PHASE EQUILIBRIA AMONG OXIDES IN STEELMAKING

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A large number of works on the phase rule and its application to various chemical systems have been published since this law was first formulated by J. Willard Gibbs in 1876. Most comprehensive among these is the famous Roozeboom’s monograph entitled *Die heterogenen Gleichgewichte vom Standpunkt der Phasenlehre*, started by Bakhuis Roozeboom and continued after his death by Aten, Büchner, and Schreinemakers. A number of textbooks and monographs dealing with the same subject have appeared since that time, for instance those of Masing, Ricci, Rhines, Vogel, and Zernike.

Similarly, several compilations of phase diagrams for various types of systems are available, for instance those of Hall, Insley, McMurdie, and Levin for oxides and halides, and that of Hansen for metals. These compilations are very comprehensive, and have found widespread use among chemists, ceramicists, metallurgists, and geoscientists. In these compilations, however, discussions or commentary on diagrams as applied to specific problems are not practical, and because of the very wide areas covered, many details of the diagrams which would be useful to workers seeking more thorough information in selected fields of specialization are often left out.

The field of specialization dealt with in the present book is that of the oxide phases appearing most commonly in iron- and steelmaking processes. Impetus for the writing of the book came mainly from the association of the authors with a research project entitled “Phase Equilibrium Studies of Steelplant Refractories Systems,” which the American Iron and Steel Institute has sponsored in the College of Mineral Industries at The Pennsylvania State University since 1949. During the 14 years which have elapsed since the initiation of this project, a large number of phase equilibrium diagrams for binary, ternary, and quaternary oxide systems have been published from our laboratories as well as from other laboratories. It has been the experience of the present authors that users of these diagrams often lack the ability to apply theoretical knowledge to the diagrams, and thus fail to extract from them all the useful practical information which they contain. The main purpose of the present book is to bridge this gap and thus increase the usefulness of these diagrams.

The presentation is aimed at metallurgical and ceramic engineers who have an interest in applying available phase equilibrium data to the fullest extent in predicting and explaining reactions among oxide phases in steelmaking operations. Although not primarily intended as a textbook for college students, some of the material presented in this book may be found useful as a practical or theoretical guide to the study of high-temperature equilibrium problems for those working in one of the interdisciplinary fields of metallurgy, ceramics, materials science, and geosciences.

A geometrical approach has been used in the presentation of equilibrium data throughout this book. Thermodynamic principles are not used explicitly in any of the discussions except in Chapter 2, but a person with knowledge of physical chemistry will be able to transform some of the data into meaningful thermodynamic functions if he so desires. Because of an emphasis on the practical applications of the phase equilibrium data presented in this book, compositions are usually expressed in weight percent.
In a geometrical approach to presentation of equilibrium data, diagrams tell more than words. Hence a large proportion of the space in this book is taken up by diagrams showing phase relations in actual, known oxide systems of importance in iron- and steelmaking. Representative types of these diagrams are discussed in considerable detail, while others are presented without much explanation or interpretation, as background material for the interested reader who desires to apply phase equilibrium data to his own specific problems. The diagrams given do not represent a complete coverage of all oxide systems which may be of importance in iron- and steelmaking processes. However, the data used have been critically reviewed, and the diagrams presented are thought to represent the best up-to-date picture of the phase relations available at the time of this writing.

The authors have drawn on many sources for the diagrams presented in this book. Appropriate reference to the original publications has been given in each instance. In some cases, when several different versions of a diagram have been published, the authors have used the diagram judged to be most reliable. All diagrams taken from the literature have been redrawn to conform with the style and symbols used by the authors of this book.

A number of organizations and individuals have contributed in various ways to make this book possible. Our thanks go first to the American Iron and Steel Institute and its Vice President for Research and Development, C. M. Parker. For many years this institute has generously supported in our laboratories research programs on oxide equilibria from which many of the factual data contained in this volume were derived and during which most of the ideas and interpretations originated. The receipt from the American Iron and Steel Institute of a grant to defray expenses in the preparation of the manuscript for this book is also acknowledged. Cooperation, encouragement, and advice from the Research Subcommittee of the Refractories Committee of the Institute during the course of the research program as well as during the preparation of the manuscript for this book was a source of continuous stimulation to the authors. Members of this committee at one time or another during the period since initiation of the research project in 1949 have been: W. S. Debenham, B. L. Dorsey, J. J. Hazel, H. M. Kraner, P. H. Schroth, and R. B. Snow. H. M. Kraner, the liaison between the Institute and the research project, has been particularly helpful in giving freely of his long experience and knowledge of oxide equilibria, throughout the period of our association with the American Iron and Steel Institute.

The American Institute of Mining, Metallurgical, and Petroleum Engineers and Interscience Publishers generously permitted the reproduction of several diagrams as well as parts of the text from the authors' writing in Chapter 18 on physical chemistry of steel-plant refractories in the recent book entitled Electric Furnace Steelmaking.

Thanks go to Hildegard Muan for her search of the literature and the drawing of many of the diagrams. The drafting of the diagrams was handled by Clifford R. Warner.

University Park, Pennsylvania
February 1964

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A. THE PHASE RULE AND ITS APPLICATION TO VARIOUS CHEMICAL SYSTEMS


**B. COMPILATIONS OF PHASE DIAGRAMS**


**C. GENERAL**


LEGENDS TO COMMON LINE SYMBOLS AND PHASE NOTATIONS USED IN DIAGRAMS

A. Line Symbols

The majority of the phase diagrams presented in this book illustrate phase relations over a considerable temperature range, with emphasis on the liquidus temperature region. In such diagrams, heavy lines usually represent boundary curves separating the various phase areas, with arrows indicating directions of decreasing temperatures, heavy lines with crosshatching on one side designate outlines of areas within which liquid immiscibility occurs, and light lines represent liquidus isotherms (in ternary, quaternary, and multicomponent systems). The above-mentioned sets of lines are drawn solid where their locations have been determined experimentally with a degree of accuracy practically attainable with present-day techniques, whereas the lines are dashed where their locations are less accurately known or inferred only.

![Diagram](image)

1. = BOUNDARY CURVES
2. = OUTLINES OF TWO-LIQUID REGIONS
3. = LIQUIDUS ISOTHERMS

Examples of the lines explained above are shown in sketches (a) and (b) above, representing simple hypothetical binary and ternary systems, respectively.

Other line symbols which are less commonly used are explained in the legend to each diagram where they occur, or in the text.
B. Phase Notations

The phases present are designated by their mineralogical names when such are available and well-known. The use of such mineral names does not imply that the phase has the stoichiometric composition of the ideal end member compound of the mineral in question. For instance, the term worstonite is used to designate the low-temperature form of calcium metasilicate whether this phase occurs as essentially stoichiometric CaSiO$_3$ within the binary system CaO-SiO$_2$, or as a solid solution within the system CaO-MgO-SiO$_2$ with Mg$^{2+}$ partly replacing Ca$^{2+}$ in the structure. In cases where very extensive or complete solubility prevails between the end members, the names of both end members are commonly reflected in the designation of the solid solution series. For instance, the term magnesiowüstite is used to designate the solid solution series between MgO (magnesia) and "FeO" (wüstite).

In other cases it has been found most consistent with accepted terminology to use a structural group name to designate a phase. Examples of this are the use of the terms olivine, pyroxene, and spinel to designate the solid solutions (Mg, Fe, Ca)$_2$SiO$_4$, (Mg, Fe, Ca)SiO$_3$, and (Mg, Fe) (Fe, Al, Cr)$_2$O$_4$, respectively.

Phases not being named according to any of the systems explained above are usually represented by chemical formulas, for instance Ca$_2$SiO$_4$ for dicalcium silicate. The use of such a formula, similar to the situation prevailing when mineral names are used, does not preclude the possibility of the phase having a composition deviating from that of the stoichiometric compound by virtue of foreign ions substituting in part for the parent cations in the structure. In cases where such substitution is extensive, however, the substituting species is included in the formula [for instance (Mn, Al)$_2$O$_3$] or the notation as (for solid solution) is appended in parentheses behind the formula.

Many of the diagrams presented in this book would not be legible if abbreviations were not used to designate the phases present. Attempts have been made to use a specific abbreviation for each phase consistently throughout the book, although space limitations on some diagrams and other considerations have made it impractical to adhere strictly to this rule. However, it is thought that no confusion will arise from this, as the abbreviations used have been explained in the legend of each diagram where they occur.

Oxide formulas are used to represent points on the composition axes of the diagrams. It is emphasized that these formulas relate to compositions only and carry no implication regarding the possibility of experimentally realizing a phase of such composition, or regarding the stability or instability of such a phase if it can be made. For instance, FeO and FeSiO$_3$ are used as composition points in many diagrams for iron oxide-containing systems even though the former composition cannot be attained experimentally and a phase of the latter composition is known to be unstable at elevated temperatures and ordinary pressures. For a correct use of phase-equilibrium diagrams, it is extremely important to keep clear this distinction between the true compositions of phases and the composition points of mixtures as expressed along the composition axes of the diagram used to represent the system. Whereas the phase compositions, assuming that equilibrium conditions prevail, are properties of the system itself, the composition points in the diagrams can be chosen by the investigator in order to illustrate the phase relations geometrically in what he considers to be the clearest representation in each particular instance. It is hoped that these relations will become clear to the reader from the subsequent detailed discussions of the various projection methods used in this book.
INTRODUCTION

The extraction of iron from ores and the refining of this iron to steel are highly complex heterogeneous reactions involving gas, metal, and oxide phases. Although the extractive metallurgist is concerned primarily with the metal phase, he cannot ignore the other phases present. The compositions and properties of the latter not only determine the purity and hence the properties of the final metal, but without them the practical iron- and steelmaking processes would be impossible. It is nothing less than a miracle that hundreds of tons of liquid steel at a temperature of 1600°C or higher can be contained in any vessel without breaking out. The materials which make these processes possible are the refractory linings of the huge iron- and steelmaking furnaces. Almost equally astonishing is the fact that these large tonnages of steel can be made to specified compositions with very small tolerances. This is made possible by the careful adjustment of the slag and by controlled blowing of oxygen-containing gases into the metal bath. As an undesirable by-product of the latter process there arise nonmetallic inclusions in the metal which, depending upon their composition, shape, and distribution, may impair the properties of the steel to a larger or smaller extent.

The present book deals with important aspects of the chemistry of these auxiliary oxide phases. A starting point for an understanding of reactions in these systems is provided by phase-equilibrium data for various oxide combinations. Equilibrium data have the obvious shortcoming of not telling whether a reaction will actually occur or not, but only whether or not it is possible. However, at the high temperatures of steelmaking processes, a close approach to equilibrium is often realized. Phase-equilibrium data therefore constitute a reliable guide from which important judgments on courses of reactions can be made.

The discussion of phase equilibria in the present book is divided into two main parts. The first part describes equilibria existing in a large number of oxide systems of importance in steelmaking. The second part deals with the applications of these equilibria to slag, inclusion, and refractory phases in steelmaking. Each of these two main parts is subdivided into various sections. In part one appears first a chapter dealing with the stabilities of oxides relative to other possible phases in steelmaking furnaces. This is followed by a systematic treatment of phase relations in various oxide systems, starting with one-component and proceeding through two-, three- and four-component systems, concluding with a few remarks about systems in which the number of components exceeds four. Within each of these groups one or more “model” systems is described in some detail to demonstrate the reasoning involved in the application of the phase rule to the systems being discussed in the book. The remaining systems within each group are discussed only briefly by pointing out some of their most characteristic features.
The second main part of the book is divided into three sections. The first of these deals with slag systems, starting with blast furnace slags and concluding with slags in various steelmaking processes. Application of phase diagrams to oxide inclusion problems follows next, starting with simple deoxidizers and proceeding to complex deoxidizers where several oxide components are present in the deoxidation product. The last section of part two is devoted to equilibria existing among oxides in steelplant refractories. For purpose of systematization, these refractories are classified and discussed in terms of the following groups, in order: silica, alumina-silica, chrome, chrome-magnesia, magnesia, dolomite, and forsterite refractories.
STABILITIES OF OXIDES

One of the principal reasons for the extensive use of oxide materials in the steel industry is their high stabilities at elevated temperatures. A number of possible reactions must be considered in order to evaluate these stabilities quantitatively. We will consider in successive order the following: A, Stabilities relative to the elements; B, Stabilities relative to hydroxides, carbonates, sulfides, nitrides, and carbides; C, Vaporization; D, Melting.

It is recognized that the usefulness of oxides in high-temperature processes depends also on their favorable physical and mechanical properties. Tabulations of such data are beyond the scope of this book, however, and the reader is referred to recent textbooks dealing with properties of ceramic materials.¹,²

A. Stabilities Relative to the Element

A quantitative measure of the stability of an oxide relative to the elements is the standard free energy of formation ($ΔG^0$). A graph showing this quantity (per mole of oxygen consumed) as a function of temperature for a number of important oxides in steelmaking is shown in Fig. 1.³⁻⁵ The larger the negative value of $ΔG^0$ is, the greater is the stability of the oxide with respect to its elements. Hence, the farther down on the graph a curve is located, the more stable is the oxide represented by that curve. It is seen, for instance, that calcium and magnesium form oxides of high stabilities, nickel and copper form oxides of relatively low stabilities, and iron and chromium are intermediate with respect to the stabilities of their oxides.

It is often useful to express these stabilities also in terms of the oxygen pressure $p_{O_2}(\text{eq})$ of the gas phase with which the metal and its lowest oxide coexist in equilibrium. This equilibrium oxygen pressure is related to the standard free energy of formation by the equation

$$ΔG^0 = -2.3 \cdot RT \log p_{O_2}(\text{eq}). \quad (2-1)$$

Lines of equal log $p_{O_2}(\text{eq})$ values are shown as a series of dash-dot curves in Fig. 1. The intersection of such a curve with a solid line defines the oxygen pressure prevailing when metal and its lowest oxide coexist in invariant equilibrium. If the solid line representing equilibrium coexistence of a metal-metal oxide pair is located below a chosen dashed curve at any particular temperature, the oxide is the stable phase at the chosen oxygen pressure. Conversely, if the solid line is located above the dashed line, the metal is the stable phase.

One feature of particular interest in the diagram of Fig. 1 is that of the slopes of the free-energy curves. It will be noticed that most curves have a positive slope, the curve for CO₂ is practically horizontal and the curve for CO has a negative slope. These
Fig. 1. Solid curves showing standard free energies of formation of various oxides from the elements as a function of temperature, based mainly on data summarized by Coughlin (3) and by Elliott and Gleiser (4). The curve for SiO₂ has been drawn on the basis of new data presented by Chipman (5). Light dash-dot curves are lines of equal oxygen pressures (atm) of the gas phase, as labeled on each curve.
slopes are determined by the entropy change associated with the formation of the oxide from the elements, as shown by the equation

\[
\frac{d(\Delta G^0)}{dT} = -\Delta S^0.
\]  

If \(\Delta S^0\) for the reaction is negative, the standard free energy \((\Delta G^0)\) becomes less negative with increasing temperature, and hence the free-energy curve has a positive slope. If \(\Delta S^0\) is zero, the free-energy function does not change with temperature and the \(\Delta G^0\) line is horizontal. Finally, if \(\Delta S^0\) is positive, the free-energy curve has a negative slope.

It is seen that most of the oxides included in Fig. 1 belong to the first category. When the metal (crystalline or liquid) reacts with gas to form a crystalline or liquid oxide, the disappearance of the gas phase results in a large decrease in entropy and hence a positive slope of the \(\Delta G^0\) curves (CaO, MgO, FeO*, Al2O3, SiO2, etc.). The curves for K2O, Na2O, MgO and CaO are seen to be particularly steep above the boiling points of the respective metals (K, 758°C; Na, 883°C; Mg, 1103°C; Ca, 1483°C). When carbon and oxygen react to form carbon dioxide, on the other hand, one mole of gas (CO2) is formed for each mole of gas (O2) which reacts, and the entropy change is practically zero. Hence the \(\Delta G^0\) curve is nearly horizontal. The reaction between carbon and oxygen to form carbon monoxide \((2C + O_2 = 2CO)\) has associated with it a large increase in entropy, as two moles of gas (CO) are formed for each mole of gas (O2) consumed. Hence the \(\Delta G^0\) curve for this reaction has a negative slope. The location of this curve relative to those of the others in the graph demonstrates drastically the fact that C is a much stronger reducing agent for oxides at high temperatures than at low temperatures.

B. Stabilities Relative to Hydroxides, Carbonates, Sulfides, Nitrides, and Carbides

The stabilities of oxides must also be evaluated in terms of possible reactions with other constituents present in steelmaking furnaces. Some aspects of such reactions will be discussed further in later chapters of this book. As an introductory orientation it is useful to consider the stabilities of crystalline or liquid oxides relative to hydroxides, carbonates, sulfides, nitrides, and carbides which could conceivably form as a result of reactions with H2O, CO2, H2S, S2, N2, or CO, which are abundantly present in the gas phase of most furnaces. Thermodynamic data bearing on the possible reactions with these gas species are considered briefly in the following.

Equilibrium pressures of H2O and CO2, respectively, for the univariant equilibria represented by the general equations

\[
\text{MeO}_{(c)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{Me(OH)}_{2(c)} \tag{2-3}
\]

\[
\text{MeO}_{(c)} + \text{CO}_2_{(g)} \rightleftharpoons \text{MeCO}_3_{(c)} \tag{2-4}
\]

have been determined for a number of elements.6–15) Pertinent data are summarized in Fig. 2. As H2O or CO2 pressures in steelmaking furnaces usually are only a fraction of one atmosphere, it appears that reactions between these gases and crystalline oxides will not pose a problem at the high temperatures at which the iron- and steelmaking

* The lowest oxide of iron, wüstite, is represented by the formula FeO for sake of convenience. The true compositions of this phase are seen from the phase diagram for the system Fe-O to be presented in a later section.
operations are carried out. However, such reactions may very well be sources of difficulties at the lower temperatures which obtain during burning-in or shutdown of furnaces.

Considerable efforts have been devoted in recent years to determination of solubilities of H₂O in liquid silicates. Walsh, Chipman, King, and Grant(16) measured experimentally the water contents of actual steelmaking slags. An average H₂O content of 0.03% was found for basic open-hearth tapping slags and 0.01% for acid open-hearth slags. The same authors also investigated the equilibrium solubilities of water in these slags at controlled partial pressures of H₂O, and concluded that the slags were considerably short of saturation with respect to H₂O. Improved determination of H₂O-solubilities in basic open-hearth slags and in synthetic iron silicate liquids under controlled H₂O pressures as well as controlled O₂ pressures have subsequently been carried out by Uys and King.(17) They found average values of approximately 0.1% H₂O dissolved at an H₂O pressure of 0.2 atm. There was a slight decrease in H₂O solubility with increasing oxygen pressures in the iron silicate liquids investigated.

Solubilities of the same order of magnitude as above have been found in Li₂O-CaO-SiO₂ melts.(18)

Studies of solubilities of H₂O in other types of silicate systems have been carried out by glass chemists and geochemists. Russell and co-workers(19,20) have studied H₂O solubilities in glass-forming alkali silicate liquids, and geochemists(21–25) have studied water solubilities in various liquid silicates at high pressures in order to elucidate conditions prevailing during formation of minerals and rocks. Most of the latter studies were carried out on systems having much higher silica contents than those encountered.
in iron- and steelmaking slags. However, a recent investigation of water solubilities in basalts\textsuperscript{(28)} deals with systems which are sufficiently basic that the results should be correlative to those obtained for steelmaking slags. Indeed, when the data on basalts, obtained at 1100°C and H$_2$O pressures from 1000 to 6000 atm, are extrapolated to 0.2 atm on a linear square-root plot, they give the same order of magnitude for water solubility as those observed by Uys and King.\textsuperscript{(17)}

In spite of the relatively small amounts of water present in slags, they may have considerable effects on flow properties and on rates of oxygen transfer and of sulfur removal.

Solubilities of CO$_2$ in silicate and borate melts have been determined for some alkali oxide-containing systems\textsuperscript{(26–28)} at temperatures ($\sim$1000°C) considerably lower than those encountered in steelmaking. No information seems to be available regarding solubilities of CO$_2$ in slags.

Stabilities of sulfides, nitrides, and carbides of various elements are illustrated in Figs. 3 through 5 by curves showing their standard free energies of formation as a function of temperature. The stabilities of these compounds relative to those of the oxides of the same elements are illustrated in Figs. 6 and 7 by curves showing differences $\Delta(\Delta G^0)$ between the standard free energies of formation of sulfides, nitrides, or carbides and the corresponding oxides. The use of these diagrams is illustrated by the following examples:

Consider first the reaction of oxides to sulfides according to the equation

$$2\text{MeO}(e) + \text{S}_2 = 2\text{MeS}(e) + \text{O}_2,$$  

(2–5)

where one mole of oxygen exchanges position with one mole of sulfur (see Fig. 6). The less positive the $\Delta(\Delta G^0)$ value for this reaction is, the higher is the tendency for the reaction to proceed from left to right. Among the elements included in Fig. 6 the tendency for sulfide formation increases in the approximate sequence Si < Al, Ti < Mg < Mn < Fe, Ca < Ni < Cu < Na < K. The $p_{\text{S}_2}/p_{\text{O}_2}$ ratio of the gas phase in equilibrium with the two condensed phases (oxide and sulfide) according to equation 2–5 is determined by the relation

$$\log \frac{p_{\text{S}_2(eq)}}{p_{\text{O}_2(eq)}} = \frac{\Delta(\Delta G^0)}{2.3RT}.$$  

(2–6)

Since $\Delta(\Delta G^0)$ is positive for most sulfide-oxide combinations included in Fig. 6, the partial pressure of sulfur must exceed that of oxygen in the gas phase in order to form sulfides from the oxides. Only in the case of Na and K will a sulfur pressure slightly below that of oxygen stabilize the sulfide phase relative to the oxide. However, such ratios of sulfur to oxygen partial pressures are not commonly encountered in steelmaking processes, and pure sulfide phases of the common elements are, therefore, usually not present in these systems. An exception may be the appearance of sulfide inclusions in steel when the oxygen pressure is very low.

