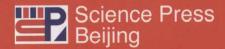Muyu Zhao

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（相图边界理论及其应用）

The Boundary Theory of Phase Diagrams and Its Application

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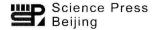
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With 72 figures

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Printed on acid-free paper

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The Boundary Theory of Phase Diagrams and Its Application
Rules for Phase Diagram Construction with Phase Regions and Their Boundaries

Preface

The phase diagram is one of the most extensively used disciplines in the Applied Sciences. They are relevant to different areas both in science and engineering, as well as to the various branches of the national economy. In many scientific and technical specialties, such as physics, chemistry, geology, materials science and technology, chemical engineering, *etc,* it is easy to find its application that strongly shows the importance of phase diagram in the science and technology today.

In the early stages of development, phase diagrams were mainly obtained from experimental measurements. With the increasing number of the system components as well as the severe demands placed on experimental materials requiring corrosion-resistant, heat-resistant, *etc,* the experimental methods were no longer able to meet these requirements, especially with respect to generating multi-component phase diagrams. The theoretical calculation of phase diagram has now become the principal method for obtaining the desired phase diagrams. This route has been especially favored by the rapid advance of research and development in computer science and technology that induced the "art" of phase diagram calculation to a new level. Under these circumstances, the continuing research on the theory of phase diagrams has recently and naturally becomes the topic of great and lasting interest, to both applied scientists and engineers alike.

Research on the theory of phase diagrams may be divided into two categories. The first category involves the research needed to study the necessary conditions that all phase diagrams must satisfy. For instance, abstracting the physical concepts from concrete phase diagrams such as the specific number of phases, the number of independent components, the degrees of freedom, *etc;* and then establishing the relationship between these parameters belong the first category work, though, that can not be used to construct a specific phase diagram, they are strict and absolute and give an universal principle in evaluating a particular phase diagram obtained from experiments. Any phase diagram violating this relationship must be incorrect. The second category of theory concerns the sufficient conditions for a concrete phase diagram; they study the quantitative relation of the thermodynamic properties of each component in specific phase equilibrium with temperature, pressure and composition, *etc.* Based on this quantitative relation, a complete and specific phase diagram can be constructed. This particular topic has attracted many scientists and researchers devoting their efforts in this subject

over recent years. The combination of these two category theories has constituted a whole theory of phase diagram.

The great thermodynamic and statistical physicist Josiah Willard Gibbs, was the founder of the theory of the first category. The "phase rule" derived by him is a typical classic work in this aspect. After Gibbs, many scientists, for example, Palatnik and Landau, and various other scholars engaged in the research undertaken by this circle, achieved some success. The great scientist and the founder of solid state chemistry, Carl Wagner, was the pioneer of the theory for the second category. Early in those years, in which the computer was becoming developed, he had pointed to the importance of studying the relation between the phase diagrams and the materials thermodynamic properties. The relation existing between the phase boundaries and the corresponding thermodynamic properties, as deduced by him, are still extensively applied today. Other scientists, for example, Hildebrand, Mitering, Richardson, *et al.*, have also made important contributions. The CALPHAD technology has played a great role for promoting the calculation of phase diagrams. It is worthy mentioning that the Chinese scholars have also made some significant contribution in both of these two category works that shouldn't be ignored.

Through his deep level research over several decades, Professor Muyu Zhao has made a significant contribution to the research on the theory of phase diagrams. For the theory of the first category, he has systematically deduced new ideas, derived a series of new relation, constructed a whole and unique systematic theory, and applied it to real phase diagrams, obtaining good results in the process. In addition to this considerable task, he has also undertaken many pioneering works, involving both experimental and theoretical research on high pressure phase diagrams.

In his book *The Boundary Theory of Phase Diagrams and Its Application*, Professor Muyu Zhao has collected the results of his research over several decades, and presented them systematically and completely, as his substantial theoretical works. Besides this work on the theory of the first category, as mentioned above, this book also contains the contents and related works on the second category. We sincerely hope that the publication of this book will bring some new energy to the phase diagram research.

Kuo-Chih Chou

Professor, University of Science and Technology Beijing
Member of Chinese Academy of Sciences

Beijing, 18 January 2008

Comment

There are two main rules governing the construction and interpretation of phase diagrams, the phase rule by Gibbs and the contact rule by Palatnik and Landau. Many years ago professor Muyu Zhao was intrigued by the fact that both rules need special instructions when applied to mixed phase diagrams, *i.e.*, diagrams with both potential and molar axes. This has caused much confusion for generations of students of materials science and has forced teachers to invent explanations that can be criticized by observant students. It is evident that there is a considerable need for better understanding of these difficulties. The reason of the difficulties is that the phase rule is strictly valid for diagrams with only potential axes and the contact rule for diagrams with only molar axes. In practice, it is more common to use a mixture of axes, *e.g.* the temperature-mole fraction diagrams, which is the type the students are first confronted with.

Professor Zhao has devoted many years of interest and energy to resolve these difficulties and he is to be congratulated finally to be able to present his results in a monograph that will give a wider audience a chance to get a coherent picture of his work.

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Stockholm, 16 March 2008

Introduction

Phase diagrams are among the most extensively used guides in materials science and engineering, and constitute the basic roadmap for alloy designers.

