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Phase Diagrams of Precious Metal Alloys and Structure Parameters of Precious Metal Compounds

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Foreword

The author's original intention for the compilation of the Chinese edition of the monograph *Phase Diagrams of Precious Metal Alloys and Structure Parameters of Precious Metals Compounds* was to provide for Chinese readers an overall, convenient and high speed searched, and reliable data including alloy phase diagrams and structure parameters of the eight elements of precious metals. This monograph has been published by Metallurgical Industry Press in January 2007.

Its publication evoked strong repercussions in the worldwide scientific circles. Academician of Academy of Sciences of China, Professor Liang Jingkui of Physical Research Institute of Academy of Sciences of China, said in his letter to the authors, "this monograph gives an important help for the research workers engaging in the investigation on the phase diagrams and metallic materials". Academician of Academy of Engineering of China, Professor Dai Yongnian of Kunming University of Science and Technology also said in his letter to the authors ,"the publication of this monograph has great significant for the readers both in China and abroad," and "this monograph involves detailed and complete data, the selection of which is conscientious, and it has full and reliable data." Professor Dai Yongnian said, this monograph could be used as an essential book in their desks of scholars in the scientific circle of phase diagraph, conveniently use it and consult it. Dr. V. Vasekin, academician of the II A and the Chief Manager of FSUE NPK "Supermetal", Russia, wrote in his letter to the authors, "the book is just global and of huge interest for experts" and "your monograph is going to be a practical manual for experts of Supermetal, as well as for many other experts developing new alloys on the basis of precious metals."

In the course of the translation, in addition to the translation of the monograph from Chinese to English, we put the stress on the following two things: firstly, we added some phase diagrams and parameters of compounds of precious metals reported recently, most of which were added in Chapter 2, Chapter 3, Chapter 4, and Chapter 5. Secondary, we think that because the three books of *Ternary alloy* Vol. 1 and Vol. 2 edited by Petzow G. and Effenberg G., and *Phase Diagrams of Ternary Gold Alloy* edited by A. Prince G. V. Raynor and D.S. Evans can be conveniently obtained by readers outside of China, therefore a series of projections were omitted but their systems were remained in this English edition. If readers want to obtain the projections, they can reference above three books. In addition to these, most of the contents in the English edition keep the same with its Chinese edition.

In the Chinese edition of the monograph, it involves 1080 systems and 2126 phase diagrams of precious metal alloys, including 403 systems and 416 phase diagrams of binary precious metal alloys; 621 systems and 1572 phase diagrams of ternary precious metal alloys; and 56 systems and 138 phase diagrams of multi-component precious metal alloys. By the complement and revision, this book includes 1109 systems and 1662 phase diagrams, including 406 systems and 424 phase diagrams of binary precious metal alloys, 645 systems and 1095 phase diagrams of ternary precious metal alloys, and 58 systems and 143 phase diagrams of multi-component precious metal alloys. At the same time, 29 binary compounds of 10 binary systems and 61 ternary compounds of 17 ternary systems were added, so 3722 compounds in total and their structure parameters were given in this English edition.

This book was translated by the authors and checked by the material expert, Professor Zhang Yongli, of Kunming Institute of Precious Metals, China. Here the authors are very glad to express our many thanks to Professor Zhang Yongli for her hard work.

We are very glad to express our thanks again to Kunming Institute of Precious Metals, China, for his support and encouragement during the publication both the Chinese edition and English edition.

The authors are willing to do our best to compile the monograph reliably, correctly and completely. But we know that it cannot be avoided that there are some disadvantages in it, and we hope you give us helpful suggestions.

Authors
December, 2007

Introduction

Materials, energy sources and information technology are the three mainstays of modern civilization generally recognized in the world. It can be seen from the history of modern science and technology that an invention of each new technique largely depends on the development of new materials. We can say that materials are milestones in the humanity progress. All the practical metallic materials (involving structural and functional materials) consist of more than two (including two) elements. The properties of these materials depend on their composition and working process. Alloy phase diagram is one of the important theoretic bases for the investigation of materials, and one of the important fields for the investigation of materials as well.