However, sulfur is an important constituent of the oxidic slags used in steelmaking practices, since metal-slag reaction is the main means of removing sulfur from the metal. Although differences in free energies of solution of the various oxides and sulfides in such slags may change slightly the order of tendency for sulfide formation as represented by the curves in Fig. 6, these curves may be expected to serve as a good guide to the relative sulfur-removing capacity of the various oxide constituents of a silicate slag. Desulfurization data which have been accumulated for many decades confirm this inference. Strong bases (for instance CaO) are much better desulfurizers than are strong acids (for instance SiO$_2$). Even more effective than CaO are the alkali oxides, Na$_2$O.
Fig. 3. Solid curves showing standard free energies of formation of various sulfides from the elements as a function of temperature, based on data tabulated by Coughlin\(^{(3)}\) and by Elliott and Gleiser\(^{(4)}\). Light dash-dot curves are lines of equal sulfur pressures (atm) of the gas phase, as labeled on each curve.
Fig. 4. Solid curves showing standard free energies of formation of various nitrides from the elements as a function of temperature, based on data tabulated by Coughlin and by Elliott and Gleiser. Light dash-dot curves are lines of equal nitrogen pressures (atm) of the gas phase, as labeled on each curve.
Fig. 5. Solid curves showing standard free energies of formation of various carbides from the elements as a function of temperature, based on data tabulated by Coughlin(3) and by Elliott and Gleiser(4). Light dash-dot curves are lines of equal carbon activities (standard state pure graphite), as labeled on each curve.
Fig. 6. Differences in free energies of formation between sulfides or nitrides and corresponding oxides, based mainly on data summarized by Coughlin (3) and by Elliott and Gleiser (4). The curves for the compounds of Si have been drawn on the basis of Chipman's new thermodynamic data for SiO_2 (5) in conjunction with the data referred to above.
Fig. 7. Solid curves showing differences in free energies of formation between carbides and oxides, based mainly on data summarized by Coughlin\textsuperscript{(3)} and by Elliott and Gleiser.\textsuperscript{(4)} The curve for SiC has been drawn on the basis of Chipman's new thermodynamic data for SiO\textsubscript{2}\textsuperscript{(5)} in conjunction with the data referred to above. The meaning of the dashed curve for C is explained in the text.
and K₂O. The high volatility of the latter constituents, as well as deleterious effect on refractories, however, limit their usefulness in steelmaking processes (compare vapor-pressure data shown later in Fig. 8).

Similar energy relations for reactions of oxides to nitrides according to the equation

\[ 2\text{Me}_2\text{O}_{(c)} + y\text{N}_2 = 2\text{Me}_2\text{N}_{y(c)} + \text{O}_2 \]  

\hspace{1cm} (2-7)

are also illustrated in Fig. 6. Each curve is drawn for a reaction in which one mole of oxygen is liberated. The \(\Delta(G^0)\) values for the elements included in the diagram are all strongly positive and show that the nitrides of these elements are very unstable relative to the oxides. The ratio \(P_{\text{N}_2}/P_{\text{O}_2}\) of the gas phase in equilibrium with oxide and nitride is determined by the equation

\[ \log \frac{P_{\text{N}_2(\text{eq})}}{P_{\text{O}_2(\text{eq})}} = \frac{\Delta(G^0)}{2.3RT}. \]  

\hspace{1cm} (2-8)

Ratios of \(P_{\text{N}_2}/P_{\text{O}_2}\) would have to exceed \(10^{10}\) at steelmaking temperatures in order to stabilize the nitrides of these elements relative to their oxides. Such conditions do not exist in practice.

The amounts of nitrogen which are dissolved in liquid silicates under steelmaking conditions have not been determined, but they may be appreciable.

The conditions for formation of carbides from oxides can be derived from the graph shown in Fig. 7. The \(\Delta(G^0)\) values represented by each of these curves are for the reaction

\[ 2\text{Me}_2\text{O} + 2y\text{C} = 2\text{Me}_2\text{C}_{y} + \text{O}_2, \]  

\hspace{1cm} (2-9)

in which one mole of oxygen is liberated.

One significant difference between the situation prevailing in the case of the carbide equilibrium (Fig. 7) and those of sulfides and nitrides (Fig. 6) is the stable existence of carbon as a crystalline phase at steelmaking temperatures, and the high stability of CO in comparison with oxides of S and N. In the presence of excess carbon, the oxygen pressure of the system Me-C-O is determined by the equilibrium

\[ 2\text{CO}_{(g)} = 2\text{C}_{(c)} + \text{O}_2_{(g)}. \]  

\hspace{1cm} (2-10)

A curve representing this equilibrium is dashed in Fig. 7.

By subtracting equation (2–10) from (2–9), the following equation is obtained:

\[ 2\text{Me}_2\text{O} + 2(y - 1)\text{C} = 2\text{Me}_2\text{C}_y + 2\text{CO}. \]  

\hspace{1cm} (2-11)

Hence it is seen that the position of the dashed curve relative to those of the solid curves in Fig. 7 represents a convenient graphical illustration of oxide-carbide-carbon equilibria. In any temperature interval where the dashed curve is located below the solid curve representing the \(\Delta(G^0)\) value for a particular element, the oxide of this element is stable relative to the carbide in the presence of carbon at a CO pressure of 1 atm. Similarly, the intersection between the dashed curve and the \(\Delta(G^0)\) curve for any particular element defines the lowest temperature at which the carbide can be formed by reaction of an oxide with carbon at a CO pressure of 1 atm. At high temperatures (>1000°C) the gas phase coexisting in equilibrium with carbon is almost pure CO (see Fig. 11, to be presented later), and hence the condition of a CO pressure of 1 atm implicit in the graph in Fig. 7 is almost identical to stipulating a total pressure of 1 atm. At low temperatures (<1000°C) a slight correction factor is necessary to account for the small amount of CO₂ present in the gas under equilibrium conditions.
Technologically important inferences can be made from the graph in Fig. 7. For instance, CaC₂ can be formed by reduction of CaO with C only at temperatures above 1830°C. Carbides of some other elements can be formed at much lower temperatures, for instance Ni₃C at ~500°C. However, the latter carbides may be metastable with respect to the assemblage metal + carbon (graphite). This is seen from the positive $\Delta G^0$ value for the standard free energy of formation of this carbide from its elements (Fig. 5).

C. Vaporization

Vaporization characteristics of oxides have been studied more intensively during the past decade than ever before. In spite of this, the amount of reliable quantitative information available on gas species and equilibria between these gas species and condensed phases for oxide systems at high temperatures is still very limited. Several excellent reviews of such data have appeared in the literature. These reviews are recommended as sources of data, as illustrations of need for more extensive data, and as sources of information on experimental techniques commonly used in vapor-pressure determinations at high temperatures. Above all, these review articles are recommended as a demonstration of the complexities and difficulties involved in experimental studies of these systems, and the uncertainties and discrepancies which still exist in the vapor-phase data for most of these systems.

No attempt will be made in the present book to cover this field thoroughly. Only a few data will be reported as general background information for the equilibria among condensed phases (crystalline and liquid) which are the main subjects of discussion in this book. The diagram in Fig. 8 summarizes vapor-pressure data for several oxides of importance in steelmaking. Included for comparison in this graph are data for some metals. The pressures plotted are total pressures resulting when the substances volatilize into a vacuum, i.e., when all the species of the gas phase originated from the condensed phase which is in equilibrium with the gas. Convenient methods for deriving the partial pressures of the various possible gas species of oxides under other conditions have been presented by Alcock. The following data were used in the construction of Fig. 8: The curves for the metals (and C) were all drawn on the basis of data summarized by Honig. The curves for CaO, MgO, and BeO were drawn on the basis of data summarized by Ackermann and Thorn. The SiO₂ curve was located by combining data tabulated by Ackermann and Thorn with the new free-energy data for SiO₂ presented by Chipman. The curve thus obtained is almost identical with that obtained from the recent data of Ramstad and Richardson. Curves for Na₂O, K₂O, and MnO were approximately located on the basis of data summarized by Brewer. Data of Wang, Dregel, Dadape, and Margrave as well as those of Grimley, Burns, and Ingham were used to construct the curve for Cr₂O₃. Results of a study by Chupka, Berkowitz, and Ingham served as a basis for plotting an approximate curve for ZrO₂.

Pertinent details regarding the mechanism of volatilization of oxides represented in Fig. 8 are as follows:

Na₂O, K₂O, CaO, MgO, MnO: Vapor-pressure data indicate that these oxides decompose mainly to the gaseous elements. Oxide species in the gas phase are quantitatively insignificant.
Fig. 8. Vapor pressures of various oxides (solid curves) and elements (dashed curves) as a function of temperature, by evaporation into a vacuum. The sources of the various data from which the curves were drawn are given in the text. Circles represent melting points of the condensed phases.
Cr₂O₃: It has long been known that chromium oxide volatilizes to a considerable extent at high temperatures. Warshaw and Keith(41) observed significant weight losses of MgO-Al₂O₃-Cr₂O₃-SiO₂ mixtures in phase-equilibrium studies of this quaternary system at 1500°C. Quantitative data for volatilization of pure Cr₂O₃ have become available only recently.(34,35)

SiO₂: The vaporization of SiO₂ under "neutral" conditions is well accounted for by the reaction(42)

\[ \text{SiO}_2(g) = \text{SiO}(g) + \frac{1}{2} \text{O}_2(g) \]

However, according to data reported by Porter, Chupka, and Inghram,(43) one may predict that the dioxide (SiO₂) is the main species of the gas phase at oxygen pressures approaching 1 atm.

ZrO₂: Chupka, Berkowitz, and Inghram(36) have shown that ZrO and ZrO₂ both exist as gaseous species in equilibrium with crystalline ZrO₂ at high temperatures (\(\sim 2100°C\)).

Oxides of importance in steelmaking which are missing in Fig. 8 include those of aluminum, titanium, and iron.

At least two oxide species of aluminum, Al₂O and AlO, have been shown to exist in the gas phase in addition to the gaseous elements Al and O.(44-46) The relative amounts of the four species above depend on the conditions under which the evaporation takes place.(31) The quantitative data on vaporization of aluminum oxide are still quite uncertain, mainly because reactions with crucible materials are difficult to avoid in experimental studies.(30,46) For this reason, a curve for Al₂O₃ is not included in Fig. 8. It probably would be located in the area between the CaO and BeO curves.

Data on titanium oxides are very fragmentary. A number of crystalline phases with varying compositions exist in the system Ti-O, and the vapor-pressure data available at present are not well defined.

Iron occurs in at least three states of oxidation in steelmaking processes, Fe⁺³, Fe⁺², and Fe⁺⁰. The highest oxide, Fe₂O₃, decomposes upon heating to lower oxides (solid or liquid), with liberation of oxygen to the gas phase. Volatilization of iron in the form of elemental Fe or a stable gaseous molecule is negligible. The decomposition to lower oxides usually takes place in two steps, first to Fe₃O₄ and subsequently to “FeO.” The latter phase decomposes mainly to the gaseous elements. The equilibrium relations among the condensed phases Fe₃O₄, Fe₅O₇, and FeO as a function of temperature and oxygen pressure will be discussed in detail in a later section dealing with the two-component system Fe-O.

**D. Melting**

Melting points of various oxides may be read from numerous phase diagrams to be presented in succeeding chapters of this book. Attention is directed in this connection to the program presently underway at the National Bureau of Standards for compiling and redetermining melting point of oxides.(47) Many melting points, especially those above 1800°C, may need considerable revision as that work progresses.
ONE-COMPONENT SYSTEMS

In one-component systems there is no composition variable, and stability relations can usually be described completely* with reference to two axes. One of these is temperature and the other a parameter expressing quantitatively the chemical potential of the component. Free energy, fugacity, or vapor pressure of the substance may be used for the latter purpose. As examples of one-component systems, we describe in the following and in some detail two systems of particular importance among oxides in steelmaking, SiO$_2$ and Ca$_2$SiO$_4$. Stability relations of other oxides (Fe$_2$O$_3$, Al$_2$O$_3$, Mn$_3$O$_4$, ZrO$_2$, TiO$_2$) occurring in more than one crystalline modification are discussed more briefly.

A. SiO$_2$

Although silicon monoxide, SiO, is an important species of the gas phase in the vaporization of silica (compare Chapter 2), the stability of SiO as a solid is still a matter of considerable doubt$^{(48-50)}$ and so is the stability of the phase Si$_2$O$_3$ reported by Dadape and Margrave.$^{(60)}$ Only SiO$_2$ seems to play an important role as a component in solid and liquid silicates. Hence the one-component system SiO$_2$ is an important basis for understanding equilibria in complex silicates.

The system SiO$_2$ is a good example of the complexities which may be hidden even in the so-called “simple” oxide systems. A tremendous amount of research effort has been expended in trying to unlock the secrets of this substance during the 50 years which have elapsed since Fenner published the results of his pioneering study.$^{(61)}$ Excellent summaries of such work have been presented by Sosman.$^{(62-64)}$ Research efforts on SiO$_2$ have been particularly intensive during the last eight years, during which time new concepts and new interpretations have been applied to previously known modifications of silica, and a whole series of new silica modifications have been synthesized and characterized. The latter development has been made possible by significant advances in experimental high-pressure techniques at high temperatures. A detailed coverage of the high-pressure modifications of silica is beyond the scope of the present book, because most steelmaking processes now or in the foreseeable future take place at total pressures in the proximity of 1 atm. A series of papers,$^{(65-74)}$ mainly by geoscientists, is recommended for the interested reader who wishes to extend his knowledge to include the high-pressure modificationscoesite and stishovite.

Even if one limits the consideration of silica stability to a total pressure of 1 atm, the relations are too complex to describe here in detail. In the following, an attempt is

* It is assumed here that variations in magnetic fields, electric fields, etc. have no appreciable effects on the equilibria.
made to delineate relations which are particularly pertinent to the occurrence of silica in steelmaking processes.

A curve illustrating the standard free energy of formation of SiO₂ from the elements was presented as part of Fig. 1 (see Chapter 2). This curve was drawn for the phases which, according to the classical picture, are stable, viz., low quartz to 573°C, high quartz from 573 to 867°C, high tridymite from 867 to 1470°C, high cristobalite from 1470 to 1723°C, and liquid above 1723°C. The free-energy curve has a change in slope at each temperature of inversion among these phases (573, 867, 1470, 1723°C). However, these changes are so small that they do not show up on the scale of the diagram of Fig. 1. A diagram which is more useful in expressing stability relations of especial interest among the various phases of SiO₂ is presented in Fig. 9. Plotted here are differences in free energy among various condensed forms of silica, using high cristobalite as reference state, as a function of temperature, again according to the classical picture of stability among the various modifications. At any particular temperature, the curve farthest down on the diagram in Fig. 9 represents the most stable form. The stability ranges of low quartz (to 573°C), high quartz (573 to 867°C), high tridymite (867 to 1470°C), high cristobalite (1470 to 1723°C), and liquid (above 1723°C) are clearly shown in this type of representation.

The structures of quartz, tridymite, cristobalite, and liquid are sufficiently different that a large energy barrier must be overcome in order to transform one of these phases

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Fig. 9. Differences in standard free energy of formation, Δ(ΔG°), among various condensed forms of SiO₂, using high cristobalite as reference state, as a function of temperature (mainly after Mosesman and Pitzer).
into another. Hence the liquid structure may be cooled to room temperature without crystallization taking place, and cristobalite and tridymite on cooling from their regions of stability may persist as metastable forms. Energy relations for these metastable equilibria are approximately described by the dashed parts of the curves in Fig. 9. In contrast to the sluggish inversions among quartz, tridymite, and cristobalite, rearrangements within one of these major structures to produce a different crystal structure is commonly easily made. Tridymite and cristobalite have several forms and quartz has two. For many of these inversions, transformation back and forth in response to alternations of temperature through the inversion point is rapid.

Several workers, beginning with Fenner himself, have observed various anomalies in the SiO₂ system which were not in accord with the picture presented above. However, it is only during the past eight years that evidence has been presented to show that the relations described above and illustrated in Fig. 9 not only represent an oversimplification of the true relations, but may even be entirely wrong in some important aspects. The main stimulus for renewed attack on the problem of silica stability came from papers by Flörke published in 1955 and 1956. He first redescribed the structural relations between tridymite and cristobalite and emphasized that they bear a polytypic relation to each other. Subsequently, he presented experimental data which he interpreted as showing that tridymite is not a stable phase in pure SiO₂, but owes its existence to the presence of foreign ions in the structure. The polytypism concept as it applies to these structures has since been generally accepted, and further details bearing on this problem have been presented by Hill and Roy. Flörke's conclusion regarding the instability of the tridymite phase in pure SiO₂, on the other hand, has stirred up a controversy which still exists at the time of this writing. Hill and Roy believe that formation of cristobalite from tridymite below the "classical" tridymite-cristobalite equilibrium temperature (1470°C) can occur only from the metastable "tridymite-M," and that "tridymite-S" is the thermodynamically stable phase in the temperature interval of approximately 867–1470°C. Because the last-mentioned work was carried out under hydrothermal conditions, there is some suspicion that water may have entered the silica structure in sufficient amounts to alter the stability relations from those of pure SiO₂. This point has been argued most enthusiastically by Holmqquist, who presented what he considered to be evidence in support of Flörke's contention that tridymite is not a stable phase in pure SiO₂. Hence, Holmqquist suggests the elimination of the stability field of tridymite, and places the temperature of coexistence of quartz and cristobalite at 1025 ± 25°C. Roy and Roy, however, on the basis of a new investigation with various additions to silica, refute the contention of Holmqquist and conclude that a rather sharp polymorphic transformation exists between stable tridymite ("tridymite-S") and stable cristobalite (with completely ordered 3C stacking) in the one-component system SiO₂, and that the temperature of this transformation is approximately 1470°C, in accordance with the "classical" picture. Roy and Roy also conducted similar experiments to establish the position of the quartz-tridymite equilibrium in the presence of various additional oxides. Although they admit that more data are needed in order to establish the relations more definitely, they conclude that quartz and stable tridymite probably coexist under equilibrium conditions in the system SiO₂ at approximately 870°C, as originally stated by Fenner.

The polytypic relations existing in and between the structures of tridymite and cristobalite make the relations in the one-component system SiO₂ far more complicated than is shown in the diagram of Fig. 9. It is established beyond doubt that sluggish, reconstructive, monotropic transformations between various polytypes take place in tridymite and cristobalite of highest purities available in the laboratory, and that the properties of these phases depend on temperature and length of heat treatment. There is good reason to suspect that these relations are at least partly responsible for dif-
ferences in the temperature of inversion between high and low cristobalite as determined by various investigators, although there may be other as yet unknown factors contributing to the difficulty of obtaining consistent data for this equilibrium.\(^{(78,83-87)}\)

In view of the new data on SiO\(_2\) reported above, it may seem desirable to present a more up-to-date picture of equilibrium relations in the SiO\(_2\) system than is represented in Fig. 9. However, until some of the discrepancies and controversies still existing in the literature are resolved, the present authors consider such a diagram premature. Diagrams representing the two main different schools of thought on SiO\(_2\) stability have been presented by Hill and Roy\(^{(78)}\) and by Holinquist.\(^{(81)}\) In spite of the shortcomings and simplifications inherent in Fig. 9, it serves as an adequate basis for discussions of SiO\(_2\) brick problems to be presented in later sections of this book.

**B. Ca\(_2\)SiO\(_4\)**

Dicaleium silicate, like silica, has several crystalline modifications and hence is of especial interest wherever it is a constituent of steelmaking systems.

Beginning with the phase-equilibrium investigation of the system CaO-SiO\(_2\) by Day and Shepherd in 1906,\(^{(88)}\) a large number of papers dealing with structure and stability relations among the various modifications of Ca\(_2\)SiO\(_4\) have appeared in the literature. Detailed reviews of this literature have been presented recently\(^{(89,90)}\) and are not repeated here. Our present concept of stability relations in this system are summarized in Fig. 10. Quantitative data for the various modifications are not available, and the stability relations are shown only qualitatively by means of hypothetical vapor pressure-temperature curves. The picture presented is essentially in accordance with that of Bredig,\(^{(91,92)}\) with slight changes for the \(\gamma-a'\) and \(\gamma-\beta\) inversion temperatures in accordance with more recent data by Roy.\(^{(90)}\) The temperature of 1450°C for the \(\alpha-a'\) equilibrium is an approximate average value based on experimental data of Newman and Wells,\(^{(93)}\) of Trömel and Möller,\(^{(94)}\) and of Welch as reported by Nurse.\(^{(95)}\)

Four crystalline modifications of Ca\(_2\)SiO\(_4\) are recognized. The three forms known as \(\alpha-, a', \) and \(\gamma-Ca_2SiO_4\) exist as stable phases over the temperature ranges indicated by solid curves in Fig. 10. The \(\beta\)-form is considered to be metastable (dashed curve) at atmospheric pressure in the entire temperature range of the diagram. On cooling from high temperatures, \(\alpha-Ca_2SiO_4\) inverts to \(\alpha'-Ca_2SiO_4\) in a rapid and reversible manner. On further cooling, the structural changes may follow one of four paths, as suggested by the curves in Fig. 10: (1) the structure of \(\alpha'-Ca_2SiO_4\) may persist to room temperature, (2) \(\alpha'\) may invert to \(\beta-Ca_2SiO_4\), which then persists to room temperature (the \(\alpha'\)- and \(\beta\)-forms occur as the natural minerals breddigite and larnite, respectively, having cooled and persisted for millions of years), (3) \(\alpha'\) may invert to \(\gamma-Ca_2SiO_4\), (4) \(\alpha'\) may invert to \(\beta\)-which in turn inverts to \(\gamma-Ca_2SiO_4\).

While useful as a basis for judging important aspects of the behavior of Ca\(_2\)SiO\(_4\) in steelmaking processes, the diagram in Fig. 10 is probably an oversimplification of the true relations in much the same way as Fig. 9 was for SiO\(_2\). Details of the nature of some of these transformations and the various parameters having a possible effect on the transformations were discussed at a recent symposium on the chemistry of cement.\(^{(96)}\)

The structures of the \(\alpha-, a', \) and \(\beta\)-phases are closely related to each other.\(^{(89)}\) The Ca\(^{2+}\) ion in all these structures has a high coordination number with respect to O\(^{2-}\) (8–10) and the phases have relatively high densities. Volume changes during inversions among these three modifications are not large enough (\(\leq 1\%\)) to cause disruption of a body containing Ca\(_2\)SiO\(_4\) as a phase. The \(\gamma-Ca_2SiO_4\) modification, on the other hand, has a structure (olivine type) which is significantly different from those of the other modifica-
Fig. 10. Schematic illustration of relative stabilities of various modifications of Ca$_2$SiO$_4$, based on data available in the literature (compare text). The vertical scale is qualitative only.

...
Three crystalline modifications of Fe$_2$O$_3$ have been reported, α (hematite), γ (maghemite), and ε. The α-form has the hexagonal (corundum type) structure and has been described repeatedly in mineralogical literature. The nature of the γ-phase has been the subject of considerable discussion for a long time. The structure of this phase is very similar to that of spinel. However, there have been controversies regarding some of the finer details and particularly regarding the possible role of impurities in stabilizing the structure. Schrader and Böttner have recently given a review of the literature on preparation and structure of the phase and in addition have provided a considerable amount of new experimental results bearing on the problem. They conclude that γ-Fe$_2$O$_3$ exists as a phase in its pure state without the presence of stabilizing foreign ions, and they confirm the previous observation of Osterhout and Rooijmans that the x-ray diffraction pattern can be indexed on the basis of a tetragonal unit cell with $a_0 = 8.33$ Å and $c/a = 3$. The cell corresponds to a stacking of three spinel unit cells on top of each other. Schrader and Böttner suggest that the formula γ-Fe$_2$O$_3$ be reserved for pure iron oxide with the structure described above, and that a similar phase stabilized with other cations and having the spinel type structure be called “stabilized iron (III) oxide of spinel type.”

Schrader and Böttner recently also identified in iron oxide aerosol produced in an electric arc under oxidizing conditions a heretofore unknown modification which they called ε-Fe$_2$O$_3$. This phase is monoclinic, with $a_0 = 12.97$ Å, $b_0 = 10.21$ Å, $c_0 = 8.44$ Å, $β = 95°20'$. Both γ- and ε-Fe$_2$O$_3$ are probably metastable with respect to hematite at all temperatures, but the relative stabilities of the γ- and ε- are unknown. The rate of conversion of the two metastable forms to hematite depends on many factors, but in general the conversions proceed rapidly at a temperature of 500°C or higher.

