国家出版基金项目
NATIONAL PUBLICATION FOUNDATION

中外物理学精品书系

引进系列·39

Phase Equilibria, Phase Diagrams and Phase Transformations: Their Thermodynamic Basis 2nd Edition

相平衡、相图和相变——其热力学基础 第二版

（影印版）

〔瑞典〕希勒特（M. Hillert） 著

北京大学出版社
PEKING UNIVERSITY PRESS

国家出版基金项目
NATIONAL PUBLICATION FOUNDATION

中外物理学精品书系

引进系列·39

Phase Equilibria, Phase Diagrams and Phase Transformations:

Their Thermodynamic Basis

2nd Edition

相平衡、相图和相变

——其热力学基础

第二版

（影印版）

〔瑞典〕希勒特（M. Hillert） 著

北京大学出版社
PEKING UNIVERSITY PRESS

著作权合同登记号　图字:01-2014-3770
图书在版编目(CIP)数据

相平衡、相图和相变:其热力学基础:第2版 = Phase equilibria, phase diagrams and phase transformations: Their thermodynamic basis: 2nd edition:英文/(瑞典)希勒特(Hillert, M.)著. —影印本. —北京:北京大学出版社,2014.8
(中外物理学精品书系)
ISBN 978-7-301-24555-2

Ⅰ. ①相…　Ⅱ. ①希…　Ⅲ. ①热力学-研究-英文　Ⅳ. ①O414.1

中国版本图书馆CIP数据核字(2014)第170620号

书　　名:Phase Equilibria, Phase Diagrams and Phase Transformations: Their Thermodynamic Basis　2nd Edition(相平衡、相图和相变——其热力学基础　第二版)(影印版)
著作责任者:〔瑞典〕希勒特(M. Hillert)　著
责任编辑:刘　啸
标准书号:ISBN 978-7-301-24555-2/O·0987
出版发行:北京大学出版社
地　　址:北京市海淀区成府路205号　100871
网　　址:http://www.pup.cn
新浪微博:@北京大学出版社
电子信箱:zpup@pup.cn
电　　话:邮购部62752015　发行部62750672　编辑部62752038　出版部62754962
印　刷　者:北京中科印刷有限公司
经　销　者:新华书店
730毫米×980毫米　16开本　33印张　629千字
2014年8月第1版　2014年8月第1次印刷
定　　价:89.00元

“中外物理学精品书系”
编 委 会

序　言

物理学是研究物质、能量以及它们之间相互作用的科学。她不仅是化学、生命、材料、信息、能源和环境等相关学科的基础，同时还是许多新兴学科和交叉学科的前沿。在科技发展日新月异和国际竞争日趋激烈的今天，物理学不仅囿于基础科学和技术应用研究的范畴，而且在社会发展与人类进步的历史进程中发挥着越来越关键的作用。

我们欣喜地看到，改革开放三十多年来，随着中国政治、经济、教育、文化等领域各项事业的持续稳定发展，我国物理学取得了跨越式的进步，做出了很多为世界瞩目的研究成果。今日的中国物理正在经历一个历史上少有的黄金时代。

在我国物理学科快速发展的背景下，近年来物理学相关书籍也呈现百花齐放的良好态势，在知识传承、学术交流、人才培养等方面发挥着无可替代的作用。从另一方面看，尽管国内各出版社相继推出了一些质量很高的物理教材和图书，但系统总结物理学各门类知识和发展，深入浅出地介绍其与现代科学技术之间的渊源，并针对不同层次的读者提供有价值的教材和研究参考，仍是我国科学传播与出版界面临的一个极富挑战性的课题。

为有力推动我国物理学研究、加快相关学科的建设与发展，特别是展现近年来中国物理学者的研究水平和成果，北京大学出版社在国家出版基金的支持下推出了“中外物理学精品书系”，试图对以上难题进行大胆的尝试和探索。该书系编委会集结了数十位来自内地和香港顶尖高校及科研院所的知名专家学者。他们都是目前该领域十分活跃的专家，确保了整套丛书的权威性和前瞻性。

这套书系内容丰富，涵盖面广，可读性强，其中既有对我国传统物理学发展的梳理和总结，也有对正在蓬勃发展的物理学前沿的全面展示；既引进和介绍了世界物理学研究的发展动态，也面向国际主流领域传播中国物理的优秀专著。可以说，“中外物理学精品书系”力图完整呈现近现代世界和中国物理