Phase diagram is a graph showing the phase equilibrium for a substance system. As a graph for the macro laws, phase diagram reflects the microstructure variation of material. The well-known metallurgist, Professor John F. Elliott in Massachusetts Institute of Technology likened the phase diagrams to the "road maps" that guide and direct metallurgists to their numerous goals—in fabrication, development, heat treatment properties, alloy design, and basic understanding. Due to the properties of materials deeply depend upon the phase number, phase proportion, phase type and phase property, so it was said that in the study of materials, the phase diagram and multi-phase structural analysis are two useful walking sticks. The properties of phase variation, such as phase formation, phase decomposition and phase change, affect materials properties greatly. The phase diagram is a real tool to provide the information mentioned above. Defining the phase diagram for an alloy, understanding the phase structure, phase relationship and phase properties are important of guiding significance to explore the material potential and to develop new materials.

In the past more than one hundred years, as people started on the investigation of phase diagrams, the investigation of phase diagrams has been an active field. In recent 15 to 20 years, the phase diagram science has developed rapidly towards two sub-areas: the experimentally determined phase diagram and calculated phase diagram.

The former is the most important and the basic method to obtain phase diagrams. The determination technology is quite perfect. The calculated phase diagram is developed progressively with the progress of the computer. The calculated phase diagram can be classified into two categories: the semi-empirically calculated phase diagram and the theoretically calculated phase diagram. Recently, the method of semi-empirically thermodynamically calculated phase diagram is ripe relatively. Other methods of semi-empirically calculated phase diagram, including Artificial Neural Network and Atomic Parameters, are developing. The theoretically calculated phase diagram by the First Principles is a comparative complex method with a certain error. However, it has been improved considerably and is developing as well.

The basic theory of phase diagrams is the Phase Rule established by Gibbs about one hundred years ago. At present, the Phase Rule is applied to summarize various phenomenon on the phase equilibrium and regulations, and to recognize the inter-relationship in different equilibrium systems, and at the same time it is a helpful guide for the investigation on the unknown equilibrium systems. However, the Phase Rule can only be used to determine the relationship between the number of components, the number of phases and degree of freedom rather than to define the relationship and rules in neighboring phase regions or their boundaries.

Professor Zhao Muyu in Jilin University, China, advanced a new theory—the Boundary Theory of Phase Diagrams to reveal how to construct an isobaric phase diagram with the phase regions and their boundaries in a system. It explained the relationship between the neighboring phase regions and their boundaries in different types of isobaric phase diagrams; concluded the empirical regulations and theory laws; deduced the calculation formulas for binary and ternary isobaric phase diagrams and calculated them. It can be used to construct roughly the quaternary, even more components horizontal sections under insufficient conditions. This new theory has been commended and recognized by the worldwide scientists in the field of phase diagrams. The book will introduce its theoretical results in detail.

Up to now, hundreds of publications dealing with phase diagrams and relative data were published (see *Bulletin of Alloy Phase Diagrams*, 1983, 3(4),413-415), and among them, the most important one is *Constitution of Binary Alloy* (1958) edited by Hansen and his coworkers, and its two supplements edited by Elliott (1965) and Shunk (1969), respectively. *Binary Alloy Phase Diagrams* (1990) in three volumes edited by Massalski and his coworkers and *Handbook of Ternary Phase Diagrams* (1995) in ten volumes edited by Villas and his coworkers are the another two significant compilations published recently. In addition, over 20 books on binary and ternary alloy phase diagrams for special metals were assessed by experts of Alloy Phase Diagram International Commission and published. But not any monograph on quaternary alloy phase diagrams has been published until now, except that for theoretic analysis. *Phase Diagrams of the Metal Systems* (with 40 issues) edited by the Institute of Science and Technology Information in former SSSR and Russia and published from 1955 to 1996 is a significant reference to obtain recent research achievements. In 1987, Professor Yu Jueqi et al., in Hunan University, China, compiled *Constitutional Graphs on Binary Alloys* which completely collects dada of binary alloy phase diagrams.

