 for the concentration of solute C_K dependent on x and t, provided that appropriate boundary and initial conditions are applied. The most appropriate method of solution for such problems is through the use of integral transforms. We will assume that a thin layer of solute, Q_0 being the mass per unit area, is deposited on the end of the semi-infinite sample of uniform cross sectional area at $t = 0$. At this time the solute is not found elsewhere in the sample. Therefore, the appropriate conditions are

$$C_K(x, t = 0) = 0,$$

$$\int_0^\infty C_K(x, t)\, dx = Q_0,$$

and $\lim_{x \to \infty} C_K(x, t)$ is finite. The method of solution is as follows. Assume that

$$\bar{C}(x, s) = \int_0^\infty C_K(x, t) e^{-st}\, dt \qquad 1.11$$

Equation 1.11 transforms the partial differential equation into an ordinary differential equation. With Eq. 1.11 and integration by parts, it is easy to show that

$$s\bar{C}(x, s) - C_K(x, t=0) = \int_0^\infty e^{-st} \frac{\partial C_K}{\partial t}\, dt \qquad 1.12$$

and it is obvious that

$$\frac{\partial^n \bar{C}}{\partial x^n} = \int_0^\infty e^{-st} \frac{\partial^n C_K}{\partial x^n}\, dt \qquad n = 1, 2, \cdots \qquad 1.13$$

Substituting Eqs. 1.11–1.13 into Eq. 1.10 and using the initial condition that $C_K(x, t=0) = 0$, Eq. 1.10 becomes

$$\frac{d^2\bar{C}}{dx^2} - \alpha \frac{d\bar{C}}{dx} - \frac{s}{D_K^*}\bar{C} = 0 \qquad 1.14$$

The Laplace transform, Eq. 1.11, has reduced the partial differential equation, 1.10, into an ordinary differential equation, 1.14. Equation 1.14 is solved by assuming a solution of the form $\bar{C} = Ae^{\gamma x}$. With this substitution one finds, assuming $\alpha \geq 0$, that

$$\gamma^2 - \alpha\gamma - \frac{s}{D_K^*} = 0 \qquad 1.15$$

However

$$\gamma = \frac{\alpha}{2} \pm \frac{1}{2}\sqrt{\left(\alpha^2 + \frac{4s}{D_K^*}\right)}$$

so that

$$\bar{C} = A_1 \exp\left\{\left[\frac{\alpha}{2} + \frac{1}{2}\sqrt{\left(\alpha^2 + \frac{4s}{D_K^*}\right)}\right]x\right\}$$

$$+ A_2 \exp\left\{\left[\frac{\alpha}{2} - \frac{1}{2}\sqrt{\left(\alpha^2 + \frac{4s}{D_K^*}\right)}\right]x\right\}. \qquad 1.16$$

When $\lim_{x\to\infty} C_K(x, t)$ is finite, one infers that $\lim_{x\to\infty} \bar{C}(x, s)$ is finite, from which one concludes that $A_1 = 0$. The other boundary condition,

$$\int_0^\infty C_K(x, t)\, dx = Q_0$$

must be transformed to $\bar{C}(x, s)$ as follows:

$$\int_0^\infty e^{-st} \int_0^\infty C_K(x, t)\, dx\, dt = \int_0^\infty \bar{C}(x, s)\, dx$$

$$= \int_0^\infty e^{-st} Q_0\, dt = \frac{Q_0}{s}$$

$$= \int_0^\infty A_2 \exp -\left\{\left[\frac{-\alpha}{2} + \frac{1}{2}\sqrt{\left(\alpha^2 + \frac{4s}{D_K^*}\right)}\right] x\right\} dx$$

$$= \frac{A_2}{\dfrac{-\alpha}{2} + \dfrac{1}{2}\sqrt{\left(\alpha^2 + \dfrac{4s}{D_K^*}\right)}} \qquad 1.17$$

Hence

$$A_2 = \frac{-Q_0}{s}\left[\frac{\alpha}{2} - \frac{1}{2}\sqrt{\left(\alpha^2 + \frac{4s}{D_K^*}\right)}\right]$$

According to LaPlace transform theory, the concentration $C_K(x, t)$ is found from the following integral in the complex plane,

$$C_K = \frac{Q_0}{4\pi i} \int_{\sigma - i\infty}^{\sigma + i\infty} e^{st} \frac{\left(\alpha - \sqrt{\alpha^2 + \dfrac{4s}{D_K^*}}\right)}{s} \exp\left[\frac{\alpha}{2} - \frac{1}{2}\sqrt{\left(\alpha^2 + \frac{4s}{D_K^*}\right)}\right] x\, dx \qquad 1.18$$

In Eq. 1.18, σ is to the right of all singularities in the function inside the integral. An analysis of the type of singularities present is aided by the substitution $4Z/D_i^* = \alpha^2 + 4s/D_K^*$ and $dZ = ds$. Then

$$C_K = \frac{-Q_0}{4\pi i} \int_{\sigma - i\infty}^{\sigma + i\infty} \frac{\exp\left[\alpha x/2 - \alpha^2 D_K^* t/4\right]\left(\alpha - 2\sqrt{(Z/D_K^*)}\right) \exp\left(Zt - x\sqrt{Z/D_K^*}\right) dZ}{\left(Z - D_K^* \alpha^2/4\right)}$$

There is a simple pole at $Z - D_K^* \alpha^2/4 = 0$, a branch point at $x\sqrt{Z/D_K^*} = 0$ and at $(\alpha - 2\sqrt{Z/D_K^*}) = 0$. One can get rid of the latter branch point by the substitution $Z = (iV)^2$, and $dZ = -2V\, dV$. This substitution, however, changes the contour of integration from that shown in Fig. 1.1 to contour C_2 in Fig. 1.2. Hence

$$C_K = \frac{Q_0}{\pi/D_K^*} \exp\left(\frac{\alpha x}{2} - \frac{\alpha^2 D_K^* t}{4}\right) I \qquad 1.19$$

试读结束：需要全本请在线购买： www.ertongbook.com