科学发展的全貌，是一部目前国内为数不多的兼具学术价值和阅读乐趣的经典物理丛书。

“中外物理学精品书系”另一个突出特点是，在把西方物理的精华要义“请进来”的同时，也将我国近现代物理的优秀成果“送出去”。物理学科在世界范围内的重要性不言而喻，引进和翻译世界物理的经典著作和前沿动态，可以满足当前国内物理教学和科研工作的迫切需求。另一方面，改革开放几十年来，我国的物理学研究取得了长足发展，一大批具有较高学术价值的著作相继问世。这套丛书首次将一些中国物理学者的优秀论著以英文版的形式直接推向国际相关研究的主流领域，使世界对中国物理学的过去和现状有更多的深入了解，不仅充分展示出中国物理学研究和积累的“硬实力”，也向世界主动传播我国科技文化领域不断创新的“软实力”，对全面提升中国科学、教育和文化领域的国际形象起到重要的促进作用。

值得一提的是，“中外物理学精品书系”还对中国近现代物理学科的经典著作进行了全面收录。20 世纪以来，中国物理界诞生了很多经典作品，但当时大都分散出版，如今很多代表性的作品已经淹没在浩瀚的图书海洋中，读者们对这些论著也都是“只闻其声，未见其真”。该书系的编者们在这方面下了很大工夫，对中国物理学科不同时期、不同分支的经典著作进行了系统的整理和收录。这项工作具有非常重要的学术意义和社会价值，不仅可以很好地保护和传承我国物理学的经典文献，充分发挥其应有的传世育人的作用，更能使广大物理学人和青年学子切身体会我国物理学研究的发展脉络和优良传统，真正领悟到老一辈科学家严谨求实、追求卓越、博大精深的治学之美。

温家宝总理在 2006 年中国科学技术大会上指出，“加强基础研究是提升国家创新能力、积累智力资本的重要途径，是我国跻身世界科技强国的必要条件”。中国的发展在于创新，而基础研究正是一切创新的根本和源泉。我相信，这套“中外物理学精品书系”的出版，不仅可以使所有热爱和研究物理学的人们从中获取思维的启迪、智力的挑战和阅读的乐趣，也将进一步推动其他相关基础科学更好更快地发展，为我国今后的科技创新和社会进步做出应有的贡献。

“中外物理学精品书系”编委会 主任

中国科学院院士，北京大学教授

王恩哥

2010 年 5 月于燕园

Phase Equilibria, Phase Diagrams and Phase Transformations

Their Thermodynamic Basis

Second Edition

MATS HILLERT
Department of Materials Science and Engineering KTH, Stockholm

CAMBRIDGE
UNIVERSITY PRESS

Preface to second edition

The requirement of the second law that the internal entropy production must be positive for all spontaneous changes of a system results in the equilibrium condition that the entropy production must be zero for all conceivable internal processes. Most thermodynamic textbooks are based on this condition but do not discuss the magnitude of the entropy production for processes. In the first edition the entropy production was retained in the equations as far as possible, usually in the form of $D\mathrm{d}\xi$ where D is the driving force for an isothermal process and ξ is its extent. It was thus possible to discuss the magnitude of the driving force for a change and to illustrate it graphically in molar Gibbs energy diagrams. In other words, the driving force for irreversible processes was an important feature of the first edition. Two chapters have now been added in order to include the theoretical treatment of how the driving force determines the rate of a process and how simultaneous processes can affect each other. This field is usually defined as irreversible thermodynamics. The mathematical description of diffusion is an important application for materials science and is given special attention in those two new chapters. Extremum principles are also discussed.

A third new chapter is devoted to the thermodynamics of surfaces and interfaces. The different roles of surface energy and surface stress in solids are explained in detail, including a treatment of critical nuclei. The thermodynamic effects of different types of coherency stresses are outlined and the effect of segregated atoms on the migration of interfaces, so-called solute drag, is discussed using a general treatment applicable to grain boundaries and phase interfaces.

The three new chapters are the results of long and intensive discussions and collaboration with Professor John Ågren and could not have been written without that input. Thanks are also due to several researchers in his department who have been extremely open to discussions and even collaboration. In particular, thanks are due to Dr Malin Selleby who has again given invaluable input by providing the large number of computer-calculated diagrams. They are easily recognized by the triangular *Thermo-Calc* logotype. Those diagrams demonstrate that thermodynamic equations can be directly applied without any new programming. The author hopes that the present textbook will inspire scientists and engineers, professors and students to more frequent use of thermodynamics to solve problems in materials science.

