Introduction to

PHASE EQUILIBRIA IN CERAMIC SYSTEMS

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Floyd A. Hummel

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EQUILIBRIA IN CERAMIC SYSTEMS

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PREFACE

As W. Eitel states in his Preface, "There is no lack of textbooks on heterogeneous equilibria." Among the early classics were "The Phase Rule" by Alexander Findlay and "The Phase Rule and Phase Reactions" by S. T. Bowden and two books which are now out-of-print, "The Phase Rule" by A. C. D. Rivett and "Principles of Phase Theory" by D. A. Clibbens. More recently, the very fine books by Eitel, Ricci, and Rhines have furnished rather comprehensive geometrical approaches to heterogeneous equilibria in silicate, aqueous salt, and metal systems. The books by Prince, Gordon, and Reisman are some of the best examples of the use of the thermodynamic approach with the phase diagram. Each of these books must be regarded as excellent and having its own special strength.

However, none of these texts are completely adequate for use in teaching phase equilibria to undergraduates in Ceramic Science and Engineering. In Gordon's Preface he lists five comments on other texts: "(1) they are heavily oriented toward the viewpoint of the chemist, and therefore, though they treat the systems involved thermodynamically, they give the area of materials systems little attention; (2) they are highly mathematical, with a language and symbolism outside the realm of easy familiarity to the materials engineer; (3) they are treatises rather than texts; (4) they deal only briefly with phase diagrams as one of many subjects in a book of a more general nature; or (5) they give only what might be called the geometrical and phenomenological approach to phase diagrams, with little or no discussion of the thermodynamic foundations."

Comment (1) applies to all of the early classics such as Findlay, comment (2) applies to certain first-rate, top-level books such as Ricci where the language and symbolism are outside the realm of easy familiarity to the materials scientist

or engineer, and comment (3) applies to many modern textbooks because they lack examples and problems. The many excellent books on calculus and other subjects in mathematics are excellent because abundant sets of problems have been provided for use by the experienced or inexperienced instructor. Comment (4) is discussed in Sec. II. A. of Chapter 1. Many textbooks in ceramics contain a single chapter on phase equilibria and the book on "The Defect Solid State" with the excellent chapter by D. E. Rase is a prime example of Gordon's #4 comment. With respect to comment (5), it is simply necessary for a student to know the basic geometry *before* working on the thermodynamics of phase diagrams. The student usually becomes acquainted with general thermodynamics while taking physical chemistry and other courses in his major discipline. Later, it may be necessary to study the specific thermodynamics of phase diagrams.

Other comments can be applied. The very fine textbook of F. N. Rhines, "Phase Diagrams in Metallurgy," is obviously written for metallurgists and therefore stresses metal systems, which, in general, react more rapidly and contain phases of higher crystallographic symmetry than ceramic systems. Solid solubility is emphasized, whereas the intermetallic compound is not; this has been traditional for the metallurgist, whereas the ceramist has long been acutely aware of the intermediate compound but only more recently of the tremendous importance and effects of solid solution on phase transitions and the chemical and physical properties of compounds. Rhines very appropriately emphasizes the importance of the *application* of phase diagram information and the need to develop space perception. Eitel very appropriately emphasizes the great importance of *non-equilibrium* in silicate systems. in more recent years, this latter notion has been extended to oxide systems of all types including simple oxides, borates, silicates, phosphates, titanates, and other "ceramic" systems.

Ceramics, metallurgy, and polymers have always had a few close relationships, but since ceramic, metallurgical, and polymer science and engineering are now combined as materials science and engineering in many universities, certain phase-related aspects of the three disciplines are becoming closer and closer as time continues, similar to crystal structure and crystal chemistry relations.