Unfortunately, monographs on phase diagrams of precious metal alloys are very few. The book *Platinum Metals and Their Alloys* edited by E. M. Wise in 1942 is the earliest monograph on binary alloy phase diagrams of platinum metals, where less than 20 phase diagrams were involved. During the 1960s to the 1980s, several monographs on phase diagrams of precious metal alloys were compiled and published by former SSSR, including *Благододоны меаллы справочник* edited by E.M. Savitskii (the first edition was published in 1984) and its English issue *Handbook of Precious Metals*, which collects a large number of phase diagrams of precious metal alloys. It is worth to pay close attention to that a series of monographs on precious metal alloy phase diagrams were compiled and published by Alloy Phase Diagram International Commission, such as *Ternary Alloys*, Vol. 1 (Ag-Al-Cu to Ag-Cu-P) (1988) and Vol.2 (Ag-Cu-P to Ag-Zn-Zr) (1988) edited by G. Petzow and his coworkers; *Phase Diagrams of Binary Gold Alloys* edited by H. Okamoto and his coworkers; *Phase Diagrams of Ternary Gold Alloys* edited by A. Prince and his coworkers. In China, two important monographs on precious metal alloy phase diagrams, *Phase Diagrams of Precious Metal Alloys* (in Chinese and English) and *Phase Diagrams of Precious Metal Alloys First Supplement* (1976—1985), were compiled and published in 1983 and 1993, respectively by Professor He Chunxiao and his coworkers of Kunming Institute of Precious Metals, China, *Phase Diagrams of Precious Metal Alloys* gathered 520 binary, ternary and quaternary alloy systems of the 8 elements of precious metals reported before 1975. These two books collected 754 alloy systems of precious metal phase diagrams. It may be said that these books are the first two about precious metal alloy phase diagrams in the world.

Since 1980, alloy phase diagrams of about 5000 binary and ternary systems have been assessed by experts invited by Alloy Phase Diagram International Commission including more than 1000 systems of precious metal alloy phase diagrams. It is believed that these phase diagrams are relatively reliable. It is a very significant achievement and a great contribution to the material science. However, a large number of phase diagrams were reported in various publications, such as *Bulletin of Alloy Phase Diagrams, Journal of Phase Equlibria, Journal of Phase Equlibria and Diffusion* (from 2004), and *Journal of Alloy Phase Diagrams* and so on. As a result, it is very inconvenient to apply these phase diagrams. For the phase diagrams that have not been evaluated, we agree the opinion of H.Okamoto and T.B. Massalski, who said that a "suspect phase diagram" or even a "partially wrong phase diagram" may be better that "no diagram" (see Journal of Phase Equilibria, 1994,15(5), 500-521).

Precious metal materials possess the unique properties and higher prices. Therefore, it is used only in the cases that the non-precious metal materials can not meet the requirements for special properties. Investigation, collection and collation of the precious metal alloy phase diagrams are particularly significant to excavate the potential of precious metal materials and to develop the novel precious metal materials, and it is an important fundamental assignment.

In order to make scientists and technologists to conveniently use phase diagrams of precious metal alloys, Li Guanfang, He Chunxiao, Luo Yanbo and Li Yanan of Kunming Institute of Precious Metals, China, undertook the constitution of *Database of Precious Metals Alloy Phase Diagrams* in 1997 under the support of Natural Science Fund of Yunnan Province, China. The project was completed in Oct., 2000 and corresponding CD-Room was produced for the restrict application. In order that the extensive researchers in the field of precious metal alloy phase diagrams and the scientists and technologists in the field of materials in the world could use the data easily, the authors compiled the present monograph, *Phase Diagrams of Precious Metal Alloys and Structure Parameters of Precious Metals Compounds*, according to the *Database of Precious Metals Alloy Phase Diagrams*. This work was completed under the encouragement of Metallurgy Industry Press, Beijing, China, and the support of Kunming Institute of Precious Metals, China. This monograph combined the authors'experiences during the investigation on precious metal alloy phase diagrams for many years, especially collected and systemized the achievements in China, including those in Kunming Institute of Precious Metals and the achievements of Prof. He Chunxiao himself.