The ε-phase has never been recognized in the steel plant. Similarly, the γ-phase (maghemite) probably plays no important role in high-temperature iron- and steel-making processes, but it may be a common constituent in some iron ores. It is probably formed in nature either by slow oxidation of magnetite (Fe$_3$O$_4$) at low temperatures or by dehydration of lepidocrocite (γ-Fe$_2$O$_3$ · H$_2$O).

A bewildering number of different crystalline modifications of Al$_2$O$_3$ have been reported in the literature. The α-form (corundum) with hexagonal structure is probably the only one which is thermodynamically stable at elevated temperatures, and the only modification which is of importance in steelmaking.

The true nature of the many reported metastable modifications of Al$_2$O$_3$ and their interrelations are still unsettled issues. The reported modifications may be related to each other by order-disorder sequences, or they may be discrete crystalline phases, or impurities (for instance water) may play prominent roles in their structures. The major reported modifications, as listed in a recent review, are the γ-form (cubic, tetragonal, or orthorhombic); δ- (orthorhombic); κ- (orthorhombic); η- (cubic); θ- (hexagonal); χ- (approximately cubic). In addition, the two forms β- and ε- are often listed among the modifications of Al$_2$O$_3$, although it is now well established that the existence of these two phases depends on the presence of other ions in the structure (Na$^+$, K$^+$, Mg$^{++}$, Ca$^{++}$, or Ba$^{++}$ in case of β-; Li$^+$ in case of ε-).

The various metastable modifications of Al$_2$O$_3$ convert to the α-form, either directly or through several intermediate steps, upon heating in the temperature interval ~400–1000°C.

Zirconia (ZrO$_2$) is potentially a very attractive material for use at high temperatures because of its high chemical stability (see Fig. 1) and high melting point (~2730°C). Its use is restricted, however, not only because of cost limitations, but also because of poor thermal shock resistance. The latter difficulty is caused by transformation from a low-temperature monoclinic to a high-temperature tetragonal structure. The tem-
temperature of equilibrium coexistence of these two modifications is still uncertain, in
spite of numerous investigations on this problem. On the basis of the most recent
data\(^{(102, 103)}\) it appears that the transformation occurs at a somewhat higher tem-
perature than previously assumed. However, a hysteresis problem still remains. Whereas
the transformation during heating is observed at \(\sim 1170^\circ C\), it occurs during cooling at
\(\sim 1040^\circ C\). The phenomenon has a striking similarity with that of the inversion in
cristobalite. The volume change accompanying the monoclinic-tetragonal transforma-
tion in \(ZrO_2\) is \(\sim 9\%\). This is enough to disintegrate a refractory body composed of
\(ZrO_2\) if temperatures fluctuate around the inversion temperature. The inversion from
the tetragonal to the monoclinic modification is so rapid that the former cannot be
preserved by quenching to room temperature.

The oxide \(Mn_3O_4\) exists in two different crystalline modifications, a high-temperature
cubic (spinel type) structure and a low-temperature tetragonal structure. The two
phases coexist in stable equilibrium at \(\sim 1160^\circ C\).\(^{(104)}\) The transformation between the
two modifications is very rapid, and the cubic (high-temperature) form cannot be pre-
served at room temperature even by fast quenching.

The dioxide of titanium, \(TiO_2\), exists in at least three crystalline modifications.\(^{(97)}\)
The tetragonal form of rutile is probably stable relative to the other two modifications,
anatase (tetragonal) and brookite (orthorhombic), at all temperatures encountered in
steelmaking. The structural interrelations among the three modifications have been
discussed in detail in the literature.\(^{(105, 106)}\)
TWO-COMPONENT SYSTEMS

A. Systems in Which a Gas Phase
   Plays an Important Role

The two-component systems of greatest importance for an understanding of oxide
equilibria in iron- and steelmaking are C-O and Fe-O. In both these systems, one
component (Fe or C) is a condensed phase and the other component (O) is a gas at
steelmaking temperatures. However, the systems differ in one important respect.
Whereas the oxides of carbon (CO and CO₂) are gases at steelmaking temperatures,
the oxides of iron ("FeO," Fe₃O₄, Fe₂O₃) are condensed phases (liquid or crystalline)
under the same conditions. Equilibria existing among the phases in these two systems
will be discussed in considerable detail below. Other two-component systems involving
a gas phase will be discussed only briefly.

1. C-O

Reactions among the various species present in the two-component system C-O at
steelmaking temperatures are expressed by the equations

\[ 2\text{CO}(g) = \text{C(graphite)} + \text{CO}_2(g), \]  

(4–1)

for which the equilibrium constant may be written

\[ K_1 = \frac{p_{\text{CO}_2} \cdot a_c}{p_{\text{CO}}^2}, \]  

(4–2)

and

\[ 2\text{CO}_2(g) = 2\text{CO}(g) + \text{O}_2(g), \]  

(4–3)

for which the equilibrium constant may be written

\[ K_2 = \frac{p_{\text{O}_2} \cdot p_{\text{CO}}^2}{p_{\text{CO}_2}^3}. \]  

(4–4)

An analysis of the above equilibria (4–1, 4–3) in terms of the phase rule shows the
following situation to exist: If the two phases carbon (graphite) and gas coexist in
equilibrium, the system possesses two degrees of freedom:

\[ (P + F = C + 2 = 4; \quad F = 4 - 2 = 2). \]

Hence, when two of the independent variables have been chosen, the system is com-
pletely defined. For instance, if temperature and CO pressure of the gas phase are
chosen, the partial pressures of CO₂ and O₂ of the atmosphere and hence also the total
pressure, are fixed. Conversely, if temperature and total pressure are chosen, the partial pressures of CO, CO₂, and O₂ of the gas phase are fixed. This divariant equilibrium situation is illustrated graphically by the heavy dashed cross curve in Fig. 11, showing CO₂/CO ratios of the gas phase in equilibrium with graphite as a function of temperature at a total pressure of 1 atm. The shaded area below this curve represents conditions (CO₂/CO ratios) which cannot be realized experimentally if equilibrium prevails. In other words, if at a chosen temperature an attempt is made to achieve a CO content of the gas in excess of that prevailing on the curve, carbon will precipitate out and the CO₂/CO ratio will be that represented by the solid curve at that temperature.

The unshaded area above the curve represents conditions under which a gas phase is in stable equilibrium without precipitation of carbon, at a total pressure of 1 atm. Because the number of phases present has decreased by one from the previous case considered, the system now possesses an additional degree of freedom:

\[ P + F = 4; \quad F = 4 - 1 = 3. \]

With temperature and total pressure chosen, the partial pressures of CO, CO₂, or O₂ are all fixed if one of them or the ratio between two of them is chosen. Curves of constant oxygen partial pressures as a function of CO₂/CO ratios are presented in the diagram of Fig. 11.

2. Fe-O

The most extensive discussion of stability relations existing among metallic iron and its oxides is found in papers by Darken and Gurry in 1945 and 1946. They summarized results of earlier work in addition to providing a large amount of new data. The following account is based mainly on their work, but is supplemented with additional data which have become available since that time.

Because of the large number of possible condensed phases present, the presentation of phase relations in the system Fe-O requires more elaborate representations than was the case in the system C-O. The first illustration of stability relations existing among the various phases in the system Fe-O is given in Fig. 12, where temperature and partial pressure of oxygen of the gas phase have been chosen as variables. In any area of the diagram where one condensed phase coexists with gas, the system possesses two degrees of freedom:

\[ P + F = C + 2; \quad F = 4 - 2 = 2. \]

This means that temperature and oxygen pressure may both be varied (within certain limits) without the number of phases changing. Along a boundary curve, on the other hand, the system possesses only one degree of freedom, since two condensed phases coexist with gas. Hence, if temperature is chosen, the oxygen pressure is fixed and vice versa.

The diagram shown in Fig. 12 is not the most practical illustration of phase relations in the system Fe-O, for two reasons. First, it will be noticed that the oxygen pressures of the gas phase in equilibrium with condensed phases vary over a very wide range as temperatures vary between 0 and 1600°C. The lowest oxygen pressures shown in Fig. 12 have little physical meaning. More meaningful parameters are obtained by combining the Fe-O equilibrium with the C-O equilibrium or similar equilibria. The resulting three- or four-component systems will be discussed in succeeding chapters of this book.

The second serious drawback of the diagram in Fig. 12 is that it does not show compositions of condensed phases. This situation is remedied in the type of diagram
Fig. 11. Curves showing oxygen pressures (atm) as a function of temperature and CO₂/CO ratios at a total pressure of 1 atm, based on data tabulated by Coughlin (3) and by Elliott and Gleiser (4). The shaded area below the dashed cross curve represents metastable conditions (compare text).
Fig. 12. Stability relations among the various condensed phases in the system Fe-O as a function of temperature and oxygen pressure, based on data of Darken and Gurry.\textsuperscript{(107,108)}

presented in Fig. 13, where the stability ranges of the various condensed phases present are shown as a function of temperature and total composition of condensed phases.\textsuperscript{(100)} A family of dash-dot curves are included in the diagram to show partial pressures of oxygen of the gas phase coexisting in equilibrium with the condensed phases.

The two types of representations used in Figs. 12 and 13 have contrasting features which must be kept clearly in mind when using the diagrams. Whereas areas in Fig. 12 represent situations where only one condensed phase is present and curves represent situations where two condensed phases are present, the areas in Fig. 13 represent conditions under which either one or two condensed phases are present in equilibrium with a gas phase. These observations are not in conflict with each other. In Fig. 12
Fig. 13. Phase relations in the system FeO-Fe$_2$O$_3$, based mainly on data of Darken and Gurry$^{107,108}$ and supplemented by new data for the magnetite and hematite regions.$^{110}$ Heavy lines are boundary curves separating stability fields of the various condensed phases, and light dash-dot lines are oxygen isobars.$^{109}$ The heavy dashed curves in the upper right corner of the diagram show the probable, approximate positions of the hematite liquidus and solidus curves in a region which has not been studied experimentally.
there is no axis representing compositions of condensed phases. Hence, although the
two phases coexisting with gas along a boundary curve have different compositions,
they are recorded by the same point in this diagram. In Fig. 13, on the other hand,
the horizontal axis represents compositions of condensed phases, and the two phases
coexisting in equilibrium with gas at any particular temperature are therefore recorded
by two separate points in this diagram. It is as if the boundary curve in Fig. 12 were
“pulled out” to form an area in Fig. 13. Hence in the latter diagram one-phase (one
condensed phase) areas are separated by two-phase (two condensed phase) areas.

The general features of the oxygen isobars in Fig. 13 are readily understood by a
simple application of the phase rule to the system. Two degrees of freedom exist when
one condensed phase is in equilibrium with gas. Temperature and oxygen pressure of
the gas may therefore be varied independently (within certain limits) under these
conditions. Hence, the oxygen isobars run diagonally across one-phase areas of the
diagram. Where two condensed phases are present together in equilibrium with gas,
however, the system possesses only one degree of freedom. Under such circumstances
a choice of temperature fixes the oxygen pressure and vice versa. Hence the oxygen
isobars cross two-phase areas as straight lines parallel to the horizontal (composition)
axis.

The diagram in Fig. 13 is so important for an understanding of later sections of this
book that a couple of examples of the use of the diagram will be given. It is expedient
at this time to introduce the concept of path of equilibrium crystallization. Although
commonly used only in connection with ternary and quaternary systems, the term will
be used here on the system Fe-O to show more clearly the relations between two-com-
ponent systems and the multicomponent systems to be treated in later sections of this
book. As originally introduced by petrologists, the term path of equilibrium crystallization
was defined as the course along which the liquid composition changes during crystal-
lization under equilibrium conditions. In a wider meaning, however, the path of crystal-
lization also takes into account the changes taking place in compositions of gas and
crystalline phases during the process. It is in this wider meaning that the term is used
in this book. Hence the path of equilibrium crystallization is nothing but a description
of the phase changes which take place as heat is withdrawn from the system and equilib-
rium is maintained throughout the process. Similarly, the equilibrium path of melting
may be defined as a description of the phase changes taking place as heat is supplied to
the system and equilibrium is maintained throughout the process.

Consider as an example the path of equilibrium crystallization of a mixture m shown
in Fig. 14. It is convenient to derive the relations under two idealized conditions.

Assume first that the equilibrium cooling is carried out under such conditions that
the total composition of condensed phases remains constant. This situation is
approximated in a closed system when the volume of the gas phase is small in comparison
with that of the condensed phases, and if no reaction takes place between the sample
and the material of the container. The path of crystallization under these conditions
is read directly off the diagram by following a vertical line (constant composition line =
isopleth) from high to low temperature. Liquid oxide is the stable condensed phase
from 1700 to 1540°C; magnetite and liquid coexist in equilibrium from 1540 to 1424°C;
liquid, magnetite, and wüstite are present together in equilibrium at 1424°C; wüstite
and magnetite coexist from 1424 to 560°C; wüstite, magnetite, and α-iron are present
together at 560°C; and magnetite and α-iron is the stable phase assemblage below 560°C.
The relative amounts of each phase at any chosen temperature are determined by the
lever rule. For instance, at 600°C the mixture consists of ∼30% wüstite and ∼70%
magnetite. The oxygen pressure of the gas phase decreases continuously with decrease
in temperature, from ∼10⁻² atm at 1700°C to ∼10⁻²⁶ atm at 560°C.
Fig. 14. Diagram showing paths of equilibrium crystallization of a mixture \( m \) in the system FeO-Fe\(_2\)O\(_3\) under two idealized conditions as explained in text: constant total composition of condensed phases (solid line), and constant oxygen pressure (dashed line).

Contrast this behavior with the path of crystallization of the same mixture \( m \) cooled under such conditions that the oxygen pressure of the atmosphere remains constant \( (10^{-2} \text{ atm}) \). This can be done experimentally at high temperatures in an open system by adjusting the compositions of gas mixtures (compare Fig. 11). The path of crystallization of mixture \( m \) is now derived by following the dash-dot \( 10^{-2} \text{ atm} \) oxygen isobar from high to low temperatures in Fig. 14. It is seen that the liquid phase is stable down to \( \sim 1580^\circ \text{C} \), magnetite and liquid coexist at \( 1580^\circ \text{C} \), magnetite is the only crystalline phase present between \( 1580^\circ \text{C} \) and \( \sim 1250^\circ \text{C} \), magnetite and hematite exist in stable equilibrium at \( 1250^\circ \text{C} \), and hematite is stable below \( 1250^\circ \text{C} \).

One important difference between the two crystallization paths discussed above should be noted in particular. Two condensed phases (for instance magnetite and liquid) coexist in equilibrium over a range of temperatures during crystallization at
constant total composition of condensed phases, whereas the same phases (magnetite
and liquid) coexist in equilibrium with gas only at one temperature during crystallization
at constant oxygen pressure. That these situations must prevail is easily understood
by application of the phase rule. In the case of crystallization at constant oxygen
pressure, one degree of freedom is expended in choosing this oxygen pressure of the
gas phase. However, no degree of freedom is expended in fixing constancy of total
composition of the condensed phases, because the phase rule is concerned only with the
chemical potentials, and hence the compositions, of each individual phase present. A
change in total composition (within certain limits) changes the relative amounts of two
coeexisting condensed phases, but not their compositions.

The paths of melting of mixtures in the system Fe-O, similarly, are derived by follow-
ing isopleths or oxygen isobars from low to high temperatures under heating at constant
total composition of condensed phases or at constant oxygen pressure, respectively.

3. H-O

Equilibrium relations existing in the system H-O at elevated temperatures are simpler
than those just considered because no condensed phase is present. The relative amounts
of the gas species H₂O, H₂, and O₂ at any temperature can be calculated from thermo-
dynamic data for the reaction

\[ 2\text{H}_2\text{O}_{(g)} = 2\text{H}_2_{(g)} + \text{O}_2_{(g)}, \]

for which the equilibrium constant may be written

\[ K = \frac{P_{\text{O}_2} \cdot P_{\text{H}_2}^2}{P_{\text{H}_2\text{O}}^2}. \]

The results, for a total pressure of 1 atm, are shown in Fig. 15. Values of H₂O/H₂
ratios given in these diagrams are those prevailing at the equilibrium temperature.
Similarly to the situation existing in the system C-O, these ratios are practically identi-
tical to room-temperature mixing ratios, except in the upper right corner of the diagram.
Experimental methods for mixing H₂O and H₂ in desired proportions have been de-
scribed in detail by Chipman and coworkers.¹¹¹,¹¹²

4. METAL-OXYGEN SYSTEM OTHER THAN Fe-O

Equilibrium relations in metal-oxygen systems where only one valence state pre-
dominates are well represented by the free energy-temperature diagram shown in Fig. 1
(Chapter 2). Equilibrium data for binary systems of oxygen and transition metals with
several states of oxidation are very scarce, except for Fe-O. Parts of the systems Mn-O,
Ti-O, V-O, and Cr-O have been studied in some detail, but the data available at the
present time are far from sufficient to construct reliable phase diagrams of the type
shown for Fe-O in Fig. 13.

A graph comparing the stabilities of manganese oxides¹¹³ with those of iron is
shown in Fig. 16. The most notable feature of the diagram is the much wider stability
range of the oxide of divalent manganese than that of divalent iron. It is seen that
MnO is not reduced to metallic manganese at oxygen pressures far below those of the
Fe/FeO equilibrium, and at the same time MnO is not oxidized to Mn₃O₄ at oxygen
pressures above those for the FeO/Fe₃O₄ equilibrium.

Magneli and co-workers¹¹⁴–¹¹⁷ have reported a large number of discrete oxide
phases in the system Ti-O and have delineated the structural relations existing among
these phases. Since no reliable information is yet available regarding the range of
Fig. 15. Curves showing oxygen pressures (atm) as a function of temperature and $\text{H}_2\text{O}/\text{H}_2$ ratios at a total pressure of 1 atm, based on data tabulated by Coughlin\(^3\) and by Elliott and Gleiser\(^4\).
Fig. 16. Comparison of stability relations among the oxides of iron and manganese as a function of temperature and oxygen pressure, based on data of Darken and Gurry\(^{107,108}\) and of Hahn and Muan\(^{113}\).

oxygen pressures over which the alleged phases are stable, or regarding the melting relations of these phases, it seems premature to draw a phase diagram for the system Ti-O which has any significance beyond being “not impossible.” Such a diagram has been suggested by DeVries and Roy\(^{118}\).

A situation similar to that of Ti-O seems to exist in the system V-O. Magneli and coworkers\(^{119,120}\) have identified a large number of oxide phases prepared in the temperature range 650–1000°C, and Gel’d, Alyamovskii, and Matveenko\(^{121}\) have made observations on V-O samples quenched from 1400°C. However, it is not possible to draw a phase diagram for the system on the basis of data available at the present time.

In the system Cr-O, the sesquioxide Cr\(_2\)O\(_3\) with corundum type structure is probably the only stable oxide phase at temperatures below 1600°C regardless of oxygen pressure in the range from 1 atm to that below which metallic chromium is stable. Hilty, Forogeng, and Folkman\(^{122}\) have shown that another oxide phase, Cr\(_3\)O\(_4\) with distorted spinel structure, exists and probably is stable under strongly reducing conditions above 1600°C. In addition to the above, a number of phases with higher oxygen contents (CrO\(_2\), Cr\(_5\)O\(_9\), Cr\(_7\)O\(_5\), Cr\(_3\)O\(_8\), CrO\(_3\)) have been reported to exist in the system Cr-O\(^{123}\). Some of these phases are metastable only, and certainly none is stable at high temperatures unless the oxygen pressure is high (see for instance recent equilibrium data on CrO\(_2\)\(^{124}\)). These phases therefore play no role in iron- and steelmaking processes.
B. Systems in Which a Gas Phase Plays No Important Role

1. GENERAL CONSIDERATIONS

Systems containing only very stable oxides (for instance CaO, MgO, Al₂O₃, SiO₂; compare Fig. 1) as components can be adequately represented in diagrams showing compositions of condensed phases as a function of temperature, at a constant total pressure of 1 atm. The compositions of the condensed phases vary only slightly with variation in composition of the gas phase, and hence the latter can usually be ignored in representation of phase relations in such systems. Consequently, the total composition of the condensed phases may be assumed to remain constant as phase assemblages change in response to temperature changes, and the paths of equilibrium crystallization or paths of equilibrium melting of selected mixtures in these systems may be read directly off the diagrams by following isopleths from higher to lower temperatures, or vice versa, in accordance with the first idealized condition discussed for the system Fe-O in a previous section.

A number of such binary systems will be presented in the following. The appearance of the phase diagrams depends mainly on the solubility relations existing between the

![Diagrams](image)

**Fig. 17.** Sketches of various hypothetical phase diagrams for a binary system A-B, as discussed in the text. The symbols α, β, and γ represent solid solution phases, and the abbreviation L denotes liquid.
two components in the solid and in the liquid state, and on the tendencies for compound formation between the components.

It is useful as an introduction to consider a number of idealized situations, as shown schematically by the hypothetical diagrams presented in Fig. 17. The first diagram (a) in this figure shows the extreme case of a system in which there is no mutual solubility between the two components either in the liquid or in the solid state, and no compound formation. The melting relations of each component in these circumstances is unaffected by the presence of the other component, and liquidus and solidus temperatures are represented by horizontal lines. The second diagram (b) in Fig. 17 shows the other extreme: a system in which there is complete solubility between the two components both in the liquid and in the solid state. Several intermediate stages between these two extremes are possible, as indicated by examples shown in Fig. 17 (c)–(e). The sketch in (c) shows a situation where there is partial solubility in the liquid state, and no solubility in the solid state, (d) shows complete solubility in the liquid and no solubility in the solid state, and (e) shows complete solubility in the liquid and partial solubility in the solid state. The three remaining diagrams in Fig. 17 are sketches of hypothetical systems in which an intermediate compound AB is present. In (f) this compound is assumed to melt congruently, in (g) it is assumed to melt incongruently, and in (h) the incongruently melting compound appears in a system with limited solubility in the solid state.

Actual diagrams often approximate one of the simplified idealized diagrams sketched above or, more commonly, combine two or more of the features represented in separate diagrams in Fig. 17. Among the diagrams to be presented in the remainder of this chapter, Cr₂O₃-SiO₂ approximates the diagram sketched in 17(a), Al₂O₃-Cr₂O₃ represents that of 17(b), and CaO-MgO resembles that of 17(d). The other diagrams include features from several of the simplified type diagrams above. In particular, there is commonly a large number of compounds present as stable phases in the systems.

Because of the dominant role of silica in oxide structures, the systems to be presented below are divided into two groups, those with SiO₂ as a component and those without SiO₂ as a component. The two systems CaO-SiO₂ and Al₂O₃-SiO₂ will be presented first, partly because of their central roles in silicate chemistry, and partly because they constitute good examples of application of phase equilibrium considerations to binary systems. The diagrams for the remainder of the oxides components are arranged, within each group, approximately in order of increasing field strengths of the cations; viz., K₂O, Na₂O, CaO, MgO, Al₂O₃, Cr₂O₃, TiO₂, P₂O₅. The systems are discussed in various degrees of detail, depending on their complexity, their significance in steelmaking, and the reliability of the diagrams.