For example, at one time "powder" and "glass" were not very important aspects of metallurgy, but now "powder metallurgy" and "metallic glasses" are becoming as important as conventional fusion techniques, at least to the basic science of metals. In contrast, ceramics is now deeply involved in the production of single crystals and polycrystalline materials by fusion, relative to its historical powder methods of producing sintered porous or vitreous products and relative to its conventional methods of producing (noncrystalline) glasses, glazes, and enamels by fusion. With respect to phase equilibria, current technology increases the need for knowing the liquid-solid relationships of one atmosphere phase diagrams, but very often the vapor phase must also be considered or not neglected. For example, chemical vapor deposition (CVD) is an established method of pro-

ducing solid (crystalline or noncrystalline) films. Eventually, each of the three disciplines will require a knowledge of phase relationships which involve not only the liquid and "solid state," but like all basic phase equilibria, the solid, liquid, and vapor state relationships' (p-T-X) diagrams. The pressure variable is becoming more important in "ceramic" systems as time goes on and eventually two, three, and higher order systems will have to be treated in terms of the (p-T-X) type of diagram. However, at the present time, most ceramic operations are carried out at or near one atmosphere and it is only necessary to discuss the influence of pressure in one-component systems and at rare intervals in later chapters.

At this point, one concludes that there is still a need for a textbook for undergraduates in Ceramic Science and Engineering which will contain sufficient geometrical analyses to enable the student to move into any of the more highly specialized textbooks or treatises with great ease. For example, the examination of ceramic systems under controlled oxygen pressure is now very important in the fields of slags, pigments, ferroelectrics, and ferromagnetics, and a knowledge of the principles set out in the Muan and Osborn book, "Phase Equilibria Among Oxides in Steelmaking," is an invaluable supplement in these areas.

Phase equilibria is interwoven (sometimes in a very intricate way) with crystal chemistry and at appropriate points in the text, this interrelationship will be illustrated through the use of examples of real systems, following the practice of Eitel and Rhines and others.

The author wishes to acknowledge the good fortune to have studied physical chemistry under Professor T. R. Briggs of Cornell, who was an associate of Professor Wilder D. Bancroft, founder of the "Journal of Physical Chemistry." Professor Bancroft was, in turn, one of the persons responsible for communicating the papers of Roozeboom, Schreinemakers, Buchner, and Aten, who were the interpreters of the great works of Gibbs. This chain was in a large measure responsible for placing the Phase Rule and all of its ramifications in a position where the American chemist, physicist, geologist, geochemist, mineralogist, metallurgist, and ceramist could apply it to real systems.

Finally, I wish to thank Dr. J. J. Brown, Professor of Materials Engineering at Virginia Polytechnic Institute and State University, for contributions to Chapters 1 and 2 which resulted in better organization and better discussion of the Phase Rule, Mrs. Nancy Bierly of Aaronsburg, Pa., for typing assistance and Mr. Clifford Warner of Cepiad Associates, Boalsburg, Pa., for drafting figures in chapters 2, 3, 5-8.

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CONTENTS

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INTRODUCTION AND DEFINITIONS

I. HISTORICAL

A. General

The entire field of chemical equilibria involving the application of the simple equation $F = C - P + 2$ stems from the original thermodynamics of J. Willard Gibbs (1), most particularly his paper on the "Equilibrium of Heterogeneous Substances" (2). The student is urged to read the account of the life and work of this outstanding genius as recorded by one of his students (3).

The basic mathematical and thermochemical treatment of Gibbs remained obscure and little used until the interpretations of Roozeboom (4), Shreinemakers (5), and Bancroft (6) appeared. Through the efforts of these writers, the Phase Rule was placed in position for the widespread application to all types of chemical systems. The later texts of Tamman (7) and Vogel (8) deserve special mention. Since the early work, many excellent textbooks have been written, most of them in the field of metallurgy or aqueous solution chemistry.

In more recent times, the work of the Geophysical Laboratory of the Carnegie Institution of Washington, D.C. has been of special significance and considerable use to ceramists and others working in the field of high temperature silicate and oxide chemistry. An account of the history, methods, and achievements of this Institution is available (9), as well as a list of specific systems which have been studied (10). The names of Adams, Day, Bowen, Morey, Shepherd, Rankin, Wright, Merwin, Greig, and Kracek are associated with most of the early work of this laboratory, while those of Schairer, Osborn, Tuttle, Keith, Yoder, Roedder, and Schreyer are prominent in later publications. Morey

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(11,12) wrote two papers on the analysis and interpretation of phase diagrams, especially for glass technologists, high temperature oxide chemists and ceramists.