The main differences between the monograph, *Phase Diagrams of Precious Metal Alloys and Structure Parameters of Precious Metals Compounds*, and *Database of Precious Metals Alloy Phase Diagrams* (*Database* for short) are as follows. For the *Database* it contented the number of alloy, number of figure, phase diagram, composition of experimental materials, range studied, method of experiment, compound and its structure parameters and references, et al. The data and storage were carried out strictly according to the working table. In the *Database* all types of phase diagrams were collected whether it was experimental phase diagrams or calculated phase diagrams, or it was achieved by different authors. But in the present monograph only the alloy systems with phase diagrams, mainly the experimental phase diagrams, were collected, and their calculated phase diagrams were generally not involved. The partial amplified figures in the *Database* were omitted in this monograph. Readers can refer to original copies if necessary. Some disadvantages in the *Database* were corrected and a certain number of phase diagrams were added, and the coordinates in the phase diagrams were unified according to the national standards to make the monograph having better suitability and accuracy.

The present monograph collected the alloy phase diagrams of the eight elements of precious metals (platinum, palladium, rhodium, iridium, osmium, ruthenium, gold and silver), and the structure parameters of the precious metal compounds reported before 1996 and assessed or corrected before 2007 (including 2007), the achievements reported by researchers in China before 2004 were also involved in it. 1109 systems, 1662 phase diagrams of precious metal alloys and 3722 precious metal compounds were included in the monograph. It consisted of the following five chapters: chapter 1 Phase Diagrams of Precious Metal Binary Alloys with 406 systems and 424 figures; chapter 2 Phase Diagrams of Precious Metal Ternary Alloys with 645 systems and 1095 figures; chapter 3 Phase Diagrams of Precious Metal Multi-component Alloys with 58 systems and 143 figures;chapter 4 Binary Compounds of Precious Metals and Their Structure Parameters and chapter 5 Ternary Compounds of Precious Metals and Their Structure Parameters. In addition, an Introduction and 4 appendixes including Appendix 1 Contrast of Abbreviations of Partial References Cited in the Monograph and Their Corresponding Full Titles, Appendix 2 Conversion of the Mass Percentage to Mole Percentage and Vice Versa for Binary Systems, Appendix 3 Conversion of the Mass Percentage to Mole Percentage and Vice Versa for Ternary Systems and Appendix 4 Conversion of the Mole Percentage to Atom Percentage and Vice Versa for Pseudo-binary Systems, and an Index of Phase Diagrams, were also given. A short Introduction was put in front of every chapter to introduce the fundamental conceptions, present investigation situation and development approaches for references. Structure parameters of precious metal compounds contained the alloy system, name of phase, chemical formula, crystal structure, structure symbol, prototype, Pearson symbol, lattice parameter and reference. All the data were checked with those in ICDD and selected. The phase diagrams and the compounds were arranged alphabetically for readers to easily search.

The following principles are complied with during the collection and selection:

(1) "Complete".It means that the alloy systems in the monograph are relatively complete. Binary, ternary, quaternary and multi-component precious metal systems and structure parameters of compounds were all involved. Especially, it reflects the research achievements produced by Chinese research workers in the field of phase diagrams of precious metals (up to the beginning of the year of 2005).

(2) "Accuracy". It means that under the requirement of "complete"the data were relatively accurate. The authors believed that the phase diagrams assessed by experts invited by Alloy Phase Diagram International Commission are certainly reliable, and these phase diagrams are selected firstly. Of cause, the phase diagrams collected will be modified and supplemented in the future with the development of science and technology.

(3) "New". It means that under the requirement of "complete". The reassessed or the nearest reported data were selected.