2. SYSTEMS WITH SiO₂ AS A COMPONENT

CaO-SiO₂: The diagram for the system CaO-SiO₂ shown in Fig. 18⁶⁰⁶,¹²⁵⁻¹³⁹ incorporates several of the features discussed in section 1, as well as features discussed in connection with one-component systems: Two immiscible liquids coexist in equilibrium in a certain composition-temperature region of the system CaO-SiO₂; several compounds between the end members have stable existence within the system; several of these compounds occur in different modifications. Many of these features have important bearings on the chemistry of steelmaking processes. Some of these aspects will be touched upon here, while others will be discussed in later sections of the book.

The liquidus curve is seen to rise steeply from the tridymite-pseudowollastonite eutectic toward the plateau where two liquids are in equilibrium with cristobalite. The amount of liquid present in a mixture of chosen composition increases very little as temperature increases from that of the eutectic (1435°C) to that of two-liquid formation
**Fig. 18.** Phase diagram for the system CaO-SiO₂, based mainly on the work of Day, Shepherd, and Wright,\(^{125}\) of Rankin and Wright,\(^{126}\) and of Greig,\(^{127}\) with revisions based on more recent data.\(^{99,128,129}\)

(1707°C). For instance, a 97% SiO₂ 3% CaO mixture is ~8% liquid at 1436°C and 11% liquid at 1706°C. The liquid formed is highly viscous because it contains a relatively large amount of SiO₂.

Lime (CaO) is not in any circumstances in equilibrium with liquids within this binary system at steelmaking temperatures (~1600°C), because of the formation of very stable crystalline silicate phases (Ca₃SiO₅, Ca₂SiO₄). Other components must be added to CaO and SiO₂ in order to obtain a liquid slag saturated with CaO at 1600°C.
Dicalcium silicate, Ca$_2$SiO$_4$, is seen to appear in three different modifications. Because there is no appreciable mutual solubility in the solid state among the phases in the system CaO-SiO$_2$, the stability relations among the Ca$_2$SiO$_4$ modifications are analogous to those described for the one-component system Ca$_2$SiO$_4$ in Fig. 10. Hence boundary curves in Fig. 18 appear as straight lines between two adjacent areas differing in phase assemblages only as a result of different Ca$_2$SiO$_4$ modifications being present in the two areas. Similarly, straight horizontal lines denote modification changes in SiO$_2$ (compare Fig. 9) and in CaSiO$_3$.

Mixtures with compositions in the vicinity of the CaO-end of the system have high solidus and liquidus temperatures. No liquid is developed until a temperature of 2050°C is reached if the CaO to SiO$_2$ ratio of the mixture is higher than 2:1. However, the possibilities of using as refractory bodies mixtures where Ca$_2$SiO$_4$, Ca$_3$SiO$_5$ or CaO are present as phases are severely reduced by the “dusting” tendency of the former (compare page twenty-six) and the high susceptibility to hydration of the latter two.

Al$_2$O$_3$-SiO$_2$: The system Al$_2$O$_3$-SiO$_2$ is one of the truly “classic” binary silicate systems. It was studied in great detail as early as 1924 by Bowen and Greig,$^{(130)}$ and the availability of data for this system represented a milestone in the development of alumina-silica and high-grade silica brick.

On the basis of more recent work,$^{(131-134)}$ it appears that the original diagram as presented by Bowen and Greig should be changed slightly with respect to the melting relations of mullite (3Al$_2$O$_3$·2SiO$_2$). The most probable diagram is presented in Fig. 19. It should be noted, however, that there is still no general agreement on the behavior of the mullite phase at high temperatures, and a recent symposium devoted entirely

![Diagram](image_url)

**Fig. 19.** Phase diagram for the system Al$_2$O$_3$-SiO$_2$, based mainly on the original work of Bowen and Greig,$^{(130)}$ with modifications based on more recent data, as explained in the text.$^{(131-134)}$
to this subject\textsuperscript{(135)} testifies to the controversial views on this problem and the importance of the mullite phase in ceramic technology. Whether mullite under equilibrium conditions in the binary system Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} melts congruently or not, the technologically important inferences made by Bowen and Greig are still valid. For instance, the detrimental effect of Al\textsubscript{2}O\textsubscript{3} on a silica brick is readily apparent from an inspection of the SiO\textsubscript{2}-end of the system. The liquid which is in equilibrium with cristobalite and mullite at the eutectic temperature of 1590°C contains only 6% Al\textsubscript{2}O\textsubscript{3}. Hence a relatively small amount of Al\textsubscript{2}O\textsubscript{3} present as an impurity in SiO\textsubscript{2} severely damages refectoriness of this brick.

It is furthermore evident from the diagram in Fig. 19 that the most refractory mixtures are those whose compositions are in the range between mullite (\textasciitilde~72\% Al\textsubscript{2}O\textsubscript{3}) and Al\textsubscript{2}O\textsubscript{3}. A liquid phase will develop in these mixtures only at temperatures above 1840°C. Below this temperature, mixtures in this composition range consist of mullite and corundum if heated to equilibrium. In mixtures containing less Al\textsubscript{2}O\textsubscript{3} than mullite a liquid forms as temperature exceeds 1590°C. The phases present in such mixtures, at lower temperatures, are mullite and either cristobalite or tridymite.

\textbf{K\textsubscript{2}O-SiO\textsubscript{2}:} The diagram shown in Fig. 20\textsuperscript{(136,137)} represents phase relations in mixtures of the system K\textsubscript{2}O-SiO\textsubscript{2} containing more than 30\% SiO\textsubscript{2}. No data are available for the extreme K\textsubscript{2}O-end of the system. The diagram is characterized by three binary compounds, two of which have more than one crystalline modification, and a liquidus

![Phase Diagram](https://example.com/phase_diagram.png)

\textbf{Fig. 20.} Phase diagram for a part of the system K\textsubscript{2}O-SiO\textsubscript{2}, based on data of Kracek, Bowen, and Morey.\textsuperscript{(136,137)} Abbreviations used have the following meanings: \(h\) = high, \(l\) = low, Trid = tridymite, Crist = cristobalite, Qtz = quartz, KS = K\textsubscript{2}SiO\textsubscript{3}, KS\textsubscript{2} = K\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}, KS\textsubscript{4} = K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9}, \(L\) = liquid.
Fig. 21. Phase diagram for a part of the system Na2O-SiO2, based on data of Morey and Bowen (138) and of Kracek (139). Abbreviations used have the following meanings: h = high, l = low, Trid = tridymite, Crist = cristobalite, Qtz = quartz, N2S = Na4SiO4, NS = Na2SiO3, NS2 = Na2Si2O5, L = liquid.

curve which falls off drastically as K2O is added to SiO2. There is no liquid miscibility gap present as was the case in the system CaO-SiO2. It is evident that K2O is an extremely strong fluxing agent of SiO2.

Na2O-SiO2: Similarly to the preceding diagram, that for the system Na2O-SiO2 (Fig. 21) (138,139) shows a drastic lowering of the liquidus temperature as the alkali oxide is added to SiO2. Clearly, Na2O has a strong fluxing action on SiO2.

MgO-SiO2: Phase relations in the system MgO-SiO2 are illustrated in Fig. 22 (127,140,141,142). The effect of MgO on lowering the SiO2 liquidus curve is seen to be very similar to that of CaO (Fig. 18). A two-liquid plateau exists near the SiO2-end of the diagram, and a small amount of MgO added to SiO2 causes a relatively small amount of liquid to form. The amount of liquid increases only slightly as temperature increases from 1543 to 1703°C. Bodies containing excess MgO over the 2:1 ratio of forsterite (Mg2SiO4) develop liquid only at temperatures exceeding 1850°C, and hence are very suitable for high-temperature refractory applications. It is also seen that the refractoriness of forsterite mixtures decreases rapidly as silica is present in excess of the stoichiometric ratio (2:1).

Cr2O3-SiO2: The system Cr2O3-SiO2 as shown in Fig. 23 (143,144) is characterized by extremely small mutual solubilities between the two components both in the crystalline and in the liquid state. Hence the components are relatively “inert” to each other,
Fig. 22. Phase diagram for the system MgO-SiO₂, mainly after Bowen and Andersen,\textsuperscript{140} incorporating modifications of Greig,\textsuperscript{127} and with protoenstatite shown as the high-temperature stable form of MgSiO₃ in accordance with data of Foster\textsuperscript{141} and of Atlas.\textsuperscript{142}

and the solidus and liquidus curves both extend as horizontal lines almost all the way across the diagram from one side to the other.

**TiO₂-SiO₂:** The phase diagram for the system TiO₂-SiO₂ is shown in Fig. 24.\textsuperscript{145} The SiO₂-end of the system is similar to that of Al₂O₃-SiO₂ (compare Fig. 19). Addition of TiO₂ to SiO₂ causes liquidus temperatures to drop from 1723 to 1550°C, as compared with 1590°C when Al₂O₃ is added to SiO₂. The liquid present in equilibrium with rutile and cristobalite at the eutectic in the TiO₂-SiO₂ system, however, contains considerably more SiO₂ (~11%) than does the liquid existing in equilibrium with mullite and cristobalite (~6%) at the eutectic in the system Al₂O₃-SiO₂. Hence TiO₂ is not as serious a flux of silica as is Al₂O₃.

A large concentration range at the TiO₂-end of the system is characterized by the equilibrium existence of two liquid phases at temperatures above 1780°C. The rutile liquidus curve rises steeply up to this temperature, and the liquid phase contains relatively little TiO₂.
Fig. 23. Phase diagram for the system Cr$_2$O$_3$-SiO$_2$, based on data of Bunting$^{(143)}$ as discussed by Keith.$^{(144)}$

Fig. 24. Phase diagram for the system TiO$_2$-SiO$_2$, after DeVries, Roy, and Osborn.$^{(145)}$
Fig. 25. Phase diagram for the system CaO-MgO, mainly after Doman, Barr, McNally, and Alper. The melting points of the end members CaO and MgO have been placed at 2570 and 2800°C, respectively, in accordance with data of Kanolt, pending results of the series of melting-point determinations presently in progress at the National Bureau of Standards.

3. SYSTEMS WITHOUT SiO₂ AS A COMPONENT

CaO-MgO: Approximate phase relations in the system CaO-MgO are shown in Fig. 25. Notable features are the limited mutual solubilities between the two end members in the solid state and the high solidus and liquidus temperatures prevailing over the entire composition range.

CaO-Al₂O₃: Phase relations in the system CaO-Al₂O₃ have been studied and re-studied by numerous investigators during the past 40 years. The equilibria prevailing in this complicated system now seem to be reasonably well established, thanks to concentrated efforts in many laboratories during recent years. The information is summarized in the diagram shown in Fig. 26. It is seen that although the end members both have very high melting points (CaO ~ 2570°C, Al₂O₃ ~ 2020°C), liquids form at as low a temperature as 1370°C in the binary system. Clearly, the simultaneous presence of large amounts of CaO and Al₂O₃ is undesirable in oxide bodies where high refractoriness is required. In the binary silicate systems shown earlier, glasses form only of compositions near the SiO₂-end. In contrast, calcium aluminate glasses form only of compositions in the central part of the system CaO-Al₂O₃.

CaO-TiO₂: Phase relations in the system CaO-TiO₂ are illustrated in Fig. 27. The lowest temperature of liquid formation is approximately 1460°C in TiO₂-rich mixtures. A somewhat different diagram, showing equilibrium existence of the phase Ca₄Ti₅O₁₀, has been proposed by Roth.
Fig. 26. Phase diagram for the system CaO-Al₂O₃, based mainly on the original work of Rankin and Wright(126) and modified in accordance with more recent data of Goldsmith,(151) of Filonenko,(162) and of Gloria and Burdese.(153) The melting points of the end members CaO and Al₂O₃ are in accordance with Kanolt(149) and Burdick,(154) respectively. Abbreviations used have the following meanings:
C₃A = Ca₃Al₂O₆, C₁₂A₇ = Ca₁₂Al₁₄O₃₃, CA = CaAl₂O₄, CA₂ = CaAl₄O₇, CA₆ = CaAl₁₂O₁₉, Cor = corundum, L = liquid.

Fig. 27. Phase diagram for the system CaO-TiO₂, after DeVries, Roy, and Osborn.(155)
CaO-P₂O₅: The phase diagram for the system CaO-P₂O₅ (157-163) is reproduced in Fig. 28. A large number of intermediate compounds exist between the two end members. Liquidus temperatures are high near the CaO-end and low near the P₂O₅-end of the system.

A revision of the diagram in the composition range between 2CaO-P₂O₅ and 3CaO-P₂O₅ has been proposed recently by Welch and Gutt. (164) This change involves partial solid solution of 2CaO-P₂O₅ in 3CaO-P₂O₅ and a transformation in the latter phase at about 1450°C. These possible features are of little consequence in our discussions and are left out of Fig. 28 in order to avoid undue cluttering of the diagram.

Fig. 28. Phase diagram for the system CaO-P₂O₅, as summarized by Trömel and Fix. (163) Abbreviations used have the following meanings: C₄P = Ca₄P₂O₉, C₃P = Ca₃P₂O₈, C₂P = Ca₂P₂O₇, CP = CaP₂O₆, C₂P₃ = Ca₂P₆O₁₇, CP₂ = CaP₄O₁₁, L = liquid.
Fig. 29. Phase diagram for the system MgO-Al₂O₃, based mainly on data of Rankin and Merwin,¹⁴⁶ of Clark, Howe, and Badger,¹⁶⁶ of Roy, Roy, and Osborn,¹⁶⁷ and of Alper, McNally, Ribbe, and Doman.¹⁶⁸ The melting points of the end members MgO and Al₂O₃ have been placed at 2800°C¹⁴⁹ and 2020°C,¹⁶⁴ respectively, pending results of redetermination of melting points of refractory oxides.¹⁴⁶

Fig. 30. Sketch showing phase relations in the system MgO-Cr₂O₃, based mainly on data of Alper, McNally, Doman, and Keihm.¹⁶⁹
**MgO-Al₂O₃**: Equilibrium relations existing in the system MgO-Al₂O₃ are shown in Fig. 29. The lowest temperature of liquid formation is much higher than in the system CaO-Al₂O₃. Hence MgO and Al₂O₃ are much more compatible than are CaO and Al₂O₃ in bodies where high refactoriness is required. The extensive solid solubility among the components is a particularly noteworthy feature of the diagram.

**MgO-Cr₂O₃**: An approximate phase diagram for the system MgO-Cr₂O₃ is shown in Fig. 30. High liquidus and solidus temperatures prevail throughout the entire composition range of the system.

**MgO-TiO₂**: The phase diagram for the system MgO-TiO₂ is shown in Fig. 31. The lowest temperature of equilibrium existence of a liquid phase is approximately 1600°C.

**Al₂O₃-Cr₂O₃**: The two sesquioxides Al₂O₃ and Cr₂O₃ form a complete solid solution series at high temperatures, as shown by the diagram in Fig. 32. Liquidus and solidus temperatures are high throughout the system, decreasing continuously from ~2265°C for Cr₂O₃ to ~2020°C for Al₂O₃.

**Al₂O₃-TiO₂**: Phase relations in the system Al₂O₃-TiO₂ are shown in Fig. 33. One intermediate compound is formed between the end members, and the lowest liquidus temperature is approximately 1700°C.

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Fig. 31. Phase diagram for the system MgO-TiO₂, after Coughanour and DeProsse.
Fig. 32. Phase diagram for the system Al$_2$O$_3$-Cr$_2$O$_3$, after Bunting.$^{(171)}$

Fig. 33. Phase diagram for the system Al$_2$O$_3$-TiO$_2$, after Lang, Fillmore, and Maxwell.$^{(174)}$ Some uncertainty still prevails regarding the melting relations of the phase Al$_2$TiO$_5$, as indicated by the two alternative versions of the diagram presented for this region.
A. Systems in Which a Gas Phase Plays an Important Role

The three systems to be treated in detail in this section will be arranged in order of increasing complexity with respect to the condensed phases present. In the first system to be described (C-H-O), only one condensed phase, carbon (graphite), is present. In the next system (Fe-C-O), metallic iron and iron oxides are present in addition to carbon. Finally, in the last system (Fe-Si-O), silica and iron silicates appear as phases in addition to metallic iron and iron oxides.

Other ternary systems similar to the above will be discussed only briefly.

1. C-H-O

Equilibrium relations existing among the various gas species formed by the components C, H, and O may be evaluated by combination of equilibrium data for the reactions

$$2\text{CO}_2(g) = 2\text{CO}_2(g) + \text{O}_2(g)$$  \hspace{1cm} (5-1)

and

$$2\text{H}_2\text{O}(g) = 2\text{H}_2(g) + \text{O}_2(g).$$ \hspace{1cm} (5-2)

The equilibrium constants for reactions 1 and 2 may be written

$$K_1 = \frac{p_{\text{O}_2} \cdot p_{\text{CO}}^2}{p_{\text{CO}_2}^2}$$ \hspace{1cm} (5-3)

and

$$K_2 = \frac{p_{\text{O}_2} \cdot p_{\text{H}_2}^2}{p_{\text{H}_2\text{O}}^2},$$ \hspace{1cm} (5-4)

respectively, and from this the equilibrium constant $K$ for the reaction

$$\text{CO}_2(g) + \text{H}_2(g) = \text{CO}(g) + \text{H}_2\text{O}(g)$$ \hspace{1cm} (5-5)

is expressed as

$$K = \frac{p_{\text{CO}} \cdot p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} \cdot p_{\text{H}_2}} = \left(\frac{K_1}{K_2}\right)^{1/2}$$ \hspace{1cm} (5-6)

The numerical values of $K_1$ and $K_2$ are small ($\sim 10^{-12}$ to $\sim 10^{-8}$) in the temperature range of particular interest in our discussion, 1200–1600°C, whereas the numerical value of $K$ in the same temperature range is close to unity.

In experimental laboratory studies as well as in practical steelmaking it is desirable to establish the relation between the oxygen partial pressure of the system and the
proportions of the various gas species present in the system. Consider as an example a gas mixture consisting of CO\textsubscript{2} and H\textsubscript{2} at room temperature. Let \( p_{\text{CO}_2(i)} \) and \( p_{\text{H}_2(i)} \) be the initial partial pressures of the two species in the gas mixture at room temperature, and let \( p_{\text{CO}_2}, p_{\text{H}_2}, p_{\text{CO}}, p_{\text{H}_2\text{O}}, \) and \( p_{\text{O}_2} \) be the equilibrium partial pressures of the various gas species at elevated temperature. The following relationship is apparent from the requirement of conservation of matter:

\[
\begin{align*}
\frac{p_{\text{CO}_2(i)}}{p_{\text{CO}_2}} &= \frac{p_{\text{CO}}}{p_{\text{CO}}}, \\
\frac{p_{\text{H}_2(i)}}{p_{\text{H}_2}} &= \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}}},
\end{align*}
\]  

(5-7)

(5-8)

Hence, the original gas mixing ratio, \( r = \frac{p_{\text{CO}_2(i)}}{p_{\text{H}_2(i)}} \), can be expressed as

\[
\begin{align*}
r &= \frac{\frac{p_{\text{CO}_2} + p_{\text{CO}}}{p_{\text{H}_2} + p_{\text{H}_2\text{O}}}}{\frac{p_{\text{CO}}[1 + (p_{\text{CO}_2}/p_{\text{CO}})]}{p_{\text{H}_2\text{O}}[1 + (p_{\text{H}_2}/p_{\text{H}_2\text{O}})]}} \\
&= \frac{1 + (p_{\text{CO}_2}/p_{\text{CO}})}{1 + (p_{\text{H}_2}/p_{\text{H}_2\text{O}})}.
\end{align*}
\]  

(5-9)

Because the constants \( K_1 \) and \( K_2 \) are numerically small in comparison with \( K \), \( p_{\text{CO}} \) can be set equal to \( p_{\text{H}_2\text{O}} \), and hence

\[
r \approx \frac{1 + (p_{\text{CO}_2}/p_{\text{CO}})}{1 + (p_{\text{H}_2}/p_{\text{H}_2\text{O}})}.
\]

(5-10)

If this equation is combined with equation 5-6, \( p_{\text{CO}_2}/p_{\text{CO}} \) or \( p_{\text{H}_2}/p_{\text{H}_2\text{O}} \) can be eliminated. For simplicity, set \( p_{\text{CO}_2}/p_{\text{CO}} = x \) and \( p_{\text{H}_2}/p_{\text{H}_2\text{O}} = y \). From the two equations

\[
r = \frac{1 + x}{1 + y}
\]

(5-11)

and

\[
K = \frac{1}{x \cdot y},
\]

(5-12)

\( r \) can be expressed as

\[
r = \frac{x(1 + x)}{x + (1/K)}.
\]

(5-13)

The only unknown in this equation is \( x \), which is easily determined. The value of \( x \) is then inserted into equation 5-3, and \( p_{\text{O}_2} \) is calculated as \( K_1 \cdot x^2 \). A diagram showing relations among oxygen partial pressures, CO\textsubscript{2}/H\textsubscript{2} mixing ratios, and temperatures at a constant total pressure of 1 atm is presented in Fig. 34.

At very low oxygen pressures of the system, disproportionation of CO with precipitation of carbon may occur, according to the equation

\[
2\text{CO} = \text{C} + \text{CO}_2.
\]

(5-14)

Ratios \( p_{\text{CO}_2}/p_{\text{H}_2} \) of the gas phase in equilibrium with carbon as a function of temperature are shown by the heavy dash-cross curve in Fig. 34. The shaded area below this curve represents gas compositions which cannot be realized experimentally if equilibrium prevails in the system.

2. Fe-C-O

Equilibrium data for the two systems Fe-O and C-O can be combined to express stability relations existing in the system Fe-C-O. As an example, the equilibrium

* In order to make this exact, a small correction factor would have to be introduced to account for the very slight volume change accompanying reactions 5-1 and 5-2 at constant pressure. However, this factor is negligible, because \( K_1 \) and \( K_2 \) are small in comparison with \( K \).
Fig. 34. Curves showing oxygen pressures of $\text{CO}_2/\text{H}_2$ mixtures as a function of mixing ratios and temperature, at a constant pressure of 1 atm. The heavy dash-cross curve represents equilibrium between the gas phase and carbon (graphite), and the shaded area below the latter curve represents metastable conditions of the gas phase.
constant $K$ for the reaction

$$\text{FeO}_1 + \text{CO}_1 = \text{Fe}_0 + \text{CO}_2$$

(5-15)

is derived by a combination of the following equilibrium equations:

$$\text{FeO}_1 = \text{Fe}_0 + \frac{1}{2}\text{O}_2; \quad K_3 = \frac{pO_2^{1/2} \cdot aFe}{aFeO},$$

(5-16)

$$\text{CO}_2 = \text{CO}_0 + \frac{1}{2}\text{O}_2; \quad K_4 = \frac{pO_2^{1/2} \cdot pCO}{pCO_2}.$$  

(5-17)

The expression for $K$ is

$$K = \frac{K_3}{K_4} = \frac{pCO_2 \cdot aFe}{pCO \cdot aFeO}.$$  

(5-18)

If pure condensed phases whose activities can be set equal to one are assumed, the expression for $K$ is reduced to

$$K = \frac{pCO_2}{pCO}.$$  

(5-19)

Analogous derivations can be carried out for pairs of iron oxide phases, such as FeO-Fe$_3$O$_4$ and Fe$_3$O$_4$-Fe$_2$O$_3$. The equilibrium relations in the system Fe-C-O can thus be summarized in a diagram showing the condensed phases present as a function of temperature and $pCO_2/pCO$ ratio of the gas phase, as presented in Fig. 35. The heavy dash-cross line represents $CO_2/CO$ ratios of the gas phase which is in equilibrium with carbon

![Fig. 35. Stability relations among metallic iron and iron oxides, as a function of CO$_2$/CO ratios and temperature, at a total pressure of 1 atm. The dash-cross curve represents equilibrium between the gas phase and carbon (graphite), and dash-dot lines are oxygen isobars.](image-url)
Fig. 36. Phase relations among metallic iron and iron oxides as a function of temperature and CO₂/CO ratios of the atmosphere, at a total pressure of 1 atm. Heavy solid lines are boundary curves, light dash-dot lines are curves of equal CO₂/CO ratios of the gas phase, and the heavy dash-cross line is the carbon deposition curve. The cross-hatched area below the latter curve represents metastable conditions.