The equilibrium work of Insley, McMurdie, Geller, Bunting, Lang, Levin, Roth, Waring, Robbins, and Schneider at the National Bureau of Standards deserves special mention, since the systems studied have direct application to optical glass, glazes, special refractory bodies and ceramic dielectric wares. Apparently no tabulation of the systems studied has been published, but most of them have been incorporated in the Levin, Robbins, and McMurdie compilations (13a,b).

B. Significance to Ceramic Science and Engineering (The Orton Lectures)

It is noteworthy that the first Orton Memorial Lecture was delivered to the American Ceramic Society in 1933 at Pittsburgh, Pennsylvania, by Edward W. Washburn on "The Phase Rule in Ceramics". Several subsequent Orton Lectures on this topic or on closely related topics such as "Natural and Artificial Ceramic Products" (Arthur L. Day, 1934), "Petrology and Silicate Technology" (Norman L. Bowen, 1943), and "Spark Plug Insulation" (Frank H. Riddle, 1959) attest to the general significance of the Phase Rule in ceramic science and engineering.

The first collection of phase diagrams, consisting of 178 diagrams, was published by F. P. Hall and Herbert Insley as the October, 1933 issue of the Journal of the American Ceramic Society. They received the first Ross Coffin Purdy Award in 1949 for this outstanding contribution to ceramic literature and for laying the cornerstone for all subsequent collections.

Subsequent compilations include the following:

Year	No. of Diagrams	Collectors
April, 1938*	154 (Supplement to 1933)	Hall and Insley
Nov., 1947*	507 (Part II of Nov. Jour)	Hall and Insley
Dec., 1949*	25 (Supplement to 1947)	McMurdie and Hall
1956	811	Levin, McMurdie and Hall
1959	462 (Supplement to 1956)	Levin and McMurdie
1964	2066	Levin, Robbins and McMurdie
1969	2082	Levin, Robbins and McMurdie
1975	850	Levin and McMurdie
1981	590	Roth, Cook and Cleek

*Part of regular issues of the Journal of the American Ceramic Society. Since 1956 the collections of diagrams have appeared as special bound publications.

Originally, the collection was confined to oxide and silicate systems, but starting in 1947, sulfide, fluoride and many other types of systems important to ceramic technology have been included.

At the present time, the significance of phase studies in ceramic systems no longer has to be justified. Every year, a certain amount of equilibrium studies and new phase diagrams appear in a great variety of journals throughout the world, and there are long-range plans for keeping the collection of "Phase Diagrams For Ceramists" up to date.

II. LITERATURE SOURCES

A. Textbooks in Ceramics

Various general and specialized textbooks have recognized the contributions of the equilibrium diagram and have devoted one or more chapters to a discussion of the application to a particular subject. Examples are Chapter 4, "Modern Glass Practice" by S. R. Scholes; Chapter 13, "Elements of Ceramics" by F. H. Norton; Chapter 13, "Refractories" by F. H. Norton; Chapter 3, "Enamels" by A. I. Andrews; Chapter 2, "Ceramic Whitewares" by R. Newcomb, Jr., several chapters in "Steelplant Refractories" by J. H. Chesters; Chapters 9 and 11, "Introduction to Ceramics" by W. D. Kingery; and Chapter 10, "Chemistry and Physics of Clays and Other Ceramic Materials" by R. W. Grimshaw.

It is interesting to quote from the extended Chapter 7 on Melting, Fusion, and Crystallization in "Ceramics: Clay Technology" written by Hewitt Wilson in 1927:

> Raw and dried clay is largely composed of colloidal and amorphous material. High temperatures tend to eliminate the colloidal phases and to replace them with the corresponding silicate glasses, together with small amounts of the more easily and quickly formed crystalline mullite which has been found in low-temperature paving brick and high-temperature porcelain bodies. Although as in chinaware bodies, the crystalline material such as feldspar and quartz may amount to 50 percent of the composition, yet but little of this is obtained as crystalline matter after heating, because the rate of cooling in ceramic furnaces and kilns is too fast for the crystalline growth of most silicates. THE CERAMIC INDUSTRY AS A WHOLE IS PRIMARILY INTERESTED IN THE PRODUCTION OF AMORPHOUS MATERIALS. The structural pottery industries wish to produce ceramic bodies which are hard and strong, that is, with a large content of glass bond, but which have sufficient rigidity at the maximum temperature of the kiln to resist deformation or loss of shape. On the other hand, these viscous bodies afford very little opportunity for the development of crystals, and mullite appears to be the only one active enough to develop in the ordinary clay mixture.