(4) For the system with both experimental and calculated phase diagrams, it was preferred to select the experimental phase diagram. Besides, the reference for every phase diagram and compound was given for readers to learn more information.

Another distinguishing feature of this monograph is that the recently reported theories and rules are introduced and summarized in the Introduction of corresponding chapters. May be, readers will interested in them.

Most of the data in the monograph were cited from literatures and relative compilations in the world, especially those edited by H. Okamoto, T. B. Massalski, G. Petzow, G. Effenberg, A. Prence, G. V. Rener, D. S. Evans and E. M. Savitskii, some of the data were quoted from the secondary references *Phase Diagrams of the Metal Systems* and other journals or books. Professor V. Vasakin and Vitali Poulikov in "Supermetal", Russia, presented us a lot of valuable Russian information, and Beijing National Library and Beijing Science and Technology University provided useful original literatures to us. The authors express our grateful thanks to them for their help. In addition, we will give our many thanks to Yunnan Province Natural Science Fund Committee and Kunming Institute of Precious Metals, China, for their support, concern and helps. Particularly, we express heartfelt gratitude to Kunming Institute of Precious Metals, China, for active leading and organization. Finally, the thanks will be given to Metallurgy Industry Press for his hard work during the publication of this monograph.

The compile work of this monograph was divided as follows: He Chunxiao was in charge of writing the introduction, the introductions of chapter 1, 3, 4 and 5, and collection of phase diagrams in chapter 3; Li Guanfang was in charge of the writing of introductions of chapter 2, and collection of phase diagrams in chapter 2 and 5, inaddition she took part in the collection and the edition of this monograph. Luo Yanbo was in charge of collection of chapter 1 and 4, and Li Yanan was in charge of design of the software for the *Database of Precious Metals Alloy Phase Diagrams*. Chen Liangwei was in charge of addition and correction of the data of the compounds. The correction, arrangement and finalization of the manuscript were carried out by He Chunxiao.

The authors are willing to do our best to compile the monograph reliably, correctly and completely. But we know that it cannot be avoided that there are some disadvantages in it, and we hope you give us helpful suggestions.

Authors
May, 2005

Contents

Phase Diagrams of Precious Metal Binary Alloys 1

The fundamental conceptions were introduced. The theory of phase diagrams was introduced with the emphasis on the Boundary Theory of Phase Diagrams—Rules for Phase Diagrams Construction with Phase Regions and Their Boundaries. The expression of coordinate in phase diagram, the expression of intermediate phases and the calculation and prediction of phase diagrams were presented. The experimental determination of phase diagram was introduced. The reliability of phase diagrams was discussed. The present research situation on phase diagrams of precious metal binary alloys was briefly analyzed. It was concluded that several regulations between the construction of phase diagrams of precious metal binary alloys with the position of the elements in the Periodical Table and the Mendeleev number were existed. 406 systems and 424 phase diagrams of binary precious metal alloys were given.

1. 1 Introduction

1.1.1 Fundamental conception and phase diagram theory

Phase diagram is a geometric description of component, substance phase and interaction of external conditions for one system existing under equilibrium conditions.

In the discussion of thermodynamics, a system means the collection of substances which are separated from the environment and contended in a defined boundaries (the substance number could be more or less). In other words, it is a part of "isolated" substance selected in any way as one object to be studied. The "isolation" means that the quantity of the substance selected as the object to be studied and its composition keep constant. When one or more than one kind of substances are closed to study their changes under certain environmental conditions, then this one or more than one substances compose a system.

Any systems consist of chemical substances more or less, such as various elements or compounds, and these chemical substances are called constitute. However, it does not mean constitute is always independent. Some constitutes may be produced by the chemical reactions of different constitutes in the system. In one system, constitute which can change independently is called a component. The number of the component in a system is the minimum number of constitute needed for each phase and independently changing in the constructed equilibrium system. If one system consists of only one component, the system is called a single component system; if it consists of two components, this system is called binary system. The rest may be deduced by analogy.