(graphite). The shaded section to the left of this curve represents conditions which cannot be realized experimentally if equilibrium prevails.

The diagram in Fig. 35 has the same shortcoming as Fig. 12, in that it does not show compositions of the condensed phases. This shortcoming is eliminated in the diagram presented in Fig. 36, where stability ranges of condensed phases are shown as a function of their total composition and of temperature. Heavy solid lines in this diagram are boundary curves, light dash-dot lines are curves of equal CO₂/CO ratios of the gas phase in equilibrium with the condensed phases, and the heavy dash-cross curve is the carbon deposition curve. The intersection of the latter curve with the FeO-Fe boundary curve defines the lowest temperature (≈620°C) at which metallic iron can be made by reduction of iron oxide with carbon, at a total pressure of 1 atm.
3. Fe-Si-O

a. General considerations. The two ternary systems discussed so far (C-H-O, Fe-C-O) could be adequately described by using only one composition axis, because carbon and the various oxides of iron were the only condensed phases present. In the system Fe-Si-O, however, condensed phases are formed in which all three components are present. In this case it is therefore necessary to introduce an additional composition axis in order to describe the phase relations adequately.

An equilateral triangle is the most suitable figure for representing compositions in a ternary system. The composition triangle for the system Fe-Si-O is shown in Fig. 37(a), with one component at each apex. Because oxygen is a gas and Fe and Si are condensed phases at the temperatures of interest in the present discussion, the O apex of the triangle assumes a role different from those of the other two in the use of the diagram. Consider the situation existing when compositions of condensed phases change in response to changes in the oxygen pressure of the gas phase. During such a process an exchange of oxygen takes place between gas and condensed phases such that the Si/Fe ratio of the latter phases remains constant. This constancy of Si/Fe ratios is described by a family of straight lines radiating from the O apex of the triangle in Fig. 37(a). In accordance with previously adopted terminology, these lines will be referred to as oxygen reaction lines.

The area FeO-Fe₂O₃-SiO₂ in Fig. 37(a) is of particular interest in discussions of equilibria among oxides in steelmaking. For purposes of clear illustration of the phase relations, it is advantageous to draw this area enlarged and in the form of an equilateral triangle, as shown in Fig. 37(b). The oxygen reaction lines are seen as dash-dot lines extending from left to right across the diagram.

Phase relations in the system FeO-Fe₂O₃-SiO₂ will be discussed in considerable detail in the following, both because certain composition areas of the system have an important bearing on silica brick problems, and because the application of the phase rule to ternary systems is particularly well illustrated in this system. The equilibria will be discussed by means of three different types of representations: the liquidus surface, the solidus surface, and isothermal sections.

![Fig. 37. Composition triangles for the systems (a) Fe-Si-O and (b) FeO-Fe₂O₃-SiO₂, as discussed in text.](image)
**b. The liquidus surface.** Three diagrams are presented in order to illustrate adequately the phase relations existing at liquidus temperatures. It would have been possible but not practical to combine these three diagrams into one. The resulting diagram would hardly be legible because of too many lines.

The first of these diagrams (Fig. 38) is a projection of the liquidus surface showing liquidus isotherms as light lines and boundary curves separating the various primary phase areas as heavy lines. This diagram shows relations between temperature and compositions of liquids coexisting in equilibrium with crystals. For instance, the 1400°C

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* A primary phase area comprises compositions of all mixtures having as the first ("primary") crystalline phase to appear during equilibrium cooling the phase labeled for that area in Fig. 38.
liquidus isotherm represents compositions of all liquids that can exist at 1400°C in equilibrium with magnetite in the magnetite primary phase area, with tridymite in the tridymite primary phase area, and with magnetite and tridymite on the boundary curve between the two areas.

The second diagram (Fig. 39) is a projection of the liquidus surface showing fractionation curves as medium dashed lines and boundary curves as heavy lines. The fractionation curves illustrate in a convenient way interrelations between liquid and crystalline phases coexisting in equilibrium. The significance and use of the fractionation curves are best understood by reference to their construction from conjugation lines. The latter are straight lines connecting two points representing compositions of two condensed phases (in our case, one crystalline and one liquid) coexisting in equilibrium.

Fig. 39. Projection of the liquidus surface of the system FeO-Fe₂O₃-SiO₂\(^{175}\) showing boundary curves as heavy lines and fractionation curves as medium dashed lines.
Fig. 40. Examples of conjugation lines showing compositions of wüsite and liquid phases coexisting in equilibrium in the system FeO-Fe₂O₃-SiO₂.

Examples of conjugation lines in the wüsite field of the system FeO-Fe₂O₃-SiO₂ are shown in Fig. 40. For instance, liquid a₁ is in equilibrium with wüsite crystals of composition a'₁, and liquid a₂ is in equilibrium with wüsite a'₂. Fractionation curves are constructed from the conjugation lines in such a manner that the latter are tangents to the former. An example of a fractionation curve in Fig. 40 is f-f". Each point on this fractionation curve represents the composition of a liquid coexisting with a wüsite phase whose composition is determined as the point of intersection between the join FeO-Fe₂O₃ and the tangent to the fractionation curve at the point representing the composition of the liquid. Clearly, a₁-a'₁ and a₂-a'₂ are examples of such tangents.

A family of fractionation curves for the system FeO-Fe₂O₃-SiO₂ is shown in Fig. 39. In the field of silica (cristobalite or tridymite), and in the field of magnetite to the left of the FeO-Fe₂O₃-SiO₂ join, the fractionation curves are straight lines. This is because the compositions of the crystalline phases in equilibrium with liquids in these areas are constant (corresponding to the chemical formulas SiO₂ and FeO-Fe₂O₃, respectively). Only in the wüsite field and in the magnetite field to the right of the join FeO-Fe₂O₃-SiO₂ do the fractionation curves have finite radii of curvature, because the crystalline phases in equilibrium with liquids in these areas have variable compositions. Fractionation curves have not been drawn through the upper, two-liquid area of Fig. 39. Mixtures within this area at liquidus temperatures consist of cristobalite (of composition SiO₂) and two liquids whose compositions are represented by points along the outlines of this area. No liquid of composition within this area is stable at liquidus temperatures. If the straight-line fractionation curves in the SiO₂ primary phase area were extended into the two-liquid region, they would represent the combined composition of the two liquid phases coexisting with SiO₂. Because it is sometimes of special interest to have this information readily available in graphical form, the fractionation curves have been drawn through the two-liquid region in at least one recent publication.¹⁷₆
Fig. 41. Projection of the liquidus surface of the system FeO-Fe₂O₃-SiO₂\(^{175}\) showing boundary curves as heavy lines and oxygen isobars (in atm) as light dash-dot lines.

The third diagram needed for adequate description of phase relations in the system FeO-Fe₂O₃-SiO₂ is shown in Fig. 41. Here, lines of equal oxygen pressures (to be referred to as oxygen isobars) at liquidus temperatures are drawn as dash-dot curves and boundary curves as heavy lines. The significance and use of the oxygen isobars in this system are best visualized by comparison with the previous discussion of analogous relations for the system Fe-O (see Fig. 13). Consider the use of the phase rule in the situation prevailing at the intersection between a chosen oxygen isobar and the liquidus curve in the latter system. Since three phases (one crystalline, one liquid, and one gas) coexist under these conditions, the two-component system has only one degree of freedom \((F = C + 2 - P = 2 + 2 - 3 = 1)\). In choosing the oxygen pressure, this degree of freedom is expended, and the temperature at which the chosen phase assemblage exists under equilibrium conditions is fixed. When SiO₂ is added as a third component to the system Fe-O, however, one additional degree of freedom exists if the
number of phases remains the same. Hence another variable may be independently chosen, for instance the SiO$_2$ content of the liquid. Temperature and the Fe$_2$O$_3$/FeO ratio of the liquid are then fixed. It follows that for each chosen oxygen pressure the oxygen isobar extends along the liquidus surface of the ternary system FeO-Fe$_2$O$_3$-SiO$_2$ from the point of intersection between the oxygen isobar and the liquidus curve in the system Fe-O. Each point along this isobar in the ternary system represents the composition of a liquid which is in equilibrium with one crystalline phase (or two crystalline phases where the oxygen isobar intersects a boundary curve) and a gas phase of constant oxygen pressure.

c. Paths of equilibrium crystallization. Paths of equilibrium crystallization of mixtures within the system FeO-Fe$_2$O$_3$-SiO$_2$ depend critically on the conditions under which the process is carried out. In analogy with the previous discussion of the system Fe-O, two idealized conditions will be considered.

The first is crystallization under such conditions that total composition of the condensed phases remains constant. This situation is approximated in a closed system when the volume of the gas phase is small. The paths of crystallization in this case are derived from the projections of the liquidus surface by methods which have been described extensively in the literature (see, for instance, papers from the Geophysical Laboratory of the Carnegie Institution of Washington$^{126,177-179}$) and applied specifically to the system FeO-Fe$_2$O$_3$-SiO$_2$. An example of this type of crystallization path is shown in Fig. 42, illustrating phase relations adjacent to the FeO apex of the composition triangle. Consider a mixture $A$ located in the primary phase area of wüüstite. As heat is withdrawn from the system and equilibrium is maintained, the liquid composition changes first along the curved path $A-a_1$ and subsequently along the wüüstite-fayalite boundary curve from $a_1$ to $a_2$. The liquid disappears at the temperature of the latter point. The wüüstite composition during this process changes first from $\alpha$ to $\alpha_1'$ and subsequently from $\alpha_1'$ to $\alpha_2'$. The composition of fayalite is constant, corresponding to the formula 2FeO-SiO$_2$. The relative amounts of each phase present at any temperature are determined from the position of the point ($A$) representing the constant total composition relative to the positions of the points representing compositions of coexisting condensed phases, as illustrated by the sketches in Fig. 43. For instance, when only two condensed phases, such as wüüstite ($\alpha_2'$) and liquid ($\alpha_2$), are in equilibrium, their relative amounts are determined from the well-known "lever rule" as shown in Fig. 43(a): the amount of wüüstite is $100 \cdot Aa_2'/a_2a_2'$% and the amount of liquid is $100 \cdot Aa_2'/a_2a_2'$%. An example of the geometrical relations involved in determining relative amounts in the case of coexistence of three condensed phases, wüüstite ($\alpha_4'$), fayalite (2FeO-SiO$_2$), and liquid ($\alpha_p$), is illustrated in Fig. 43(b). The amount of wüüstite is $100 \cdot AN/NA_4'$%, fayalite $100 \cdot AF/F-2\text{FeO-SiO}_2$%, and liquid $100 \cdot AL/a_pL%$. It is readily seen that these amounts can also be expressed as $100 \cdot W'-2\text{FeO-SiO}_2/a_p'2\text{FeO-SiO}_2$%, $100 \cdot a_pF'/a_p-2\text{FeO-SiO}_2$, and $100 \cdot a_pL'/a_pL'$, respectively, where $W'$, $F'$, and $L'$ are points of intersections between the sides of the triangle $a_p-a_p'-2\text{FeO-SiO}_2$ and straight lines through $A$ parallel to the sides of the triangle.

The triangle formed by the three conjugation lines connecting points representing the three coexisting condensed phases (Fig. 43b) is commonly referred to as a three-phase triangle. In the example of crystallization path given above, the composition triangle "moves" as temperature decreases, because the compositions of the liquid and the wüüstite phases vary. One specific position of the three-phase triangle was represented in Fig. 43(b). Examples of other positions of the three-phase triangle are shown in Fig. 43(c). In one of these, 2FeO-SiO$_2$-$\alpha_1$-$\alpha_4'$, point $A$ is located on the wüüstite-liquid join, and hence fayalite is just on the verge of appearing as a phase (corresponding to point $a_1$ in Fig. 42). In the other situation, point $A$ is located on the wüüstite-fayalite
join, and the liquid is just disappearing as a phase (corresponding to point $a_2$ in Fig. 42). Hence the solidus temperature in a ternary system where one or more solid solution phases are involved in the equilibrium is either that of an invariant point or that of a point along a univariant boundary curve representing the composition of a liquid which is in equilibrium with two crystalline phases such that the conjugation line for the latter two phases passes through the point representing total composition of the mixture. If the crystalline phases involved in the equilibrium have fixed compositions (no solid solutions formed), the point representing liquid composition is the only apex of the three-phase triangle which moves during crystallization. In this case the solidus

Fig. 42. Diagram of a part of the system FeO-Fe$_2$O$_3$-SiO$_2$ shown in order to illustrate paths of equilibrium crystallization under conditions of constant total composition of condensed phases. In addition to boundary curves, liquidus isotherms, and oxygen isobars which can be identified by comparison with Figs. 38 and 41, the heavy solid line is the equilibrium crystallization curve, medium dashed lines are fractionation curves and light dashed lines are conjugation lines.
temperature is that of a ternary invariant point, usually either a eutectic or a peritectic, although it may be the temperature of a maximum point on a boundary curve. If more than one such invariant point is present in the system, the solidus temperature for a mixture of chosen composition is that of the invariant point at which the liquid is in equilibrium with crystalline phases whose composition points form a triangle (composition triangle) within which point A (representing the constant total composition of the mixture) is located.

Crystallization under conditions of constant oxygen pressure is radically different from that just considered. The liquid composition during equilibrium crystallization must follow the oxygen isobar corresponding to the chosen constant oxygen pressure. As the condensed phases react with the gas phase during this process, oxygen is added to or subtracted from the condensed phases. The total composition of the condensed
phases therefore changes during the process, but only with respect to their oxygen content. As explained previously (see Fig. 37), this composition change is described by the oxygen reaction lines radiating from the O apex of the triangle Fe-Si-O, of which FeO-Fe₂O₃-SiO₂ is a part.

The path of crystallization of an iron oxide-silica mixture at constant oxygen pressure is illustrated in Fig. 44, where mixture C in the primary phase field of wüstite is used as an example. As heat is withdrawn at constant oxygen pressure and equilibrium is maintained, the liquid composition first changes along the oxygen isobar from C to c₁ as wüstite crystallizes out. Wüstite, magnetite and liquid c₁ coexist in equilibrium at temperature t₁. As more heat is withdrawn from the system, wüstite disappears and

![Diagram of the system FeO-Fe₂O₃-SiO₂](image)

**Fig. 44.** Diagram of the system FeO-Fe₂O₃-SiO₂ shown in order to illustrate paths of equilibrium crystallization at constant O₂ pressure. In addition to the line symbols explained for Fig. 42, the dash-cross line represents changes in total composition of condensed phases during crystallization.
magnetite crystallizes out, with liquid composition changing along the oxygen isobar from c1 to c2. At the temperature of the latter point the liquid is saturated with silica, and the three condensed phases, tridymite, magnetite, and liquid, coexist in equilibrium. One phase must disappear before the temperature can change because the system has only one degree of freedom, and the oxygen pressure has been chosen. Because \( t_c \) is the lowest liquidus temperature on the chosen oxygen isobar, it is the liquid phase which disappears at \( t_c \). The end product of crystallization is thus a mixture of tridymite and magnetite, and thus the total composition of the crystalline aggregate must lie on the FeO-Fe_2O_3-SiO_2 join. The total composition of the condensed phases during the crystallization has changed along the dash-cross oxygen reaction line from C to C'.

It follows as a general rule that in ternary oxide systems where changes in oxidation states take place, the lowest temperature of liquid existence at constant oxygen pressure is that of intersection between a boundary curve and the oxygen isobar in question. Only when the oxygen isobar happens to pass through a ternary invariant point is the temperature of the latter the solidus temperature.

d. Composition sections through the system FeO-Fe_2O_3-SiO_2. It is often convenient and informative to present phase relations in the system iron oxide-silica in diagrams which are simpler than those shown in the preceding figures (Figs. 38 through 44). This is possible when the experimental conditions used are such as to restrict the compositions of condensed phases to lines or relatively narrow bands through the composition triangle FeO-Fe_2O_3-SiO_2. Two examples of such simplified diagrams are discussed below and illustrated in Fig. 45. The first and best known of these diagrams, (a), is that for the system "FeO"-SiO_2 as determined by Bowen and Schairer. They developed a special experimental technique for studying this system some 30 years ago. The oxide phases were contained in iron crucibles in a "neutral" purified nitrogen atmosphere. Hence metallic iron was always present as a phase, and the compositions of the oxide phases present in equilibrium were those of the boundary curve between iron and the oxide phases wüstite, fayalite, and silica in Fig. 38. The phase relations were illustrated by projecting the compositions of the condensed phases along oxygen
reaction lines onto the iron oxide-SiO₂, which is close to the iron boundary curve. This amounts to the same as recalculating all iron as FeO. The resulting diagram, shown in Fig. 45, has the appearance of a binary system and also can be treated as a binary system as far as path of equilibrium crystallization is concerned. The second diagram (Fig. 45b) shows phase relations in the system iron oxide-SiO₂ in air (pO₂ = 0.21 atm (1175, 109)). In this case the true compositions of liquids at liquidus temperatures are those of the 0.21 atm oxygen isobar in Fig. 41. For sake of simplicity, compositions along this isobar are projected along oxygen reaction lines onto the iron oxide-SiO₂. This amounts to the same as recalculating all iron as FeO·Fe₂O₃. Again, the resulting diagram has the appearance of a binary system and may be treated as such in derivations of equilibrium crystallization paths.

In anticipation of later application of the diagrams in Fig. 45 to the problem of reactions between silica brick and iron oxides, it is of interest to note the effect of changes in oxygen pressure on the location of the two-liquid region of the system. It is seen by a comparison of the two diagrams that the lower temperature limit of existence of two liquids decreases and the SiO₂ content of the low-silica liquid decreases as the oxygen pressure increases. The implication of these relations in silica-brick technology will be explained in a later chapter.

e. The solidus surface. A projection of the solidus surface for the system FeO-Fe₂O₃-SiO₂ is shown in Fig. 46. Heavy solid lines outline composition areas within each of which all mixtures at solidus temperatures have as crystalline phases those labeled for the particular area, and light dashed lines are solidus isotherms representing lowest temperatures of liquid existence. The various features of the solidus surface are visualized by comparison with the paths of equilibrium crystallization of selected mixtures as discussed above. Two different types of areas are seen to exist among those present in the diagram of Fig. 46. One is characterized by the coexistence of three crystalline phases with liquid and gas at the solidus temperature. Since this phase assemblage corresponds to an invariant situation \( F = C + 2 - P = 3 + 2 - 5 = 0 \), there is only one temperature at which each such assemblage can exist in equilibrium. Hence the solidus temperature is constant within such a triangle (see numbers labeled on the diagram). There are four triangles of this type in the diagram of Fig. 46, each corresponding to one of the three ternary liquidus invariant points present in the system FeO-Fe₂O₃-SiO₂ (compare Fig. 38). One is the triangle SiO₂-FeO·Fe₂O₃-2FeO·SiO₂ formed by the composition points representing the three crystalline phases coexisting with liquid at 1140°C (see Fig. 38). The solidus temperature for all mixtures within this area is 1140°C. The second is the triangle 2FeO·SiO₂-FeO·Fe₂O₃-w for which the solidus temperature is 1150°C. Point w of this triangle represents the composition of the wüstite phase which, together with fayalite (2FeO·SiO₂) and magnetite (FeO·Fe₂O₃), is present in equilibrium with liquid at 1150°C. The third triangle is SiO₂-Fe₂O₃-x, with a solidus temperature of approximately 1455°C. Point x in this diagram represents the composition of the magnetite phase which is in equilibrium with hematite, silica (tridymite), and liquid (compare Fig. 38). Adjacent to the FeO-SiO₂ join between 2FeO·SiO₂ and FeO is an area with a solidus temperature of 1177°C and coexistence of fayalite (2FeO·SiO₂), wüstite of composition y, metallic iron, and liquid. This area is part of a larger triangle representing the ternary system Fe-Si-O, of which FeO·Fe₂O₃-SiO₂ is a part.

Wedge between the above triangles are two triangles comprising compositions of mixtures which have two crystalline phases coexisting with a liquid phase at the solidus temperatures. Since the system under these conditions has one degree of freedom \( F = C + 2 - P = 3 + 2 - 4 = 1 \), the solidus temperature varies as the composition of at least one of the crystalline phases varies in such an area. One of these areas (y-w-2FeO·SiO₂) is characterized by the coexistence of fayalite (2FeO·SiO₂)
and wüsite with liquid in the temperature range 1150–1177°C. The other (FeO·Fe₂O₃-x-SiO₂) is characterized by the simultaneous presence of silica (tridymite, SiO₂), magnetite, and liquid in the temperature range 1140–1456°C.

In addition to these wedge-shaped areas, a straight line (labeled 1155) separates the two areas with solidus temperatures of 1140 and 1150°C, respectively. This straight line represents the coexistence of fayalite, magnetite, and liquid of composition at the maximum of the fayalite-magnetite boundary curve. Because the crystalline phases present in this equilibrium have constant compositions, the wedge-shaped area as discussed above has “shrunk” into a line.

Application of the phase rule to the equilibria illustrated in Fig. 46 reveals the following relations regarding oxygen isobars along the solidus surface: Because the situation is invariant when three crystalline phases, liquid, and gas are present together, the oxygen pressure of the gas phase is constant within each of the first type of triangles discussed above. Numerical values of these oxygen pressures are given (numbers in

![Diagram](image)

**Fig. 46.** The solidus surface for the system FeO-Fe₂O₃-SiO₂. The various features of the diagram are discussed in the text. Abbreviations used have the following meanings: W = wüsite, F = fayalite, M = magnetite, H = hematite, T = tridymite.
parentheses) for each triangle in Fig. 46. In contrast, oxygen pressures of the gas phase for the phase assemblages existing in the second type of triangles in Fig. 46 vary. The oxygen isobars in these areas are represented by straight lines parallel to the solidus isotherms. The former curves have not been drawn in Fig. 46, however, in order to avoid the confusion caused by too many lines.

f. Isothermal sections through the system FeO-Fe₂O₃-SiO₂. It frequently happens that phase relations at one temperature are of special interest. In this case it is useful and instructive to draw a diagram showing explicitly and in detail the phase relations prevailing at that temperature. Such diagrams are commonly referred to as isothermal sections.