At present, however, interest is being displayed in those crystal-line forms which are useful in refractory work because of their rigidity under pressure at temperatures close to their melting points and because of the greater inertness of crystalline materials to the action of active agents such as slags and glasses. The electrical-insulator industry has recently introduced a high content of mullite into spark-plug bodies because of the better resistance to a combination of electrical and thermal stresses. The Corning Glass Company* and others are engaged in commercial experiments of a revolutionary character. Mullite is melted in an electric furnace and cast directly in sand molds to produce glass tank shapes. These are carefully annealed to prevent strain and thus produce a solid mass of interlocking crystals, with the maximum resistance to load and slag or glass action at high temperatures. Heretofore, mullite, corundum, and other crystalline masses have been crushed, bonded with plastic fire clays, milk of lime, etc., and refired in ordinary combustion kilns. In some cases, as in silica and special mullite brick, a second interlocking crystallization could be produced. In most cases, however, the bond was amorphous and the character of the product very largely depended on this bond. Recrystallized silicon carbide refractory products have been on the market for many years. The second growth of crystals is produced in electric resistance furnaces without a silicate bond. Silicon carbide has no melting point but rather a dissociation temperature at $2240°C$.

Other crystalline ceramic forms include corundum, Al_2O_3, in aluminous bauxite and diaspor, calcium silicates and aluminates in different cements, periclase in magnesia brick, and spinel, $MgO \cdot Al_2O_3$, in the "Diamel" brick of the Vitrefrax Company. In selecting such high-temperature refractories for casting wares, it is necessary to obtain fluidity with comparatively low vapor pressure over a workable temperature range, together with rapid crystallization. Magnesia and lime vaporize very fast, and, while quartz melts at comparatively low temperatures, it crystallizes too slowly from its melt. Fused silica finds its best service in the production of amorphous silica glass wares. With the recent rapid commercial development of the electric furnace, we will soon have more data on the behavior of these high-temperature compounds. The delayed solution of the lime problem may be found in the production of some high-temperature compound of this cheap, abundant, very refractory, but as yet, far too unstable and active material for high-temperature service.

The influence of clay and the technology of its heat treatment is already evident in the title of the book, but the three paragraphs quoted above emphasize how few materials besides clay (and mullite) were thought to be of interest at that time. After mullite, only a small group of materials are mentioned, name-

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*Anonymous: "Tank Block Problem Solved at Corning", Glass Ind., 7, 257 (1926).

ly silica, silicon carbide, corundum, spinel, MgO, calcium aluminates, and calcium silicates. Moreover, it was said that "THE CERAMIC INDUSTRY AS A WHOLE IS PRIMARILY INTERESTED IN THE PRODUCTION OF AMOR-PHOUS GLASSY MATERIALS," which even at that time was not true.

These statements form a striking contrast with our present wide interests, in crystalline or glassy borates, aluminates, silicates, titanates, zirconates, stannates, vanadates, phosphates, niobates, chromates, molybdates, tungstates, fluorides, and sulfides. Regardless of the form in which these compositions are desired, such as single crystals, fibers, foams, as finely divided sintered aggregates, or as finely divided aggregates in a glassy matrix, it demonstrates the tremendous effort which is being put forth to discover new phases, determine their equilibrium and non-equilibrium relationships in various systems, and to measure a wide variety of their chemical and physical properties.

The whole movement represents a transition period (started around 1943 during WWII) in Ceramics with less and less emphasis on easily formed clay products which can meet only limited general technological requirements and more and more emphasis on a great variety of difficult-to-form (in general) special compositions which meet severe and highly specific scientific and technological requirements.

B. Textbooks on Phase Equilibria

The general textbooks in Ceramics mentioned in Section B1 above cannot adequately cover the subject of phase equilibria in oxide systems in one or two chapters. The reading list on phase equilibria given at the end of this chapter includes most of the easily accessible books written in English. The instructor may wish to supplement the reading in this book with some specialized material in one of the fourteen texts listed. The most recent book of Ehlers contains some very useful material for ceramists, although it is directed toward geologists, as the title implies.