A phase means a homogeneous part in physical and chemical properties in a system. Different phases are divided by interface. Every phase has its own characteristics, and at least it can be distinguished theoretically from the other parts in the system. A phase can be either a simple substance or a mixture of several substances. A gas phase consisting of either one kind of gas or a mixture of several kinds of gases is always a single phase substance. For the liquid, the homogeneous liquid (such as unsaturated sugar solution or salt solution) is a single phase as well, except the component in the liquid are immiscible. A solid solution is a homogeneous solid with the same physical and chemical properties, which is produced by the dissolution of one or more substances in anther substance. For example, the Pt-Rh alloy and Os-Ru alloy belong to the single phase. But when the same one substance possesses variety states and crystal structures under different temperatures and pressures, in those cases it dose not belong to the same phase but to the different phases.

The environmental conditions include temperature, pressure, electric field, magnetic field, attraction field and so on. In addition to the temperature and pressure, the other conditions do not or in less certain affect equilibrium of two phases.

If the properties of one system do not change with the time, in other words, the change rates of two or more than two types of phases are the same, in this case, this system is in equilibrium state. In a multi-phase equilibrium system, the temperature and pressure of various phases in equilibrium state must be the same and at the same time the chemical potential of every component in the phase must be the same as well.

The degree of freedom is the number of independent variable in an equilibrium system under certain conditions, in other words, it is the minimum number of thermodynamic parameters that lead to neither increase nor decrease of the number of phase. The thermodynamic parameters involve composition and environmental conditions. For a single component system, the composition is not a variable, but for a binary system, one of the compositions is a variable, and for a ternary system two of the compositions are variables. The rest may be deduced by analogy.

The most important theoretical foundation for phase diagrams is the Phase Rule. It was established by the outstanding physicist J. Willard Gibbs in 1875 to 1878. The letter F is used to express the degree of freedom, C the number of component that construct the substance, P the number of phases of the substance. The Phase Rule could be express as the following formula under the influences of temperature and pressure:

$$F = C + 2 - P$$

Any substance systems in an equilibrium state must obey this rule.

When the degree of freedom is zero, one point may be drawn in a phase diagram; when the degree of freedom is 1, a line is drawn in a phase diagram; when the degree of freedom is 2, a region is drawn in a phase diagram.

In metals or alloys, generally liquid state and solid state are studied, but the state of gas is scarcely studied. This liquid or solid is called condensed state. In this case, the influence of pressure on temperature is so slight that it could be neglected. Even though ,when the variation of pressure is as large as several atmosphere pressures, the phase change point does not change much. In this case, the pressure could not be considered in the Phase Rule. Thus:

$$F = C + 1 - P$$

In analysis of phase diagrams of metals or alloys, the Phase Rule for the condense state is used. However, in recent years the investigation on high pressure materials is developed. In this case, the influence of pressure could not be neglected. The following formula must be applied:

$$F = C + 2 - P$$

The equilibrium of the conversion from a solid state to a liquid state is easy to be reached. But in the solid state, it needs very long time to reach the equilibrium, generally due to the slow diffusion rate of atoms in solids. Therefore, in most cases the discussion on phase diagrams is related to the phase relationship in a near equilibrium state.

Under a constant pressure, there are two independent parameters in binary phase diagrams: temperature and composition of one of components. One line coordinate is enough to express the composition in a binary system. Thus, a binary phase diagram is a plane figure.

Professor Zhao Muyu (Zhao, 1988; Zhao, Song,2004) pointed out that the Phase Rule could only be applied to treat the real thermodynamic system in a equilibrium state, and it is a qualitative rule rather than a quantitative one. The Phase Rule could only be used to study the relationship between the number of component, number of phase with degree of freedom, and it could not reflect the relationship and the regulation between the neighboring phase regions and their boundaries. Therefore, since the establish of the Phase Rule by Gibbs, a lot of investigations have been carried out by scientists leading to cumulate a series of empirical regulations and to deduce two general rules, they are the Gorden Boundary Rule (1986) and Palatnuk-Landau Phase Contact Rule. These two rules could not solve the problems theoretically because their disadvantages.

