Phase Equilibria, Phase Diagrams and Phase Transformations

Second Edition

Thermodynamic principles are central to understanding material behaviour, particularly as the application of these concepts underpins phase equilibrium, transformation and state. While this is a complex and challenging area, the use of computational tools has allowed the materials scientist to model and analyse increasingly convoluted systems more readily. In order to use and interpret such models and computed results accurately, a strong understanding of the basic thermodynamics is required.

This fully revised and updated edition covers the fundamentals of thermodynamics, with a view to modern computer applications. The theoretical basis of chemical equilibria and chemical changes is covered with an emphasis on the properties of phase diagrams. Starting with the basic principles, discussion moves to systems involving multiple phases. New chapters cover irreversible thermodynamics, extremum principles and the thermodynamics of surfaces and interfaces. Theoretical descriptions of equilibrium conditions, the state of systems at equilibrium and the changes as equilibrium is reached, are all demonstrated graphically. With illustrative examples – many computer calculated – and exercises with solutions, this textbook is a valuable resource for advanced undergraduate and graduate students in materials science and engineering.

Additional information on this title, including further exercises and solutions, is available at www.cambridge.org/9780521853514. The commercial thermodynamic package ‘Thermo-Calc’ is used throughout the book for computer applications; a link to a limited free of charge version can be found at the above website and can be used to solve the further exercises. In principle, however, a similar thermodynamic package can be used.

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Phase Equilibria, Phase Diagrams and Phase Transformations

Their Thermodynamic Basis

Second Edition

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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, ⚠.

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