The temperature of 1200°C will be chosen as an example to demonstrate the procedures used in deriving an isothermal section from the liquidus surface projections of the system FeO-Fe₂O₃-SiO₂ illustrated in Figs. 38 through 41. Liquids in equilibrium with one or more crystalline phase(s) at 1200°C have compositions represented by points along the 1200°C liquidus isotherm (Fig. 38). This liquidus isotherm is reproduced as the curve a-b-c-d-e-f in Fig. 47, where the picture has been distorted somewhat to show the relations more clearly.

Fig. 47. Sketch illustrating methods used for constructing the 1200°C isothermal section through the system FeO-Fe₂O₃-SiO₂, as discussed in the text. The diagram has been somewhat distorted in order to show the relations as clearly as possible. Abbreviations used have the following meanings: W = wüstitite, F = fayalite, M = magnetite, H = hematite, T = tridymite, L = liquid.
It is immediately evident that the part of the liquidus surface enclosed by the curve a-b-c-d-e-f is located below the 1200°C iso thermometer plane, and hence all mixtures having compositions within this area consist of one liquid phase at 1200°C. In order to delineate the relations for the remainder of the isothermal section, it is useful to consider separately the equilibria prevailing along each section of the liquidus isotherm. Liquids of compositions along the curve a-b are in equilibrium with silica (tridymite) of constant composition, SiO₂. The area described by a straight line whose one endpoint is anchored at the SiO₂ composition point and whose other endpoint slides along the curve a-b comprises compositions of all mixtures consisting of the phases silica (tridymite) and liquid at 1200°C. This area is therefore labeled accordingly in Fig. 47. Point b on the 1200°C liquidus isotherm is located on the silica-magnetite boundary curve and hence represents a situation where liquid of this composition is simultaneously in equilibrium with these two crystalline phases. The triangle b-SiO₂-FeO-Fe₂O₃ therefore comprises compositions of all mixtures in which silica (tridymite), magnetite, and liquid are present together in equilibrium at 1200°C, as indicated by the labeling in Fig. 47. Relations similar to those described above can be derived for the sections b-c and e-f of the liquidus isotherm, giving rise to the areas labeled magnetite + liquid and fayalite + liquid, respectively. The remaining sections of the liquidus isotherms have slightly different features. Liquids along the section c-d are in equilibrium with wüstit crystals. As distinguished from silica and fayalite, the wüstit phase has variable composition. Wüstite in equilibrium with liquid c has composition c', that in equilibrium with liquid d has composition d', and wüstite crystals in equilibrium with liquids of compositions intermediate between c and d vary in composition between c' and d'. The area c-d-d'-c' thus comprises compositions of all mixtures having wüstite and liquid as equilibrium phases at 1200°C. Liquids of compositions along d-e and f-a are in equilibrium with metallic iron. The composition point for the latter phase is outside the area (FeO-Fe₂O₃-SiO₂) covered by the present composition triangle. However, the straight lines d-d', e-e', f-f' and a-a' are drawn with directions toward the Fe-apex of the composition triangle Fe-Si-O, of which FeO-Fe₂O₃-SiO₂ is a part. Thus the two areas d-d'-e-e' and a-a'-f-f' comprise compositions of all mixtures consisting of the phases metallic iron and liquid at 1200°C.

Mixtures of compositions to the right of the join SiO₂-FeO-Fe₂O₃ have no liquid phase present under equilibrium conditions at 1200°C. Because there is some solid solubility of Fe₂O₃ in magnetite at 1200°C (see Fig. 13), there is first an area of coexistence of tridymite (composition SiO₂) and magnetite of variable composition (SiO₂-FeO-Fe₂O₃-y), and then an area (SiO₂-y-Fe₂O₃) of coexistence of tridymite, magnetite and hematite.

A series of isothermal sections through the system FeO-Fe₂O₃-SiO₂ is shown in Fig. 48. The 1200°C section which was distorted in Fig. 48 for clearer illustration of the methods involved is included in its true, undistorted form in Fig. 48 to complete the picture for the temperature range 1200–1500°C.

In the application of the phase rule to isothermal sections, it must be remembered that one degree of freedom has been expended in choosing the constant temperature of the isothermal section in question. Hence, from the standpoint of the phase rule, the situation existing when one crystalline phase and liquid are in equilibrium within an area of the diagrams in Figs. 47 and 48 is very similar to that existing when two crystalline phases and a liquid are in equilibrium within an area of the diagram in Fig. 46. For instance, the oxygen isobars must be straight lines through these areas in both diagrams. Similarly, the oxygen pressure is constant in a triangle where two crystalline phases and liquid exist in equilibrium in Figs. 47 and 48, and three crystalline phases and liquid coexist in equilibrium in Fig. 46. It also follows that the oxygen isobars in the isothermal sections are curved lines only in areas where only one condensed phase is present. The all-liquid area represents such a situation in Figs. 47 and 48.
Fig. 48. Isothermal sections at 1200, 1300, 1400, and 1500°C through the system FeO-Fe₂O₃-SiO₂. Each area in the diagrams comprises compositions of mixtures consisting of the phases labeled for that area at the temperature in question. Abbreviations used have the following meanings: W = wüstite, F = fayalite, M = magnetite, H = hematite, T = tridymite, C = cristobalite, L = liquid.

If the oxygen pressure is chosen in addition to temperature, the phase relations may be referred to as “isothermal, oxygen-isobaric.” An “isothermal, oxygen-isobaric section” through the system FeO-Fe₂O₃-SiO₂ would be represented by a curve through the composition triangle representing the system. Such a curve is shown in Fig. 49. Its appearance is visualized by comparison with the preceding discussion and the diagrams shown in Figs. 47 and 48. The curve consists of three parts. Two of these (FeO-Fe₂O₃-x and y-SiO₂) are straight lines corresponding to the straight-line oxygen isobars through the two-phase areas (two condensed phases) magnetite + liquid and silica + liquid, respectively, and the third (x-y) is the curved line through the region in Fig. 48(b) in which only a liquid phase is present. Points x and y may also be identified as the points of intersection between the liquidus isotherm corresponding to the chosen temperature (see Fig. 38) and the oxygen isobar corresponding to the chosen oxygen pressure (see Fig. 41).
Fig. 49. Diagram illustrating phase relations at chosen constant temperature (1300°C) and chosen constant oxygen pressure (10⁻⁷ atm) in iron oxide-silica mixtures, as discussed in the text.

Fig. 50. Stability relations among iron oxides and metallic iron as a function of temperature (in °C) and ratios of H₂O/H₂ of the gas phase in equilibrium with the condensed phases. Heavy solid lines are boundary curves separating the various phase areas labeled in the diagram, and light dash-dot lines are oxygen isobars.
Fig. 51. Phase relations in the system Fe-O, with superimposed lines of equal H₂O/H₂ ratios (dash-dot lines) of gas phase in equilibrium with condensed phases. Heavy lines are boundary curves separating the various phase areas, as labeled on the diagram.

The oxygen reaction lines through points x and y divide the triangle into three parts, numbered 1, 2, and 3 in Fig. 49. Each of these parts comprises compositions of iron oxide-silica mixtures which upon equilibration at the chosen temperature and oxygen pressure applying to Fig. 49 give as phase assemblage those characteristic for various parts of the FeO-Fe₂O₃-x-y-SiO₂ curve, viz., magnetite + liquid in area 1, liquid in area 2, and tridymite + liquid in area 3.

4. Fe-H-O

Diagrams illustrating stability relations of metallic iron and iron oxides in H₂O-H₂ atmospheres are presented in Figs. 50 and 51. The types of representations used in these diagrams are analogous to those of Figs. 35 and 36. A comparison of the two pairs of diagrams shows striking similarities in locations of the curves. This is because the dissociation constants of H₂O and of CO₂ are almost identical in the temperature interval concerned. No curve similar to the dash-cross curves of Figs. 35 and 36 is present in Figs. 50 and 51, however, because all species in the system H-O are gases at the temperatures concerned.
5. METAL$_1$-METAL$_2$-OXYGEN SYSTEMS OTHER THAN Fe-Si-O

In general, systems similar to Fe-Si-O have not been studied sufficiently to permit the drawing of phase diagrams comparable in information to those shown in Figs. 38 through 49. Enough data are available, however, for some of these systems to illustrate phase relations in certain sections through the ternary systems. Commonly, the phase relations along the air ($p_{O_2} = 0.21$ atm) isobar and at strongly reducing conditions approaching those of equilibrium with a metal phase are known. A number of such diagrams will be discussed briefly in the following, and their relations to the ternary systems from which they originate will be illustrated in some cases.

In most cases, however, the phase relations will be illustrated as projections along oxygen isobars onto chosen joins, with the resulting diagrams having appearances similar to those of binary systems. These projected diagrams are just as well defined thermodynamically as are truly binary systems. The only information which is lost in projecting phase relations in this manner is information on ratios of the various oxidation states of the transition metal ions present (in oxygen contents) in the condensed phases. In the crystalline phases, these ratios may often be inferred, at least approximately, because of geometrical restrictions imposed by the structure in question. In the liquid phase, on the other hand, the geometrical restrictions are less severe, and the ratios must be determined by chemical analysis. Such data are available for some of the systems to be presented in the following. However, since there has been no demonstrated use of such data in practical steelmaking, this information is left out in order to avoid undue cluttering of the diagrams.

Fig. 52. Sketch showing inferred, approximate liquidus surface of the system MnO-Mn$_2$O$_3$-SiO$_2$ (compare text).
Fig. 53. Phase diagrams for the system manganese oxide-SiO$_2$ (a) in an atmosphere of CO$_2$/H$_2$ = 1$^{(181)}$ and (b) in air.$^{(182)}$ The systems are not binary. Compositions of condensed phases have been projected along oxygen reaction lines onto the joins MnO-SiO$_2$ and Mn$_3$O$_4$-SiO$_2$ in (a) and (b) respectively, because MnO is the stable phase of manganese oxide at liquidus temperatures under the atmospheric conditions prevailing in (a), and Mn$_3$O$_4$ in (b). Abbreviations used have the following meanings: (e) = cubic, (t) = tetragonal, R = rhodonite, T = tephroite, L = liquid.

**Mn-Si-O**: A triangle representing the system MnO-Mn$_3$O$_4$-SiO$_2$ is shown in Fig. 52. The method of representation is analogous to that used in the preceding discussion of the system Fe-Si-O. The triangle in Fig. 52 is part of the triangle Mn-Si-O, and oxygen reaction lines (not shown) point to the O apex of the latter triangle.

The liquidus surface of the system MnO-Mn$_3$O$_4$-SiO$_2$ is not known accurately, but the sketch in Fig. 52 is thought to illustrate the main features of the phase relations. The sketch has been made on the basis of work presently in progress in our laboratory and data previously reported for the system at two levels of controlled oxygen pressures.$^{(181,182)}$ The information available is not sufficient to justify the drawing of separate diagrams each showing liquidus isotherms, a family of fractionation curves, and a family of oxygen isobars, respectively, as was done in the case of the system FeO-Fe$_2$O$_3$-SiO$_2$. However, as a rough approximation it may be assumed that fractionation curves are essentially straight lines radiating from the composition points for the various crystalline phases, and that the oxygen isobar corresponding to air is located approximately as suggested by the dash-dot curve in Fig. 52.

Phase relations in the system manganese oxide-SiO$_2$ in equilibrium with a gas phase of CO$_2$/H$_2$ ratio equal to 1$^{(181)}$ and in air$^{(182)}$ are shown in Figs. 53(a) and 53(b), respectively. Several features of these diagrams deserve special attention. Extensive
areas of two-liquid formation characterize the SiO$_2$-rich part of the system both at low and at high oxygen pressures. Consequently, the silica liquidus surface is very steep. Manganese oxide is therefore not a very potent fluxing agent for SiO$_2$ in spite of the relatively low liquidus temperatures which prevail in the central part of the system. The high stability of Mn$^{2+}$ in comparison with that of Fe$^{2+}$ is demonstrated by the existence of tephroite (Mn$_2$SiO$_4$) and rhodonite (MnSiO$_3$) as stable phases at liquidus temperatures in air, whereas magnetite (Fe$_3$O$_4$) and silica (SiO$_2$, tridymite, or cristobalite) are the only stable crystalline phases at liquidus temperatures in air in the system iron oxide-SiO$_2$ (see Fig. 45b). Tephroite melts incongruently in air but congruently at low oxygen pressures. Silica enters into the structure of $\alpha$-Mn$_2$O$_3$ to form a solid solution phase with the mineralogical name braunite.

![Thermodynamic diagram](image)

**Fig. 54.** Phase diagram for the system FeO-Fe$_2$O$_3$-TiO$_2$ at liquidus temperatures, after Taylor.\(^{(187)}\)
Fe-Ti-O: A projection of the liquidus surface of the system FeO-Fe₂O₃-TiO₂ is presented in Fig. 54. The diagram was determined by studying mixtures which were sealed in closed containers. Hence no information is available for construction of oxygen isobars along the liquidus surface, nor is enough information available to construct fractionation curves. The most noteworthy features of the diagram are the existence of three continuous solid solutions series (magnetite-ulvöspinel, FeO-Fe₂O₃-2FeO-TiO₂; hematite-ilmenite, Fe₂O₃-FeO-TiO₂; pseudobrookite, Fe₂O₃-TiO₂-FeO-2TiO₂) and the consistent decrease in liquidus temperatures from the Fe₂O₃-TiO₂ side to the FeO-TiO₂ side of the triangle.

Diagrams showing phase relations as a function of temperature in the system iron oxide-titanium oxide under two different conditions of controlled oxygen pressures are shown in Figs. 55(a) and (b). The diagram on the left, (a), applies at the oxygen pressure where wüstite and metallic iron coexist in equilibrium and the diagram on the right, (b), applies when the atmosphere is air. The most remarkable feature of the phase relations shown is the very strong stabilizing effect of TiO₂ on the corundum.

Fig. 55. Phase relations in the system iron oxide-TiO₂ at two different levels of oxygen pressures. The diagram in (a) applies in an atmosphere defined by equilibrium between wüstite and metallic iron and the diagram in (b) applies when the atmosphere is air. The systems are not binary. Compositions of condensed phases have been projected along oxygen reaction lines onto the joins FeO-TiO₂ and FeO-Fe₂O₃-TiO₂ in (a) and (b), respectively, because wüstite is the stable crystalline phase of iron oxide in equilibrium with liquid iron oxide under the atmospheric conditions prevailing in (a), and magnetite in (b). Abbreviations used have the following meanings: W = wüstite, M = magnetite, H = hematite, U = ulvöspinel, I = ilmenite, P = pseudobrookite, L = liquid.
Fig. 56. The 1300°C isothermal section through the system FeO-Fe₂O₃-TiO₂, after Taylor. Heavy lines are boundary curves and light dash-dot lines are oxygen isobars.

Fig. 57. Phase relations in the system iron oxide-Cr₂O₃ (a) in an atmosphere consisting of a CO₂-H₂ mixture in ratio 1:1 and (b) in air. The systems are not binary. The components used to represent compositions of condensed phases were chosen on the basis of the same considerations as apply to Fig. 55.
type structure of hematite (Fe₂O₃). This is seen by the sharp rise of the boundary curves outlining the two-phase area magnetite + hematite with increasing TiO₂ contents of the mixtures (Fig. 55b).

Isothermal sections through the system FeO-Fe₂O₃-TiO₂ have been studied by several investigators. The three isothermal sections at 1000,¹⁸⁵ 1200,¹⁸⁶ and 1300°C¹⁸⁷ are all characterized by the presence of the three solid solution series referred to above. The 1300°C isothermal section presented in Fig. 56¹⁸⁷ is representative of these studies. Particular attention is called to the location of the oxygen isobars, and to the occurrence of ternary solid solutions in this system.

**Fe-Cr-O:** Phase relations in the liquidus temperature region of the system iron oxide-Cr₂O₃ at low oxygen pressures are shown in Fig. 57(a)¹⁸⁸ and those in air are shown in Fig. 57(b).¹⁸⁹ Notable features of these diagrams are the marked increases in liquidus and solidus temperatures with increasing Cr₂O₃ contents in air, the strong stabilizing effect of Cr₂O₃ on the corundum-type structure of hematite relative to the spinel-type structure of magnetite, and the slight increase in solidus and liquidus temperatures of wüstite as Cr₂O₃ is added to iron oxide at low oxygen pressures.

Phase relations for most parts of the system FeO-Fe₂O₃-Cr₂O₃ at liquidus temperatures are insufficiently known to permit the presentation of a phase diagram for this system, but Hilty, Forsgen, and Folkman¹⁹⁰ have inferred some of the general relations prevailing.

Data for the system Fe-Cr-O at 1300°C have become available recently.¹⁹¹ They are summarized by the isothermal section presented in Fig. 58.

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**Fig. 58.** The 1300°C isothermal section through the system FeO-Fe₂O₃-Cr₂O₃, after Katsura and Muan.¹⁹¹ Heavy lines are boundary curves and light dash-dot lines are oxygen isobars.
Fig. 59. Phase relations in the system iron oxide-$\text{Al}_2\text{O}_3$ (a) in contact with metallic iron, after Fischer and Hoffman,\textsuperscript{195} as well as (b) in air and (c) at 1 atm $\text{O}_2$, after Muan and Gee\textsuperscript{194} as modified by Muan.\textsuperscript{196} The systems are not binary. The components used to represent compositions of condensed phases in (a) were chosen on the basis of the same considerations as apply to Fig. 55. Compositions in (b) and (c) were projected along oxygen reaction lines onto the join $\text{Fe}_2\text{O}_3$-$\text{Al}_2\text{O}_3$ in order to show true composition of the phase $\text{FeAl}_2\text{O}_3$. Abbreviations used have the following meanings: Cor = corundum, Hem = hematite.
**Fe-Al-O:** The system Fe-Al-O has been the subject of several investigations.\(^{(192-197)}\)

Equilibria among the various oxides in this system at three different levels of oxygen pressures are illustrated in Figs. 59(a), (b), and (c). The diagram in (a) shows phase relations for the system in equilibrium with metallic iron\(^{(195)}\), the diagram in (b) shows phase relations in air,\(^{(194,196)}\) and the diagram in (c) shows phase relations at 1 atm \(O_2\) pressure.\(^{(194,196)}\) Noteworthy features are the limited mutual solubilities of the two sesquioxides hematite and corundum, the limited temperature range of stability of the phase \(Fe_2O_3\cdotAl_2O_3\), and the almost “neutral” character of \(Al_2O_3\) with respect to the hematite solid solution-magnetite solid solution equilibrium [curves outlining the area in which these two phases coexist in equilibrium are nearly horizontal in (b) and (c)].

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**Fig. 60.** Phase diagrams for the system iron oxide-manganese oxide (a) at low oxygen pressures, after Fischer and Fleischer,\(^{(198)}\) and (b) in air, after Muan and Sōmiya.\(^{(203)}\) The systems are not binary. The components used to represent compositions of condensed phases were chosen on the basis of the same considerations as apply to Figs. 53 and 55. Abbreviation used has the following meaning: Tetr = tetragonal.

**Fe-Mn-O:** The phase diagram for the system iron oxide-manganese oxide at low oxygen pressures is shown in Fig. 60(a), based mainly on the work of Fischer and Fleischer.\(^{(198)}\) The only crystalline phase present is a solid solution (mangano-wüstite) between the oxide end members FeO and MnO. Liquidus and solidus temperatures increase continuously from FeO to MnO. The diagram was obtained under two different experimental conditions. The iron oxide-rich end of the system was studied by keeping the oxide mixtures in iron crucibles, whereas equilibria in mixtures containing more than 30% MnO were studied in MnO crucibles. Fischer and Fleischer made the observation that a sudden change in slopes of solidus and liquidus curves occurred somewhere between 30 and 40% MnO. The authors were unable to find a definite explana-
Fig. 61. Sketches showing qualitatively inferred phase relations in the system Fe-Mn-O at liquidus temperatures, as discussed in the text. The upper right insert shows inferred main features of phase relations in the system Mn-O, and the circular insert on the left shows an enlarged, inferred version of the area adjacent to the Fe apex of the triangular diagram Fe-Mn-O. Abbreviation L denotes liquid. Dash lines are inferred boundary curves, and dash lines with crosshatching on one side are outlines of a composition region where two liquid phases (one metallic, one oxidic) are inferred to coexist in equilibrium at liquidus temperatures. A temperature maximum on the boundary curve between metallic iron and (Fe, Mn)O is indicated in the circular insert on the left. The location of this maximum is not known.

tion for the phenomenon, but speculated that it may be related to a small miscibility gap in the MnO-FeO solid solution. This contention is not in agreement with x-ray evidence.\(^{198-202}\) We believe that the observed phenomenon may be related to the following characteristics of the ternary system Fe-Mn-O: In the system Fe-O (Fig. 14) there exists a composition range in which two immiscible liquids coexist in equilibrium. Metallic iron is the primary crystalline phase in this region, and the wüstite-iron eutectic is on the oxygen side of the two-liquid region. Sufficient data are not available to draw a reliable phase diagram for the system Mn-O. However, some general inferences may be made on the basis of existing melting data for metallic manganese and MnO. The former melts at the relatively low temperature of 1260°C, whereas the latter melts at temperatures as high as 1875°C, depending on the oxygen pressure of the gas phase. Almost certainly, there is an extensive liquid miscibility gap between the metal and the oxide phase. Also, the liquidus temperature of the metal probably decreases with increase in its oxygen content, because the solubility of oxygen in liquid Mn metal is
probably larger than in solid Mn metal. Hence the system Mn-O probably has a phase diagram of the type shown qualitatively in the sketch in the upper right insert of Fig. 61. It will be noticed that the metal-metal oxide eutectic here is on the metal (Mn) side of the two-liquid region, in contrast to the situation prevailing in the system Fe-O. If these two binary systems are combined to form the ternary system Fe-Mn-O, the liquidus surface will probably be of the type shown qualitatively in Fig. 61. The boundary curve between the FeO-MnO solid solution and metallic iron is seen to cross the two-liquid region. The liquid phase formed during equilibration in the iron crucibles in the work of Fischer and Fleischer probably had compositions to the right of the two-liquid region in Fig. 61, whereas liquids developed in the MnO crucibles have compositions to the left of the two-liquid region. It is inferred that the discontinuity in tangent slope of liquidus and solidus curves as observed by Fischer and Fleischer resulted from this crossing over of the boundary curve through the two-liquid region.

The system iron oxide-manganese oxide in air is shown in Fig. 60(b).²⁰³ A very flat minimum appears on the liquidus and solidus curves, and extensive solid solution formation takes place among the various structures which are stable at subsolidus temperatures.

**Fe-Mg-O:** Stability relations among the various oxide phases in the system MgO-iron oxide²⁰⁴⁻²¹² at low oxygen pressures such as prevail in equilibrium with metallic iron are shown in Fig. 62(a) and those in air in Fig. 62(b). Two important facts stand out from these diagrams. First, liquidus and solidus temperatures increase drastically when MgO is added to iron oxide, both at low and at high oxygen pressures. Second, MgO

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**Fig. 62.** Phase diagrams for the system MgO-iron oxide (a) in contact with metallic iron²⁰⁹,²¹¹ and (b) in air²¹⁰. The systems are not binary. The components used to represent compositions of condensed phases were chosen on the basis of the same considerations as apply to Fig. 55.
Fig. 63. The 1400, 1500, 1600, 1700, and 1800°C isothermal sections through the system MgO-FeO-Fe₂O₃, after Phillips and Muan.\textsuperscript{(212)} Abbreviations used have the following meanings: MW = magnesiowüstite, MF = magnesioferrite, H = hematite, L = liquid.
Fig. 64. Inferred, approximate liquidus surface for the system MgO-FeO-Fe₂O₃, after Phillips and Muan. Abbreviations used have the following meanings: MW = magnesiowustite, MF = magnesioferrite, H = hematite.

has a strong stabilizing effect on phases in which iron is present predominantly or partly in the divalent state (wustite and magnetite) relative to phases in which practically all the iron is present in the trivalent state (hematite).

Data are also available for the ternary system MgO-FeO-Fe₂O₃ at several temperatures in the range from 1400 to 1800°C. A series of such isothermal sections are shown in Fig. 63. From these data (Figs. 62 and 63) and general crystal-chemical considerations it is possible to sketch an approximate liquidus surface for the system MgO-FeO-Fe₂O₃ as presented in Fig. 64.

Ca-Fe-O: Equilibrium relations at different levels of oxygen pressures have been studied in considerable detail in the system CaO-iron oxide. The diagrams reproduced in Figs. 65(a) and (b) show the phases present as a function of temperature and total composition in contact with metallic iron and in air, respectively. Striking features of these diagrams, as compared with those for iron oxide-MgO, are the low liquidus and solidus temperatures prevailing in the central part of the system, and the large number of intermediate phases (calcium ferrites) formed at the higher oxygen pressure, (b). These features are largely reflections of the greater size difference between Ca²⁺ and Fe²⁺ than exists between Mg²⁺ and Fe²⁺. The latter ions readily substitute for each other in the crystalline phases shown in Figs. 62 through 64, whereas there is only limited substitution between Ca²⁺ and Fe²⁺ (Fig. 65).

Only a small part of the liquidus surface of the system Ca-Fe-O has been studied experimentally in enough detail to permit the drawing of a phase diagram. A sketch showing probable relations for the composition triangle FeO-Fe₂O₃-2CaO-Fe₂O₃-Fe₂O₃ is presented in Fig. 66. The relatively low liquidus temperatures prevailing in large composition areas are the most characteristic feature of the diagram. There is still some uncertainty regarding the relations between the two ternary phases indicated in Fig. 66 and the binary calcium ferrites.
Fig. 65. Phase relations in the system CaO-iron oxide (a) in contact with metallic iron, mainly after Allen and Snow (219) as modified by Aukrust and Muan (227) and (b) in air, after Phillips and Muan (223). The systems are not binary. The components used to represent compositions of condensed phases in (a) were chosen on the basis of the same considerations as apply to Fig. 55. Compositions in (b) were projected along oxygen reaction lines onto the join CaO-Fe$_2$O$_3$ in order to show true compositions of the various calcium ferrites appearing in the system. Abbreviations used have the following meanings: C$_2$F = Ca$_2$Fe$_2$O$_5$, CF = CaFe$_2$O$_4$, CF$_2$ = CaFe$_4$O$_7$, H = hematite, L = liquid.

Fig. 66. Phase diagram for a part of the system Ca-Fe-O, after Phillips and Muan (226). Abbreviations used have the following meanings: C$_2$F = Ca$_2$Fe$_2$O$_5$, CF = CaFe$_2$O$_4$, CF$_2$ = CaFe$_4$O$_7$. 

TO CaO

2CaO·Fe$_2$O$_3$

40

C$_2$F

30

FeO·Fe$_2$O$_3$ 80

Fe$_2$O$_3$

800

MAGNETITE

HEMATITE

800

4CaO·FeO·8Fe$_2$O$_3$

4CaO·FeO·4Fe$_2$O$_3$

4CaO·FeO·2Fe$_2$O$_3$

2CaO·2Fe$_2$O$_3$
Fig. 67. Diagrams showing approximate phase relations in the system CaO-chromium oxide (a) under reducing conditions, essentially after Ol’shanskii, Tsvektov, and Shleપov,\(^{233}\) and (b) in air, after Ford and White.\(^{232}\) The diagram in (b) is not binary at the lowest temperatures. The compound written \(9\text{CaO}\cdot\text{Cr}_2\text{O}_3\cdot\text{4CrO}_3\) in diagram (b) may be \(9\text{CaO}\cdot\text{3Cr}_2\text{O}_5\) (see text).\(^{234}\)

**Ca-Cr-O:** The system \(\text{Ca-Cr-O}\)\(^{229-234}\) is very complicated because of the many different states of oxidation of the chromium present in the various phases which may form. Solidus temperatures in the system under reducing conditions have been reported to be above \(1500\,^\circ\text{C}\),\(^{229,233,234}\) and only one intermediate compound, \(\text{CaCr}_2\text{O}_4\), has been reported to be present. An approximate diagram is shown in Fig. 67(a).\(^{233}\) In air, a liquid phase has been reported to form at as low a temperature as \(1022\,^\circ\text{C}\), and several intermediate compounds between the end members \(\text{CaO}\) and \(\text{Cr}_2\text{O}_3\) have been reported.\(^{231}\) It is likely that in some of these phases an appreciable part of the chromium is present in oxidation states higher than \(3^+\). For instance, Ford and Rees\(^{230}\) reported a phase \(9\text{CaO}\cdot\text{4CrO}_3\cdot\text{Cr}_2\text{O}_3\) with two-thirds of the chromium having a valence of six and the other third a valence of three. Glasser and Osborn\(^{234}\) on the other hand, have suggested that the chromium in the above phase may be entirely in the pentavalent state corresponding to the oxide formula \(3\text{CaO}\cdot\text{Cr}_2\text{O}_5\). An approximate phase diagram for the system in air is shown in Fig. 67(b).\(^{231}\)

**Mn-Al-O:** Phase relations in the system manganese oxide-Al\(_2\)O\(_3\) under two different experimental conditions are shown in Figs. 68(a) and (b). The diagram in (a) applies under "reducing conditions," which unfortunately have not been well defined,\(^{235}\) and the diagram in (b) applies when the atmosphere is air.\(^{236}\) Extensive solid solution formation and high liquidus and solidus temperatures are seen to prevail at the higher oxygen pressure.
**Fig. 68.** Diagram (a) is a sketch showing probable, approximate phase relations in the system manganese oxide-Al₂O₃ under nondefined reducing conditions, based on data of Hay, White, and McIntosh.¹²¹³⁵ Diagram (b) shows phase relations in the system manganese oxide-Al₂O₃ in air, after Ranganathan, MacKean and Muan.¹²³⁶ Abbreviation used has the following meaning: Tetr = tetragonal.

**Fig. 69.** Phase diagram for the system manganese oxide-Cr₂O₃ in air, after Speidel and Muan.¹²³⁷ The system is not binary. The components used to represent compositions of condensed phases were chosen on the basis of the same considerations as apply to Fig. 53. Abbreviation used has the following meaning: Tetr = tetragonal.
**Mn-Cr-O:** Phase relations in the system Mn-Cr-O in air \((p_{O_2} = 0.21 \text{ atm})\) are shown in Fig. 69.\(^{237}\) The diagram is similar to that shown in Fig. 68(b). Remarkable is the extension of the stability field of the spinel solid solution phase (approximate composition \(\text{Mn}_3\text{O}_4-\text{MnCr}_2\text{O}_4\)) to 600°C or lower as \(\text{Cr}_2\text{O}_3\) is added to manganese oxide in air.

Data for the system manganese oxide-\(\text{Cr}_2\text{O}_3\) at low oxygen potentials are not available at the present time. Presumably the phase relations will resemble those of Fig. 68(a).

**Mn-Mg-O:** A phase diagram for the system at low oxygen pressures is not available. However, MgO and MnO form a complete solid solution series above 1000°C,\(^{199,208,235}\) and the solidus and liquidus curves must be continuous between the two end members. A sketch showing the type of diagram inferred at an oxygen pressure corresponding to the maximum melting point of MnO (compare Fig. 61) is shown in Fig. 70(a).

The diagram presented in Fig. 70(b) illustrates phase relations in the system manganese oxide-MgO in air \((p_{O_2} = 0.21 \text{ atm})\).\(^{239}\) Liquidus and solidus temperatures are seen to rise sharply as MgO is added to manganese oxide, and the \((\text{Mg, Mn})\text{O}\) solid-solution phase with periclase type structure is stable over a very large composition-temperature range.
Fig. 71. The diagram in (a) is a sketch showing qualitatively inferred phase relations in the system CaO-manganese oxide at the low oxygen pressure prevailing at the maximum melting point of MnO (compare Fig. 61). The diagram in (b) shows phase relations in the system CaO-manganese oxide in air, after Riboud and Muan. The systems are not binary. The components used to represent compositions of condensed phases in (a) were chosen on the basis of the same considerations as apply to Fig. 53. Compositions in (b) were projected along oxygen reaction lines onto the join CaO-Mn$_2$O$_3$ in order to represent compositions of the various CaO-manganese oxide compounds as closely as possible. Abbreviation used has the following meaning: Tetr = tetragonal.

Fig. 72. Phase diagram for the system iron oxide-ZrO$_2$ in contact with metallic iron, after Fischer and Hoffman. The system is not binary. The method of projection used for obtaining the diagram is the same as for FeO-SiO$_2$ (see Fig. 45a).
**Ca-Mn-O:** Equilibria in this system at low oxygen pressures have not been determined. However, continuity in slope of solidus and liquidus curves between the end members may be inferred to exist because a complete solid solution series is formed between CaO and MnO above 1000°C.(199,200,240) The qualitative sketch in Fig. 71(a) shows the type of diagram to be expected.

Phase relations existing in mixtures of CaO and manganese oxide in air ($p_{O_2} = 0.21$ atm) are illustrated in Fig. 71(b).(239) The diagram is more complicated than that for manganese oxide-MgO (Fig. 70b) as two intermediate compounds are formed between the end members.

**Fe-Zr-O:** Phase equilibrium data for the system iron oxide-zirconium oxide have been determined in contact with metallic iron.(241) The diagram shown in Fig. 72 is characterized by very limited solubility between the two components in the solid state, no compound formation between the components, and a eutectic located close to the iron oxide end of the system.

**Fe-P-O:** Equilibrium relations in the system Fe-P-O at high temperatures are difficult to determine experimentally because of the high volatility of $P_2O_5$ and the necessity of controlling the oxygen pressure of the system. Nevertheless, data for this system have been obtained under two different conditions of controlled oxygen pressures.

The diagram shown in Fig. 73(a) represents phase relations for a part of the system iron oxide-$P_2O_5$ in contact with a metal phase (Fe-P).(242) A sharp decrease in liquidus and solidus temperatures is seen to result when $P_2O_5$ is added to iron oxide. The nature of the compound labeled $X$ in the diagram has not been determined. The diagram in

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**Fig. 73.** Phase diagrams for the system iron oxide-$P_2O_5$ (a) in contact with a metal phase, after Trömel and Schwerdtfeger,(242) and (b) in air, after Wentrup.(243) The systems are not binary. The components used to represent compositions of condensed phases in (a) were chosen on the basis of the same considerations as apply to Fig. 55. Compositions in (b) were projected along oxygen reaction lines onto the join $Fe_2O_3-P_2O_5$ in order to show compositions of the various compounds between $Fe_2O_3$ and $P_2O_5$ appearing in the system. Abbreviations used have the following meanings: $F_2P = Fe_4P_2O_{11}$, FP = $Fe_2P_2O_8$, $F_2P_3 = Fe_4P_6O_{21}$, $L$ = liquid.
Fig. 73(b) shows approximate phase relations prevailing in the system in air.\(^{243}\) The work on which the latter diagram is based was done at a time when experimental techniques were not as highly developed as they are now, and the diagram should therefore be considered as a qualitative sketch only.

**B. Systems in Which a Gas Phase Plays No Important Role**

1. **GENERAL CONSIDERATIONS**

The systems discussed in this section contain as components only the relatively stable oxides made up from cations appearing in only one predominant state of oxidation. In such systems the gas phase can usually be ignored. The total compositions of condensed phases remain constant, within limits of experimental error.

Similarly to the situation prevailing in binary systems, the appearance of phase diagrams for the ternary systems is determined mainly by the mutual solubility relations existing among the components in the solid and in the liquid state, and the tendency for compound formation among the components. Since the number of components in going from binary to ternary systems increases from two to three, the number of combination possibilities increases greatly, and a classification of ternary diagrams into general types is not as simple as for binary systems (compare Fig. 17). The series of sketches presented in Fig. 74 shows projections of the liquidus surface in simplified, hypothetical systems displaying some of the possible features. Diagram (a) represents a situation in which there is no solubility in either the liquid or the solid state, (b) shows partial solubility in the liquid state and no solubility in the solid state, (c) shows complete mutual solubility in the liquid state and no solubility in the solid state, and (d) shows complete mutual solubility among the components in the liquid as well as in the solid state. The diagrams (e) through (h) show situations in which compound formation among the components takes place. In (e) and (f) the compounds are binary, with congruent melting in the former and incongruent melting in the latter. Each of the diagrams (g) and (h) shows the existence of a ternary compound, congruently melting in (g) and incongruently melting in (h). Dashed lines in diagrams (e) through (h) are joins connecting composition points for the various crystalline phases appearing in the systems. These joins divide each of the composition triangles \(A-B-C\) into so-called compatibility triangles, viz. \(A-AB-C\) and \(AB-B-C\) in (e) and (f) and \(A-ABC-B\), \(A-ABC-C\) and \(ABC-B-C\) in (g) and (h). For each compatibility triangle there is a ternary invariant point characterized by the equilibrium coexistence of liquid of composition represented by the point, and three crystalline phases whose compositions are those of the apices of the compatibility triangle in question. The invariant point is a eutectic if the liquid composition point is within the compatibility triangle [all triangles in (e) and (g), triangle \(AB-B-C\) in (f), and triangles \(A-ABC-B\) and \(A-ABC-C\) in (h)], and a peritectic if the liquid composition point is outside the compatibility triangle [\(A-AB-C\) in (f) and \(ABC-B-C\) in (h)]. Crystallization of mixtures within the system \(A-B-C\) yields as final product a mixture of the three crystalline phases whose compositions constitute the apices of the compatibility triangle within which the composition point for the mixture is located, and the temperature and composition of the last liquid present are those of the ternary invariant point associated with the compatibility triangle in question.

Actual diagrams to be presented in this section usually incorporate several of the features represented in the idealized diagrams shown in Fig. 74.

Paths of crystallization for systems in the present section follow the pattern discussed under case (a) for the system FeO-Fe\(_2\)O\(_3\)-SiO\(_2\). The geometrical relations
Fig. 74. Sketches showing in simplified form features commonly appearing in ternary systems. A hypothetical system A-B-C is used as an example (compare text).

involved in deriving solidus surface diagrams and isothermal sections are also identical to those discussed for the system FeO-Fe₂O₃-SiO₂. The system CaO-MgO-SiO₂ will be used to show examples of such diagrams. For the remaining systems, only the liquidus surface will be presented, together with brief comments on each. Similarly to the procedure used for the analogous binary systems, the ternary systems will be divided into two groups, those with and those without SiO₂ as a component. Within each of these two groups, the systems will be arranged approximately in order of increasing field strength of the cations.
2. SYSTEMS WITH SILICA AS A COMPONENT

K₂O-Al₂O₃-SiO₂: Phase relations at liquidus temperatures in the system K₂O-Al₂O₃-SiO₂ are shown in Fig. 75. (244,245,132,134) Potash is seen to have a very strong fluxing effect on Al₂O₃-SiO₂ mixtures high in SiO₂. For instance, liquidus temperatures decrease to values as low as 985°C with K₂O additions of less than 10% to a mixture containing 87% SiO₂, 13% Al₂O₃.
**Fig. 76.** Phase diagram for the system Na$_2$O-Al$_2$O$_3$-SiO$_2$, mainly after Schairer and Bowen,$^{(246)}$ with minor modifications based on recent data on the system Al$_2$O$_3$-SiO$_2$,$^{(132,134)}$ and on beta-alumina.$^{(249)}$

**Na$_2$O-Al$_2$O$_3$-SiO$_2$:** The phase diagram for the system Na$_2$O-Al$_2$O$_3$-SiO$_2$,$^{(246-249,132,134)}$ shown in Fig. 76 is very similar to that presented for K$_2$O-Al$_2$O$_3$-SiO$_2$ in the preceding figure. Sodium oxide has a fluxing action on Al$_2$O$_3$-SiO$_2$ mixtures comparable to that of potash.
CaO-MgO-SiO₂: The three oxides CaO, MgO, and SiO₂ constitute a very complicated ternary system which has been the subject of numerous investigations during the past 50 years. An up-to-date picture of phase relations at liquidus temperatures is shown in Fig. 77. An area of liquid immiscibility extends across the diagram at high SiO₂ contents, and a large number of binary and ternary crystalline phases have stable existence at liquidus temperatures. Solid solution is extensive at high temperatures between the pairs of compounds: wollastonite and diopside, diopside and protoenstatite, and monticellite and forsterite; but is essentially confined to structures of these three series and to temperatures greater than about 1000°C. Solid
Fig. 78. The solidus surface for the system CaO-MgO-SiO₂ (compare Fig. 77).

solution at liquidus temperatures as currently understood is shown on the large scale diagram published for this system.\(^{287,Plate 2}\)

The solidus surface and isothermal sections through the system are constructed in accordance with methods outlined previously for the system FeO-Fe₂O₃-SiO₂. The resulting diagrams are shown in Figs. 78 and 79.

**CaO-Al₂O₃-SiO₂**: The first studies of phase relations in this system were published 50 years ago in the classic paper by Rankin and Wright.\(^{126}\) Numerous investigations have been carried out by many researchers in many laboratories since that time, (e.g., 127-134, 131, 132, 257-261) substantiating in general the phase relations as originally determined. The diagram reproduced in Fig. 80 incorporates the most recent data for the system, and is thought to be as close to correct as is possible at the present time.
Fig. 79. Isothermal sections at 1400, 1500, 1600, and 1700°C through the system CaO-MgO-SiO₂ (compare Fig. 77). Abbreviations used have the following meanings: C₃S = Ca₃SiO₅, C₂S = Ca₂SiO₄, R = rankinite, PW = pseudowollastonite, M = merwinite, MC = monticellite, A = akermanite, P = periclase, F = forsterite, PE = protoenstatite, Trid = tridymite, Crist = cristobalite, L = liquid.
A large number of stable binary and ternary crystalline phases exist in this system. Relatively low liquidus and solidus temperatures prevail, in spite of the high melting temperatures of the three end members (SiO$_2$, 1723°C$^{(63)}$, Al$_2$O$_3$, ~2570°C$^{(149)}$; Al$_2$O$_3$, ~2020°C$^{(154)}$). Except for a small composition area adjacent to the CaO-SiO$_2$ join at high SiO$_2$ contents, liquids are miscible in all proportions within the system. Very little mutual solubility exists among the crystalline phases, however, because the ions Ca$^{2+}$, Al$^{3+}$, and Si$^{4+}$ are sufficiently different in size to prevent extensive substitution of one ion for another in the crystal lattices.
Fig. 81. Phase diagram for the system MgO-Al₂O₃-SiO₂, based mainly on the original work of Rankin and Merwin\(^{262}\) and of Greig,\(^{127}\) with modifications based on more recent work on selected parts of the system.\(^{263-267}\)

\textbf{MgO-Al₂O₃-SiO₂:} The phase diagram for the system MgO-Al₂O₃-SiO₂ has been modified many times since its first appearance in 1918,\(^{262}\) but still retains the principal features of the original diagram. A projection of the liquidus surface of this system according to our present knowledge\(^{262,127,263-267}\) is shown in Fig. 81. The diagram has many similarities with that of the system CaO-Al₂O₃-SiO₂, although it is simpler than the latter because a smaller number of crystalline phases appear in equilibrium at liquidus temperatures.
**CaO-TiO$_2$-SiO$_2$:** Phase relations in the system CaO-TiO$_2$-SiO$_2$ are illustrated in Fig. 82.\(^{(268,269)}\) Characteristic features of the diagram are the large composition area of coexistence of two immiscible liquids, the crossing of this area by the cristobalite-rutile boundary curve, and the relatively low liquidus temperatures which prevail in the central part of the system.
Fig. 83. Phase diagram for the system MgO-Cr₂O₃-SiO₂, after Keith.¹⁴⁴

**MgO-Cr₂O₃-SiO₂:** The system MgO-Cr₂O₃-SiO₂ shown in Fig. 83 was the first ternary Cr₂O₃-containing system to be studied in detail at liquidus temperatures.¹⁴⁴ The diagram is remarkable in many respects. First, the three phases chromium oxide (Cr₂O₃), picrochromite (MgCr₂O₄), and periclase (MgO) occupy almost the entire composition triangle, whereas the primary phase areas of the SiO₂-containing phases (cristobalite, SiO₂; forsterite, Mg₂SiO₄; protoenstatite, MgSiO₃) are restricted to narrow strips adjacent to the MgO-SiO₂ join. Second, a very large area comprising compositions of mixtures in which two liquid phases are in equilibrium extends across the diagram from the MgO-SiO₂ to the Cr₂O₃-SiO₂ side. This two-liquid region is intersected by the spinel-chromium oxide as well as the spinel-cristobalite boundary curves. As a result, a wedge-shaped primary phase area of spinel separates the primary phase
Fig. 84. Phase diagram for the system $\text{Al}_2\text{O}_3$-$\text{Cr}_2\text{O}_3$-$\text{SiO}_2$, after Roeder, Glasser, and Osborn.\textsuperscript{(176)}

area of cristobalite from that of $\text{Cr}_2\text{O}_3$ within the two-liquid region. Liquidus and solidus temperatures are high ($\geq 1850^\circ\text{C}$) for all mixtures within the composition triangle $\text{MgO}$-$2\text{MgO}$-$\text{SiO}_2$-$\text{Cr}_2\text{O}_3$, but considerably lower (down to $\sim 1550^\circ\text{C}$) in some mixtures located on the $\text{SiO}_2$-side of this triangle.

**$\text{Al}_2\text{O}_3$-$\text{Cr}_2\text{O}_3$-$\text{SiO}_2$:** The phase diagram for the system $\text{Al}_2\text{O}_3$-$\text{Cr}_2\text{O}_3$-$\text{SiO}_2$ shown in Fig. 84\textsuperscript{(176)} is radically different from those presented in the four preceding figures. The two components $\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$ form a continuous solid solution series at elevated temperatures (from liquidus temperatures down to about $1000^\circ\text{C}$ or lower), and only three crystalline phases (cristobalite, mullite, corundum solid solution) appear in
equilibrium with liquids. Liquidus and solidus temperatures are relatively high throughout the system, with a minimum of 1590°C in the binary Al₂O₃-SiO₂ join.