A large number of solved exercises are also available online from the Cambridge University Press website (www.cambridge.org/9780521853514). In addition, the website contains a considerable number of exercises to be solved by the reader using a link to a limited free-of-charge version of the commercial thermodynamic package Thermo-Calc. In principle, they could be solved on a similar thermodynamic package.

Preface to first edition

Thermodynamics is an extremely powerful tool applicable to a wide range of science and technology. However, its full potential has been utilized by relatively few experts and the practical application of thermodynamics has often been based simply on dilute solutions and the law of mass action. In materials science the main use of thermodynamics has taken place indirectly through phase diagrams. These are based on thermodynamic principles but, traditionally, their determination and construction have not made use of thermodynamic calculations, nor have they been used fully in solving practical problems. It is my impression that the role of thermodynamics in the teaching of science and technology has been declining in many faculties during the last few decades, and for good reasons. The students experience thermodynamics as an abstract and difficult subject and very few of them expect to put it to practical use in their future career.

Today we see a drastic change of this situation which should result in a dramatic increase of the use of thermodynamics in many fields. It may result in thermodynamics regaining its traditional role in teaching. The new situation is caused by the development both of computer-operated programs for sophisticated equilibrium calculations and extensive databases containing assessed thermodynamic parameter values for individual phases from which all thermodynamic properties can be calculated. Experts are needed to develop the mathematical models and to derive the numerical values of all the model parameters from experimental information. However, once the fundamental equations are available, it will be possible for engineers with limited experience to make full use of thermodynamic calculations in solving a variety of complicated technical problems. In order to do this, it will not be necessary to remember much from a traditional course in thermodynamics. Nevertheless, in order to use the full potential of the new facilities and to avoid making mistakes, it is still desirable to have a good understanding of the basic principles of thermodynamics. The present book has been written with this new situation in mind. It does not provide the reader with much background in numerical calculation but should give him/her a solid basis for an understanding of the thermodynamic principles behind a problem, help him/her to present the problem to the computer and allow him/her to interpret the computer results.

The principles of thermodynamics were developed in an admirably logical way by Gibbs but he only considered equilibria. It has since been demonstrated, e.g. by Prigogine and Defay, that classical thermodynamics can also be applied to systems not at equilibrium whereby the affinity (or driving force) for an internal process is evaluated as an ordinary thermodynamic quantity. I have followed that approach by introducing a

clear distinction between external variables and internal variables referring to entropy-producing internal processes. The entropy production is retained when the first and second laws are combined and the driving force for internal processes then plays a central role throughout the development of the thermodynamic principles. In this way, the driving force appears as a natural part of the thermodynamic application 'tool'.

Computerized calculations of equilibria can easily be directed to yield various types of diagram, and phase diagrams are among the most useful. The computer provides the user with considerable freedom of choice of axis variables and in the sectioning and projection of a multicomponent system, which is necessary for producing a two-dimensional diagram. In order to make good use of this facility, one should be familiar with the general principles of phase diagrams. Thus, a considerable part of the present book is devoted to the inter-relations between thermodynamics and phase diagrams. Phase diagrams are also used to illustrate the character of various types of phase transformations. My ambition has been to demonstrate the important role played by thermodynamics in the study of phase transformations.

I have tried to develop thermodynamics without involving the special properties of particular kinds of phases, but have found it necessary sometimes to use the ideal gas or the regular solution to illustrate principles. However, even though thermodynamic models and derived model parameters are already stored in databases, and can be used without the need to inspect them, it is advantageous to have some understanding of thermodynamic modelling. The last few chapters are thus devoted to this subject. Simple models are discussed, not because they are the most useful or popular, but rather as illustrations of how modelling is performed.

Many sections may give the reader little stimulation but may be valuable as reference material for later parts of the book or for future work involving thermodynamic applications. The reader is advised to peruse such sections very quickly, but to remember that this material is available for future consultation.

Practically every section ends with at least one exercise and the accompanying solution. These exercises often contain material that could have been included in the text, but would have made the text too massive. The reader is advised not to study such exercises until a more thorough understanding of the content of a particular section is required.

This book is the result of a long period of research and teaching, centred on thermodynamic applications in materials science. It could not have been written without the inspiration and help received through contacts with numerous students and colleagues. Special thanks are due to my former students, Professor Bo Sundman and Docent Bo Jansson, whose development of the Thermo-Calc data bank system has inspired me to penetrate the underlying thermodynamic principles and has made me aware of many important questions. Thanks are also due to Dr Malin Selleby for producing a large number of diagrams by skilful operation of Thermo-Calc. All her diagrams in this book can be identified by the use of the Thermo-Calc logotype,  .

Mats Hillert
Stockholm

Contents