A phase diagram consists of several phase regions and their boundaries. How is a phase diagram constructed by the neighboring phase regions and their boundaries? It has its regulation. A system represented a point in a phase region could be either a system point or an equilibrium phase point. A system point (i.e. the representative point for a system under certain conditions in a phase diagram) is a phase point, which could occupy the whole space of the phase diagram. But an equilibrium phase point (i.e. the representative point for a phase under certain conditions in a phase diagram) exists only in the single phase region and its boundaries. System points and equilibrium phase points exist on the common boundaries of the neighboring phase regions. Thus, generally the so called boundary (i.e. the collection of system points to divide the neighboring phase regions) includes both the boundaries those connect each other but have differences between them and the phase boundaries. The collection of the equilibrium phase points of a system on the boundary is defined as a "boundary" by Professor Zhao Muyu.

Professor Zhao Muyu considered that for two neighboring phase regions with a common boundary, if the number of phases in the first phase region is Φ_1 and the number of phases in the neighboring second phase region is Φ_2, and the numbers of common phases existed in these two neighboring phase regions is Φ_c, thus the total number of distinct phase in two or more than two neighboring phase regions: $\Phi = \Phi_1 + \Phi_2 - \Phi_c$.

Professor Zhao Muyu introduced a new conception, in which a boundary region is divided into boundary and phase boundary, and the total number of the boundary phase and the number of the common phase in the neighboring phase regions are introduced. It is the most important conceptions to establish his Boundary Theory of Phase Diagrams. On the basis of these conceptions, he provided a systematic new theory through logical ratiocination and mathematical argument—the Boundary Theory of Phase Diagrams. It is named Correspondence Relation Theorem. As a result, the regulation of the construction of phase diagrams with phase regions and phase boundaries is found out.

The Correspondence Relation Theorem introduces the relationship between the dimension number R_1 of phase boundary with the total number of distinct phases, Φ, in neighboring phase regions. In the phase diagrams with independent variables of temperature, pressure and composition,

$$R_1 = (N - Z - r) - \Phi + 2$$

Where, N——the number of components;

Z——the number of independent limited conditions between the concentrations of every component in the equilibrium system beyond the condition of chemical equilibrium (not including the condition of $\sum_i X_{ij} = 1$, X_{ij} means the mole percent of the component i in the phase j);

r—— the number of independent chemical reactions in a equilibrium system.

In the phase diagrams under a constant pressure,

$$R_1 = (N - Z - r) - \Phi + 1 \qquad (1\text{-}1)$$

In general isobaric phase diagrams, $r = Z = 0$, thus the formula (1-1) could be written as $R_1 = N + 1 - \Phi$, if the value of Φ is known, the value of R_1 could be obtained.

It was proved by Professor Zhao Muyu that the Correspondence Relation Theorem is the similar in form to the Phase Rule, but they are different in substance. The former is an independent rule. It is because that the Correspondence Relation Theorem points out the corresponding relationship between the dimension number R_1 of phase boundaries with the total number Φ of distinct phases in neighboring phase regions surrounded the phase boundary. But the Phase Rule used for the systems on the boundary indicates the relationship between the degree of freedom, f, of the equilibrium system on the boundary with number of phase, ϕ, in equilibrium system. ϕ is the same with Φ only in the value, but their physical means are very different.

A series of deductions could be deduced by the combination of the Correspondence Relation Theorem with several basic characteristics, leading to determine the regulation of changes and the change ranges of Φ R_1 and ϕ_c, and the relationship between their values in isobaric phase diagrams.

Deduction 1 In any *P-T-X* phase diagrams, two neighboring phase regions involve at least two phases. It means the total number of phase in a system $\Phi \geqslant 2$. Then again, because of $R_1 \geqslant 0$, thus $(N - r - Z) + 2 \geqslant \Phi \geqslant 2$. In common phase diagrams, $Z = r = 0$, thus $N + 2 \geqslant \phi \geqslant 2$.