C. General Articles

A number of articles have appeared which suggest the increased use of the quantitative calculations which can be made from the equilibrium diagram. Of general interest in this connection are the papers of Dahl (14, 15, 16, 17) and Foster (18, 19). Dahl illustrated his calculations with applications in the cement industry while Foster stressed the proper use of the diagram in the heat treatment of complex mineral assemblages, and non-equilibrium situations. He also stressed the importance of the solid state reaction in ceramics. Apler (20, 21) has edited two series of books dealing with the application of phase diagrams to various fields of ceramic science and engineering.

D. Books on Techniques of Construction and Application
of Phase Diagrams

The compilation of "Phase Diagrams for Ceramists" by Levin, Robbins, and McMurdie (13a) contains a very good list of the books and papers which are available on techniques of construction of phase diagrams (pages 32-36).

III. STATEMENT OF THE PHASE RULE AND DEFINITIONS

In the processing and manufacture of ceramic products, the reactions which occur are understood more clearly if the phase relations under equilibrium conditions are known. The chemical and physical properties of ceramic products are related to the number, composition, and distribution (microstructure) of the phases present. Temperature, pressure, and concentration are the principal variables which determine the kinds and the amounts of the phases present.

Construction of phase diagrams is based on the assumption that the system under consideration is at equilibrium. In the development of reliable information on phase relations, this condition must be satisfied. In a practical sense, however, as in the manufacture or use of a ceramic product, circumstances may not permit a condition of equilibrium to be established. In many cases, it is known that the system is driving toward or approaching equilibrium, and the knowledge of the direction in which the reaction is progressing or the direction and amount by which it deviates from equilibrium can be of great value. This gives rise to the large areas of research involving the mechanism and kinetics of reactions which are so closely related to phase equilibrium.

The phase rule developed by J. Willard Gibbs (1, 2) was derived from the first and second laws of thermodynamics. If sufficient thermodynamic data were available, equilibrium relations of the phases could be calculated. Usually, such data have not been generated. However, the understanding of the thermodynamic basis for the phase rule and the manner by which phase relations can be represented in temperature-pressure-composition diagrams is extremely helpful to ceramists, even though most phase diagrams are determined by experimental laboratory techniques.

There are numerous definitions whose meaning one must understand and which must be used repeatedly in discussing one, two, three, and four component systems. In this chapter it is the intention to introduce those which are involved in the Phase Rule itself and a few others which are needed to describe some common events which occur in simple one-component systems.

A. Equilibrium

The fundamental concept upon which the phase rule, and the phase diagram is based, is the state of thermodynamic equilibrium. Generally equilibrium in a

system can be recognized by applying the following criteria: (1) the properties of the system do not change with the passage of time, (2) the state in question can be obtained by approaching the condition from more than one direction, i.e. by temperature, pressure, or, concentration: It should be noted that there is no limit to the "time" parameter in the definition of equilibrium. Cases are known when minutes, hours, years, and even thousands or millions of years are insufficient for attainment of the equilibrium state. It is this equilibrium end-point, and only this, that is represented by the phase equilibrium diagram, drawn to conform to the phase rule.

The thermodynamic definition of equilibrium can be obtained from the Gibbs free energy equation which can be stated as

$$G = PV - TS + \mu_1 X_1 + \dots \mu_i X_i \tag{1.1}$$

where

G = Gibbs free energy
P = pressure of the system
V = volume of the system
T = absolute temperature
S = entropy
μ_i = chemical potential of ith component
X_i = mole fraction of ith component

The equilibrium state is defined as that condition when G is a minimum for a particular set of external conditions. Of course, if the external conditions are changed (i.e. temperature, pressure, etc.) the equilibrium state will change and G will strive to assume a new minimum value.

The Gibbs free energy is a function of the independent variables T, P, and X_i. The equation can be rewritten in the differential form as

$$dG = VdP - SdT + \sum_i \mu_i dX_i \tag{1.2}$$

wherein i has a maximum value of C–1 if C refers to the minimum number of components necessary to define the system. In the special case when C = 1, the third term in equation (1.2) vanishes and the equation, as it is most commonly used, becomes

$$dG = VdP - SdT \tag{1.3}$$

Because the Gibbs free energy is a measure of the available energy, it therefore represents the driving force for a reaction. For a reaction to occur spontane-