In its simple form, phase diagram consists of phase regions and their boundaries. The aim of the present text is to discuss the problem of how the phase regions and their boundaries compose a phase diagram.

We have studied the relationship among neighboring phase regions and their boundaries for nearly thirty years. Over this time, a few new concepts have been introduced, and, by application of the relevant thermodynamic principles, a systematic boundary theory of phase diagrams has been worked out. In this approach, all the relationships among the neighboring phase regions and their boundaries, for both simple and more complex, multicomponent phase diagrams, of all types, can be satisfactorily explained by reference to the so called "The boundary theory".

In this book, we contribute the most volume to discuss the isobaric T-x_i phase diagrams. However, with the generalized boundary theory for the p-T-x_i multicomponent phase diagram, this theory is easily to apply in p-T phase diagrams and those diagrams with only mole fraction axes. In the p-T-x_i multicomponent phase diagram, if we keep the pressure and temperature constant, or keep the compositions invariable, it will be the "pure" mole fraction-mole fraction, or potential P-T axes phase diagram. We have discussed these problems in Chapter 3, section 3.6 and Chapter 9, sections 9.2 and 9.3.

Moreover, we have found that there is a lot of application for the boundary theory, and thus we have written a substantial chapter to discuss the important application. In that chapter, the use of the boundary theory of phase diagrams in some specific roles, *e.g.* calculation, determination, assessment and comprehension of phase diagrams, is discussed. Based on the boundary theory, we have designed a new method for the determination of the multicomponent isothermal sections (see Chapter 7, section 7.5).

Professors at several universities in China have taught the boundary theory and its application, in those courses concerned with the phase diagram theory and its practice. One of these professors has told the author of this book: "The students are interested in this theory and, $\cdots$ via its application in some representative examples, are able to learn much from it."

Thus, in this book, we have specially concentrated on and discussed the follow-

ing 6 points:

1. We discriminate the conception of "phase point" and "system point" in phase diagrams, and find the "phase boundary", besides the "boundary" in common sense, is a real entity within the phase diagrams (see Chapter 2, subsection 2.2.8). Based on this concept and on other thermodynamic principles, we may proceed to construct a boundary theory of phase diagrams.

2. There is a certain relationship between the dimension of phase boundary and the number of total different phases in neighboring phase regions. A theorem describes this relationship. We clearly demonstrate that the "theorem of the corresponding relationship" (TCR) is indeed a fully independent theorem, and is not a variation of the phase rule (see Chapter 2, section 2.4).

3. Two equations of the relation among the dimensions of the phase boundary and the dimensions of the boundary are derived. This is the "boundary theory", the very core of this monograph, which explains well the different types of phase transitions within phase diagram. Thence, the rule of how the phase regions compose a phase diagram has been expounded (see Chapter 2, section 2.6).

4. We have compared the differences between the Palatnik-Landau's "contact rule" for the phase regions, and the "boundary theory" in details (see Chapter 3, section 3.6) and conclusions of the added value of the boundary theory can be appreciated.

5. Gupta's overlapping ZPF (Zero Phase Fraction) lines method for the construction of multicomponent isothermal sections, with limited information, is a very important method and widely applied in phase diagram calculation. The boundary theory, on the other hand, provides an alternative under the same circumstance (see Chapter 5, sections 5.3 and 5.4). To determine experimentally isothermal multicomponent sections, the boundary theory may be more useful (see Chapter 5, section 5.5). Based on the boundary theory, we have designed a new method to determine isothermal multicomponent sections (see Chapter 7, section 7.5).

6. A more general boundary theory of the multi-component p-T-x_i phase diagrams is described in Chapter 8. Applying this theory, we have worked out a thermodynamic method for calculating the multicomponent, high-pressure phase diagrams. We have been able to calculate high-pressure phase diagrams not only for binary, but also ternary alloys. The high pressure (up to several GPa) phase diagrams of the Cd-Pb-Sn and Cd-Sn-Zn systems are calculated, and verified by reference to the experimentally derived phase diagrams. These calculated high-pressure binary and ternary alloy phase diagrams agree well with the experimentally derived ones (see Chapters 8, 9, 10 and 11).

When we finally finished this book and could communicate our readers with our research results, we would like to offer our sincere thanks to all the graduate students who involved in this work: Drs Weiya Zhou, Ping Xiao, and Zezhong Fu, they did most of the calculations and/or determination of phase diagrams relevant to the boundary theory. We offer our sincere thanks to Professor Zhongyi Shen (Institute of Physics, Beijing, Chinese Academy of Sciences), for his cooperation in the high-pressure phase diagram experiments; to Professor Guanghui Rao (Institute of Physics, Beijing, Chinese Academy of Sciences), for helping me to prepare a manuscript in the early time, to Mr. Hai Huang (Science Press, Beijing), for helping us to publish this work.

Our special gratitude goes to Professor Mats Hillert (Royal Institute of Technology in Stockholm, Sweden) for his attention to and recognition of this work, and discussion with us on boundary theory over a long time; to Dr. Patrice E. A. Turchi (LLNL, Livermore, USA) for his appreciation of our work and valuable advices; and to Dr. Peter G. Lanigan (Researcher and writer, University of Sherbrooke, Canada), who gave his kind help and encouragement as a veteran industrial researcher in chemistry and metallurgy, particularly for his patient proof-reading and "text polishing" over the whole book.

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Part One
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