Deduction 2 In any *P-T-X* phase diagrams, the number of dimension of phase boundaries $R_1 \geqslant 0$. Then again, because of $\Phi \geqslant 2$, if $Z = r = 0$, thus $N \geqslant R_1 \geqslant 0$.

Deduction 3 When $N \geqslant 2$, then $Z=r=0$. In isobaric phase diagrams, if $R_1 = 0$, $\phi_c = 0$ for two neighboring phase regions, the following cases exist.

(1) "Every single-phase region intersects only at dividable common phase point".

(2) During the transition of two neighboring phase regions, if the number of common regions is $\Phi = \phi_{max} + 1 = N + 1$, thus $R_1 = 1$.

In addition, when $N \geqslant 2$, both the conditions of $R_1 \geqslant 1$ and $\phi_c \geqslant 1$ could be reached in general neighboring phase regions.

Deduction 4 In isobaric phase diagrams with $N \geqslant 2$ and $Z = r = 0$, if the number of phase boundaries for two neighboring phase regions $R_1 \geqslant 1$, thus $(\Phi - 1) \geqslant \phi_c \geqslant 1$.

Deduction 5 In isobaric phase diagrams with $N \geqslant 2$ and $Z=r=0$, when $R_1 = 0$, thus $(\Phi - 2) \geqslant \phi_c \geqslant 0$.

The boundaries existing on phase diagrams, especially on multi-component phase diagrams, mainly are the boundaries rather than the phase boundaries. When $N \geqslant 2$, ϕ_c is defined as the common phase number for neighboring phase regions, thus during the phase change, $R_1=0$. The maximum phase number in neighboring phase regions $\phi_{max} + 1$ equal to $N + 1$ phase coexisting regions, the mass of the system could be distributed in the ϕ_c common phases and in one of un-common phase. It was proved by Professor Zhao Muyu theoretically that the relationship between the number of dimension of boundaries, R_1' (i.e. the number of parameters which can change arbitrarily in physical parameters of boundary) with that of the phase boundaries R_1 obeys the following formula:

$$R_1' = R_1 + \phi_c \quad (1\text{-}2)$$

In isobaric phase diagrams with $N \geqslant 2$, the boundary (the assembly of system points of neighboring phase regions) of two neighboring phase regions meets the condition of $R_1 \geqslant 0$. In the meanwhile, the $(N + 1)$ phase coexisting region in the two neighboring phase regions does not exist. In this case, the following formula is tenable:

$$R_1' = R_1 + (\phi_c + 1) \quad (1\text{-}3)$$

The formulas (1-1), formulas (1-2) and formulas (1-3) mentioned above are the most important ones for isobaric Boundary Theory.

According to the Boundary Theory of Phase Diagrams, just replacing the number of parameters (Z) indicating the temperature (T) and pressure (P) by the number of all the parameters (K) involving temperature and pressure an so on, a Correspondence Relation Theorem of phase diagrams which is universally applicable is obtained as follows:

$$R_1 = (N - r - Z) - \Phi + K \quad (1\text{-}4)$$

For universal isobaric (or isothermal) phase diagrams, $K=1$; for phase diagrams with varied independently temperature, pressure and components, $K = 2$; if the other changeable parameters exist beside temperature and pressure, $K>2$. According to the Correspondence Relation Theorem, if Φ is known, thus R_1 could be calculated. Therefore, the following deductions are obtained.

Deduction 1 In any phase diagrams, the variation range of Φ is as follows. In two neighboring phase regions at least two phases are involved, $\Phi \geqslant 2$; and because $R_1 \geqslant 0$, the formula (1-4) could be written as:

$$(N-r-Z) + K \geqslant \Phi \geqslant 2$$

When $r=Z=0$, $N+K \geqslant \Phi \geqslant 2$.

Deduction 2 In any phase diagrams, the variation range of R_1 is as follows. Because $R_1 \geqslant 0$ and $\Phi \geqslant 2$, the formula (1-4) could be written as: