Mass transport in solids and fluids

The field of matter transport is central to understanding the processing of materials and their subsequent properties. While thermodynamics determines the final stable state towards which a material system tends, it is the kinetics of mass transport that governs how fast it gets there. This textbook gives a solid grounding in the principles of matter transport and their application to a range of materials science and engineering problems.

The author develops a unified phenomenological treatment of this subject applicable to both solids and liquids. Traditionally, mass transport in fluids is considered as an extension of heat transfer theory and uses similar methods and nomenclature. The subject can therefore appear to the student as having little relationship to diffusion in solids. By contrast, the unified approach of this text enables the student to clearly make the connection between these two important fields. The material presented assumes the student has some knowledge of thermodynamics, including the use of binary phase diagrams at a level usually presented in introductory courses on materials. It is also useful, but not essential, for students to have taken a course in partial differential equations. An appendix deals with solution methods for the diffusion equation.

This book is aimed at students of materials science and engineering and related disciplines such as metallurgy and ceramics. It contains numerous worked examples and unsolved problems. The material is suitable for advanced undergraduate and beginning graduate students, and can be covered in a one-semester course.

DAVID WILKINSON received his undergraduate education in Engineering Science at University of Toronto (1972) where he also completed a Master's degree (1974). He did his Ph.D. at Cambridge University (1978) working under the supervision of Prof. Mike Ashby FRS. The field of research was modelling and mechanism maps for pressure sintering. Following a post-doctoral fellowship at University of Pennsylvania he joined the faculty of McMaster University in 1979. He has held visiting fellowships at the Max Planck Institute für Metallforschung Stuttgart (1985/86), University of California Santa Barbara (1991/92) and Institut National des Sciences Appliqués (INSA) in Lyon (1997). He has served on the boards of both the Metallurgical Society of the Canadian Institute of Mining and Metallurgy (CIM) and the Canadian Ceramic Society. In 1996 he was awarded the prize for best materials paper in the *Canadian Metallurgical Quarterly* and in 2000 the Ross Coffin Purdy Medal of the American Ceramic Society (ACerS). Professor Wilkinson's research focusses on the processing and mechanical behaviour of heterogeneous solids, including metals, ceramics and their composites. He has published over 150 research papers. He is a Fellow of CIM and ACerS.

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The fountains mingle with the river
And the rivers with the ocean
The winds of heaven mix forever
With a sweet emotion;
Nothing in the world is single;
All things by a law divine
In one spirit mix and mingle.
Percy Bysshe Shelley, *Love's Philosophy*

Mass transport in solids and fluids

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Cover photograph: Transmission electron micrograph images of an Al–4 wt% Cu alloy during *in-situ* annealing within the electron microscope at 320 °C. These two micrographs, taken 15 minutes apart, show the progressive dissolution of platelike particles of $CuAl_2$. The field of each micrograph is about 4 μm wide. (Courtesy of Prof. G. C. Weatherly, McMaster University.)

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Preface

The field of matter transport is central to understanding the processing and subsequent behaviour of materials. While thermodynamics tells us the state in which a material system would like to exist, the kinetics of matter transport tell us how fast it can get there. The materials which we use in service are often not at equilibrium. This is particularly so in solid materials. Here kinetics are sufficiently slow that materials are almost never in complete thermodynamic equilibrium but attain a stable state which is kinetically limited. However, kinetics are equally important in fluids since the transport of matter in a liquid or gas often limits the rate at which many processes for materials fabrication can proceed. The aim of this book is to give students a solid grounding in the principles of matter transport and their application to the solution of engineering problems.

It is this emphasis on engineering application that distinguishes this text from many other books in this field. In the field of solid-state diffusion, for example, much has been written about the mechanisms of diffusion at the atomic scale. This is a fascinating topic and of great interest to materials scientists. However, only an elementary understanding is required in order to treat many practical diffusion problems. Thus, the emphasis throughout this book is on developing methods for solving problems involving the transport of matter in materials. I have attempted throughout to develop a unified view of mass transport in which the approach is independent of the state (whether solid, liquid or gas) of the transport medium. In particular, I have drawn links between the concept of counter diffusion, used to treat problems involving solid-state diffusion in concentrated alloys, and the concept of convective flow in fluids. Both result in a drift velocity which can be handled phenomenologically using the same framework.

This book is aimed at undergraduate students taking degrees in the various disciplines which come under the general umbrella of materials science and

engineering (including metallurgy and ceramics). The subject of this book has been for many years treated in a one-term course at McMaster University. It will be suitable for most students in their junior or senior years. The presentation assumes that the students have some knowledge of thermodynamics, and especially in the use of binary phase diagrams, at a level usually presented in introductory courses on materials. It is also useful, but not essential, for students to have done a course in partial differential equations. (An appendix which deals with solution methods for the diffusion equation is offered, primarily as a refresher for those familiar with the subject).

I would like to acknowledge the encouragement and assistance of many colleagues and friends in the preparation of this book. The course on which this book is based was first developed by Prof. Bob Piercy and many of his ideas are incorporated herein. I gratefully acknowledge the contributions of Prof. Gordon Irons in the area of convective mass transfer and that of Prof. Gary Purdy in multicomponent diffusion. I am grateful to both of these colleagues and to a host of students who have commented on early drafts of the book. My thanks go also to Ginnie, Laura and Jan in our Faculty Docucentre for persevering in the preparation of the text, and to Ed McCaffery and John Nychka for the production of many of the figures.

Above all, I wish to express my heartfelt gratitude to Linda, Lisa and Craig for their patience, love and understanding.

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Principal symbols

Note: In order to keep to commonly used conventions, several symbols are used with different meaning in different parts of the text. The meaning should be clear from the context however. For example, lower case p is used both for pressure and Boltzmann probability.

Symbol	Definition	Unit
a	lattice parameter	m
a	thermodynamic activity	–
A	cross-sectional area of diffusion path	m^2
C	concentration	mol/m^3
D	diffusion coefficient	m^2/s
D_v, D_a, D_s, D_i	diffusion coefficients for (respectively) vacancies, atoms (self-diffusion), substitutional solute and interstitial solute	m^2/s
D_{0v}, D_{0a}, D_{0s}, D_{0i}	pre-exponential term in Arrhenius expression for the diffusion coefficient	m^2/s
f_i	weight fraction of phase i	–
Gr'	mass transport Grashof number	–
ΔG	free energy	kJ/mol
ΔG_v^f	free energy of vacancy formation	kJ/mol
ΔG_v^m	free energy of vacancy migration	kJ/mol
ΔG_i^m	free energy of interstitial migration	kJ/mol

Symbol	Definition	Unit
j	diffusive flux	$kg/m^2\,s$
J	diffusive flux	$mol/m^2\,s$
k	Boltzmann's constant	J/atom K
k_D	mass transfer coefficient	m/s
K	equilibrium constant	–
K^*	solubility of gas in solid at 1 atm. pressure	mol/m^3
$\bar{L}$	nominal diffusion distance	m
n	total flux	$kg/m^2\,s$
N	total flux	$mol/m^2\,s$
N_0	Avogadro's number	/mol
p	pressure	Pa
p	Boltzmann probability	–
q	flow rate	mol/s or kg/s
Q	activation energy	kJ/mol
R	universal gas constant	J/mol K
Re	Reynolds number	–
$\dot{r}$	reaction rate	$mol/m^3\,s$ or $kg/m^3\,s$
Sc	Schmidt number	–
Sh	Sherwood number	–
t	time	s
t_e	exposure time	s
T	temperature	K
T_m	melting temperature	K
v	average molar velocity	m/s
v^*	average mass velocity	m/s
V	volume	m^3
X	molar fraction	–
X^*	weight fraction	–
X_v	vacancy concentration	–
X_v^o	equilibrium vacancy concentration	–
$(\Delta X)_{ln}$	log mean driving force (see eq. (7.48))	–
y	position	m
y_I	interface position	m
δ	membrane or layer thickness	m
δ_b	grain boundary thickness	m
η	viscosity	Pa s
γ	activity coefficient	–
γ^o	Henrian activity coefficient	–
Γ	jump frequency	s^{-1}
λ	mean free path	m

Symbol	Definition	Unit
ν	lattice vibration frequency	s^{-1}
ν	kinematic viscosity	m^2/s
Π	permeability	$m^3(STP)/m\,s\,atm^{1/2}$
ρ	density (mass concentration)	kg/m^3
Ω	atomic or molecular volume	m^3