**Al₂O₃-TiO₂-SiO₂**: Approximate phase relations in the system Al₂O₃-TiO₂-SiO₂ at liquidus temperatures are illustrated in Fig. 85.²⁷⁰ Only two crystalline phases, rutile (TiO₂) and Al₂TiO₅, in addition to those existing in the system Al₂O₃-SiO₂, have stable existence at liquidus temperatures in this system. The liquid miscibility gap in the system TiO₂-SiO₂ (see Fig. 24)¹⁴⁵ extends a short distance into the ternary system.
3. SYSTEMS WITHOUT SILICA AS A COMPONENT

CaO-MgO-Al₂O₃: A phase diagram for a part of the system CaO-MgO-Al₂O₃ was presented as early as 1916. This work was done at a time when many of the present-day experimental techniques were unavailable. The diagram needs some revision in light of new data which have been published on the system CaO-Al₂O₃. A sketch illustrating inferred phase relations prevailing at liquidus temperatures is presented in Fig. 86.

MgO-Al₂O₃-Cr₂O₃: A diagram showing "melting isotherms" in the system MgO-Al₂O₃-Cr₂O₃ has appeared in the literature. The data are insufficient to delineate...
phase relations quantitatively. However, there is little doubt that only the three crystalline phases periclase, spinel solid solution (approximate composition \( \text{MgO-} \text{Al}_2\text{O}_3 \)-\( \text{MgO-} \text{Cr}_2\text{O}_3 \)), and sesquioxide solid solution \( \text{Al}_2\text{O}_3 \)-\( \text{Cr}_2\text{O}_3 \) appear as crystalline phases. Liquidus and solidus temperatures are probable above 1900°C throughout the system. The type of diagram to be expected is sketched qualitatively in Fig. 87.
FOUR-COMPONENT SYSTEMS

A. General Considerations

The determination of phase relations in quaternary systems and the representation and interpretation of quaternary phase diagrams is usually more complicated than for binary and ternary systems. The complications arise, not because the application of the phase rule to four-component systems is more difficult than in the cases just considered, but because the relations are more difficult to represent geometrically. With the introduction of one more component, one additional composition variable must be accounted for, and four composition axes are necessary in order to represent the equilibria adequately.

The geometrical figure commonly used to represent four-component systems is a regular tetrahedron, with one component at each apex. Thus all three dimensions of space are expended in expressing composition variables, and there is no axis in quaternary diagrams along which the other important independent variable, temperature, is shown explicitly. Instead, temperatures are illustrated by indirect methods, as demonstrated for selected systems in the following.

It is not very meaningful to draw sketches of idealized types of quaternary systems similar to those presented for binary and ternary systems. There are at least two reasons for this. First, with the larger number of components present, a much larger number of possibilities exist, and consequently real systems seldom come close in behavior to those pictured in simplified ideal systems. Second, relatively few quaternary systems have been studied in great detail, making a classification of such systems into general types premature. However, as in the binary and ternary systems previously discussed, the mutual solubility relations among the components in the liquid and in the solid state and the tendencies for compound formation existing among the components are the main factors reflected in the diagrams of quaternary systems also.

Analogously to the approach used in the two preceding chapters, the systems to be discussed in the following are divided into two main groups: those in which the gas phase plays an important role in the equilibria, and those in which the gas phase is unimportant. In the first of these groups, the system MgO-FeO-Fe₂O₃-SiO₂ will be discussed in considerable detail. This system is relatively well known, is of considerable practical importance in steelmaking processes, and is a particularly suitable example for demonstration of the application of the phase rule to quaternary systems. Other systems similar to MgO-FeO-Fe₂O₃-SiO₂ are discussed only briefly in the remainder of the first group. In the second group, the system CaO-MgO-Al₂O₃-SiO₂ is discussed most extensively, not only because it is fundamental to an understanding of blast-furnace slag problems, but also because it is the best known quaternary system of very stable oxides and also incorporates many features suitable for the illustration of principles involved.
B. Systems in Which a Gas Phase Plays an Important Role

1. THE SYSTEM MgO-FeO-Fe₂O₃-SiO₂

a. Liquidus relations. Phase relations at liquidus temperatures in the system MgO-FeO-Fe₂O₃-SiO₂ are shown in Fig. 88. The front face of the tetrahedron has been removed for the purpose of viewing the interior. Each primary phase area in the four bounding ternary systems (the four faces of the tetrahedron) extends as a volume into the tetrahedron. All mixtures within each such volume have the same primary crystalline phase, as labeled on the diagram. The boundary surface between two adjacent

Fig. 88. Diagram showing phase relations in the liquidus temperature region of the system MgO-FeO-Fe₂O₃-SiO₂, after Muan and Osborn. Boundary curves on the four faces of the tetrahedron are drawn as light lines, and those within the tetrahedron as heavy lines.
primary phase volumes represents compositions of liquids which are simultaneously in equilibrium with two crystalline phases and gas in divariant \( F = C + 2 - P = 4 + 2 - 4 = 2 \) equilibrium. Three adjacent phase volumes intersect along a curve which represents compositions of a liquid which is in univariant equilibrium with three crystalline phases and gas \( F = C + 2 - P = 4 + 2 - 5 = 1 \). Four adjacent phase volumes meet at a point representing the composition of a liquid which coexists with four crystalline phases and gas in invariant equilibrium \( F = C + 2 - P = 4 + 2 - 6 = 0 \).

The discussion of phase relations in the system MgO-FeO-Fe₂O₃-SiO₂ is probably best understood by using as starting point the bounding system FeO-Fe₂O₃-SiO₂ and imagining the quaternary system obtained by addition of MgO to the ternary mixtures. For instance, the oxygen isobaric lines in the system FeO-Fe₂O₃-SiO₂ (see Fig. 41) extend as oxygen isobaric surfaces through the tetrahedron representing the system MgO-FeO-Fe₂O₃-SiO₂. Each of these surfaces is the loci of points representing compositions of all liquids coexisting with crystal(s), at liquidus temperatures, at the oxygen pressure of the isobar in question. The surfaces have continuously changing tangent slopes within any particular primary phase volume, whereas the tangent slopes have discontinuities where the oxygen isobaric surface crosses a boundary surface or a boundary curve. These surfaces are difficult to represent quantitatively in perspective drawings. A sketch showing approximate locations of two representative oxygen isobaric surfaces through the quaternary system at liquidus temperatures is presented in Fig. 89.

Another feature of the ternary system FeO-Fe₂O₃-SiO₂ which has its counterpart in the quaternary system MgO-FeO-Fe₂O₃-SiO₂ is the family of oxygen reaction lines. These are straight lines radiating from the O apex of the tetrahedron representing the system Mg-Fe-Si-O, of which the present system is a part. These lines describe the changes in total composition of condensed phases which take place as oxygen is added to or expelled from the condensed phases as a result of their reaction with the gas phase.

There is no simple way of extending the fractionation curves of the system FeO-Fe₂O₃-SiO₂ into the tetrahedron of Fig. 88 at the present time. This is partly because insufficient experimental data are available regarding compositions of coexisting crystalline and liquid phases within the quaternary system, partly because one of the phases occurring (magnesiowüstite) is a ternary rather than a binary solid solution (MgO-FeO-Fe₂O₃). Hence, even if the fractionation surfaces were known and could be represented clearly in a perspective drawing of the tetrahedron, the composition of the ternary solid-solution phase would not be determined by the point of intersection between the tangent to the fractionation surface and a binary join, but as the piercing point of the above tangent with the area in the face MgO-FeO-Fe₂O₃ representing the compositions of the ternary magnesiowüstite solid solution phase. Because of these complications, relations between compositions of crystalline and liquid phases coexisting in equilibrium will be considered in the following only for liquids along quaternary univariant curves or at quaternary invariant points.

b. Paths of equilibrium crystallization. The use of the phase diagram for the system MgO-FeO-Fe₂O₃-SiO₂ will be illustrated in the following by derivation of paths of equilibrium crystallization for selected mixtures. Similarly to the discussion of the system FeO-Fe₂O₃-SiO₂, two idealized conditions will be considered: crystallization when total composition of condensed phases is kept constant, and crystallization at constant oxygen pressure of the gas phase.

As a first approximation, the total composition of condensed phases may be considered constant when the crystallization takes place in a closed system when the volume of the gas phase is small. The principles involved in the derivation of paths of equilibrium crystallization under such conditions have been described in a large number
Fig. 89. Sketch showing approximate locations and shapes of two representative oxygen isobaric surfaces through the tetrahedron representing the system MgO-FeO-Fe₂O₃-SiO₂, at liquidus temperatures. The two surfaces are shown in simplified form as planes in upper right insert.

of publications (see for instance a paper by Schairer\textsuperscript{(273)}) and have also been discussed in considerable detail for the system MgO-FeO-Fe₂O₃-SiO₂.\textsuperscript{(272)} Only general features and relations which are of particular importance for the application of the diagram to steelmaking problems will be discussed here.

Take as an example a mixture of composition $A$ located on the quaternary univariant curve along which olivine, pyroxene, spinel, and liquid coexist in equilibrium, as portrayed in Fig. 90. As heat is withdrawn from the mixture at liquidus temperature, increasing amounts of the three crystalline phases separate out, and the composition of the liquid changes to the right along the boundary curve from $A$ toward $a$. The three crystalline phases are all members of solid-solution series, and hence their compositions change during the crystallization process. When the liquid composition is $A$ (beginning of crystallization), the composition of olivine, pyroxene, and spinel are $a_1$, $a_2$, and $a_3$, respectively, and when the liquid composition has reached that of point $a$ the crystalline phase compositions are $a'_1$, $a'_2$, and $a'_3$, respectively, in the same order as above. The
plane formed by the latter three points \((a_1', a_2', \text{ and } a_3')\) goes through point \(A\). Hence, the mixture of constant total composition \(A\) has completely crystallized at the temperature corresponding to this situation, and the final product of crystallization is a mixture of olivine of composition \(a_1'\), pyroxene of composition \(a_2'\), and spinel of composition \(a_3'\). The relative amounts of the phases present at any temperature between that of \(A\) (the liquidus) and that of \(a\) (the solidus) for this mixture are determined by the location of point \(A\) within the tetrahedron formed by the four points representing compositions of the four condensed phases (one liquid, three crystalline) coexisting in equilibrium at that temperature. This tetrahedron may be referred to as a four-phase volume, and plays a role in the quaternary system analogous to that of the three-phase triangle discussed for ternary systems. Inasmuch as the composition of each of the

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**Fig. 90.** Diagram illustrating path of equilibrium crystallization of a mixture \(A\) in the system \(\text{MgO-FeO-Fe}_2\text{O}_3-\text{SiO}_2\) at constant total composition of condensed phases, as discussed in text.
condensed phases coexisting in equilibrium is variable, all apices of the four-phase volume move as the crystallization proceeds, while point A, representing the constant total composition, remains stationary. An example of the geometrical relations involved is shown in the sketch of Fig. 91. Points \( \alpha_1''', \alpha_2''', \alpha_3''', \) and \( \alpha'' \) represent the compositions of olivine, pyroxene, spinel, and liquid, respectively, which coexist in equilibrium at a temperature \( t'' \) in a mixture of total composition \( A \). The amount of liquid is

\[
\alpha'' = \frac{A-x}{a''-x} \cdot 100\%,
\]

(6-1)

where \( x \) is the point of intersection between the extension of the straight line \( \alpha'''-A \) and the face of the four-phase volume opposite apex \( \alpha''' \). From the geometry of the system it is seen that the expression above is equivalent to the alternative expression

\[
\alpha'' = \frac{a''-y}{a'''-a''} \cdot 100\%,
\]

(6-2)

where \( y \) is the point of intersection between the edge \( \alpha_1''-\alpha'' \) of the four-phase volume and a plane through \( A \) parallel to the face \( \alpha_1''-\alpha_2''-\alpha_3'' \).

Similar relations obtain for the remaining three phases.

**Fig. 91.** Sketch illustrating geometrical relations involved in determining relative amounts of phases during equilibrium crystallization of a selected mixture \( A \) in the system \( \text{MgO-FeO-Fe}_2\text{O}_3-\text{SiO}_2 \) at constant total composition of condensed phases.

It follows as a general rule that the solidus temperature for a mixture of constant total composition is that of the point along the quaternary-univariant curve representing the composition of a liquid phase which is in equilibrium with three crystalline phases whose compositions are such that the plane formed by their composition points passes through the point representing the constant total composition of the mixture. If the crystalline phases have fixed compositions rather than being solid solutions, the solidus temperature is usually that of the quaternary invariant point (eutectic or peritectic) representing the composition of a liquid phase which is in equilibrium with four crystal-
line phases such that the point representing total composition of the mixture is located within the volume formed by the four points representing the compositions of the four crystalline phases. If the point representing total composition of the mixture is located in the plane formed by three crystalline phases coexisting along a quaternary univariant curve and this curve intersects the plane, then the solidus temperature is that of the maximum point on the boundary curve at its intersection with the plane.

The oxygen pressure of the system decreases continuously during crystallization in the example used above. Qualitatively, this can be visualized by a comparison with Fig. 89. The oxygen isobaric surfaces have been omitted in the diagram of Fig. 90 in order to avoid cluttering of the diagram.

Another general feature of ternary systems which has its counterpart in quaternary systems emerges from the considerations above. It is seen (Fig. 90) that the volume $b_1-b_2-b_3-SiO_2$ formed by the four points representing compositions of the four crystalline phases coexisting in equilibrium with liquid $b$ and gas at the quaternary invariant point (olivine, pyroxene, spinel, tridymite, liquid) is of particular significance so far as path of equilibrium crystallization of mixtures in the system MgO-FeO-Fe$_2$O$_3$-SiO$_2$ is concerned. It divides the tetrahedron into three subvolumes which, by analogy with the ternary system previously discussed, may be referred to as composition volumes. Mixtures located to the left (MgO side) of the volume $b_1-b_2-b_3-SiO_2$ crystallize completely at a temperature above the peritectic without the appearance of olivine as a phase in equilibrium with tridymite. Mixtures within the volume $b_1-b_2-b_3-SiO_2$ crystallize completely at the temperature of the peritectic, and mixtures to the right (iron-oxide side) of the same volume crystallize completely at a temperature on the univariant curve from $b$ to $c$. Hence, in judging solidus temperature, the composition volumes play a role in quaternary systems analogous to that of the composition triangles in ternary systems.

The course of equilibrium crystallization in the system MgO-FeO-Fe$_2$O$_3$SiO$_2$ under conditions of constant oxygen pressure is derived by methods similar to those described previously for the ternary system FeO-Fe$_2$O$_3$SiO$_2$. Two geometrical relations are particularly important in the derivation. One is the family of oxygen reaction lines radiating from the O apex of the tetrahedron representing the system Mg-Fe-Si-O, of which MgO-FeO-Fe$_2$O$_3$SiO$_2$ is a part. The other is the family of oxygen isobaric surfaces at liquidus temperatures traversing the tetrahedron MgO-FeO-Fe$_2$O$_3$-SiO$_2$. Regardless of the nature of the crystalline phases separating out during crystallization, the reaction between condensed phases and gas will force the liquid composition to stay within the oxygen isobaric surface in question if the oxygen pressure is kept constant and equilibrium prevails in the system.

The derivation of equilibrium crystallization paths is discussed in the following with the air isobaric surface as an example. This surface is drawn as a plane in Fig. 92 in order to simplify the diagram. Take as an example a mixture of composition represented by point $C$ located on the boundary curve between tridymite and spinel within the oxygen isobaric plane. As heat is withdrawn from the mixture at liquidus temperature, increasing amounts of tridymite and spinel crystallize out, and the composition of the liquid changes along the boundary curve from $C$ toward $c$. Tridymite has constant composition (SiO$_2$), whereas the spinel phase changes composition from $c'$ toward $c_1'$ as crystallization proceeds. The total composition of the condensed phases also changes as the crystallization proceeds, but only with respect to oxygen content. This change is described by the straight line $C-C''$ pointing from $C$ toward the O apex of the tetrahedron Mg-Fe-Si-O, of which the tetrahedron MgO-FeO-Fe$_2$O$_3$SiO$_2$ is a part. The mixture crystallizes completely at the temperature of point $c$, where a liquid of this composition is in equilibrium with tridymite of composition SiO$_2$ and spinel of composition $c_1'$. Point $c_1''$ is located such that the conjugation line $c_1''$-SiO$_2$ and the oxygen
reaction line \( C-C' \) intersect in point \( C' \) located in the plane \( \text{SiO}_2\)-\( \text{MgO}\)-\( \text{Fe}_2\text{O}_3\)-\( \text{FeO}\)-\( \text{Fe}_2\text{O}_3\). The relative amounts of the two crystalline phases tridymite and spinel at the solidus temperature are \( C'-c'_1/\text{SiO}_2-c'_1 \cdot 100\% \) and \( C'-\text{SiO}_2/\text{SiO}_2-c'_1 \cdot 100\% \), respectively.

The following general statements may be made regarding solidus temperatures at constant oxygen pressure: If the oxygen reaction line and the conjugation line connecting the points representing compositions of the two crystalline phases coexisting with liquids along a divariant surface intersect each other, then the solidus temperature is that of a point on the divariant surface. More commonly, the solidus temperature is that of the point of intersection between the oxygen isobaric surface and a quaternary liquidus univariant curve. Only if the oxygen isobaric surface happens to pass through a quaternary invariant point is the temperature of the latter the lowest temperature of equilibrium existence of liquid at the chosen oxygen pressure.
c. Composition sections through the system MgO-FeO-Fe₂O₃-SiO₂. It is possible and practical to present phase relations in the system MgO-FeO-Fe₂O₃-SiO₂ in diagrams which are simpler than those shown in Figs. 88 through 92. Two examples of such simplified diagrams are presented below (Figs. 93 and 94).

One is the diagram representing the system in contact with metallic iron. This diagram is best understood by comparison with the analogous type of representation used in the case of the ternary system FeO-Fe₂O₃-SiO₂ (see Fig. 38). It will be recalled that phase relations for the ternary system in contact with metallic iron were conveniently portrayed in a diagram with the appearance of a binary system (see Fig. 45a). This was done by projecting along oxygen reaction lines and onto the join FeO-SiO₂, points along the boundary curves (Fig. 38) between metallic iron and the various oxide primary phase areas (wüstite, fayalite, silica). The primary phase area of iron in Fig. 38

![Diagram](image)

**Fig. 93.** Phase relations in the system MgO-iron oxide-SiO₂ in contact with metallic iron, after Bowen and Schairer. The system is not ternary. The method of projection used in order to obtain this diagram is explained in the text.
Fig. 94. Phase relations in the system MgO-iron oxide-SiO$_2$ in air, after Muan and Osborn. The system is not ternary. The method of projection used in order to obtain this diagram is explained in the text.

extends into the tetrahedron of Fig. 88 as a thin phase volume adjacent to the MgO-FeO-SiO$_2$ face. Liquids in equilibrium with metallic iron have compositions represented by points along the surface between this phase volume and the adjacent volumes for the various oxide phases. When these composition points, as well as those representing crystalline phases in equilibrium with the liquids, are projected along oxygen reaction lines onto the face MgO-FeO-SiO$_2$, a triangular diagram is obtained, as shown in Fig. 93. The diagram is not ternary. However, so far as paths of crystallization are concerned, it can be treated like a ternary system with constant total composition of condensed phases. The total composition in question is the point of intersection between the appropriate oxygen reaction line and the face MgO-FeO-SiO$_2$.

Similar diagrams for other iron oxide-containing quaternary systems will be shown in later sections of this chapter.
The other simplified representation of the system MgO-FeO-Fe$_2$O$_3$-SiO$_2$ is presented in Fig. 94, showing phase relations in air. Here composition points in the air isobaric surface have been projected along oxygen reaction lines onto the plane MgO-FeO-Fe$_2$O$_3$-SiO$_2$, and this plane is shown in a triangular diagram. The diagram is not ternary, because compositions of all condensed phases are not represented by points located in the plane. However, so far as path of equilibrium crystallization is concerned, mixtures within this diagram can be treated just like a ternary system with constant total composition of condensed phases. The constant total composition of condensed phases for any chosen mixture in this case is the point of intersection between the chosen projection plane (MgO-FeO-Fe$_2$O$_3$-SiO$_2$) and the oxygen reaction line for the mixture in question.

Fig. 95. Phase relations in the system CaO-iron oxide-SiO$_2$ in contact with metallic iron, based mainly on data of Bowen, Schairer, and Posnjak and of Allen and Snow. The system is not ternary. The method of projection is identical to that used in Fig. 93.
Fig. 96. Phase relations in the system CaO-iron oxide-SiO₂ in air, after Phillips and Muan. The system is not ternary. Compositions of condensed phases have been projected along oxygen reaction lines onto the plane CaO-Fe₂O₃-SiO₂ in order to show true compositions of the various calcium ferrites appearing in the system.

2. OTHER FOUR-COMPONENT SYSTEMS SIMILAR TO MgO-FeO-Fe₂O₃-SiO₂

CaO-FeO-Fe₂O₃-SiO₂: The system CaO-FeO-Fe₂O₃-SiO₂ is not well enough known to permit portrayal of phase relations in terms of a tetrahedral model. However, data for the system are available at two levels of oxygen pressures, those prevailing when the oxide phases are in equilibrium with metallic iron, and that of air (0.21 atm). The diagram in Fig. 95 applies in contact with metallic iron and the diagram in Fig. 96 applies when the atmosphere is air. Both diagrams were obtained by projection methods which have been explained above. Characteristic features of the two diagrams, distinguishing them from the corresponding MgO systems, are the large number of different crystalline phases present, the relatively limited extent of solid
solution among these phases, and the relatively low liquidus (and solidus) temperatures prevailing over large composition areas of the diagrams.

**FeO-Fe₂O₃-Al₂O₃-SiO₂**: A perspective drawing of a tetrahedron illustrating phase relations in the system FeO-Fe₂O₃-Al₂O₃-SiO₂ at liquidus temperatures\(^{278,279}\) is shown in Fig. 97. A relatively small number of crystalline phases occur in the system, because Al\(^{3+}\) and Fe\(^{3+}\) substitute for each other to a considerable degree in the crystal lattices.

Phase relations among the components of this system have been studied in considerable detail at the following three levels of oxygen pressures: those of contact with metallic iron,\(^{280-283}\) air (0.21 atm),\(^{284}\) and 1 atm O₂.\(^{279}\) Diagrams showing these relations are presented in Figs. 98, 99, and 100, respectively.

Notable features of the diagrams in Figs. 97 through 100 are the relatively low liquidus (and solidus) temperatures prevailing in most composition areas of the system, particularly at the lowest oxygen pressures.

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Fig. 97. Perspective drawing of tetrahedron representing the system FeO-Fe₂O₃-Al₂O₃-SiO₂ and showing phase relations at liquidus temperatures, after Muan.\(^{279}\)
Fig. 98. Diagram showing phase relations at liquidus temperatures in the system iron oxide-Al$_2$O$_3$-SiO$_2$ in contact with metallic iron, based mainly on data of Schairer and Yagi$^{(282)}$ with minor changes based on recent data for the system Al$_2$O$_3$-SiO$_2$$^{(132,134)}$ and composition areas adjacent to the latter join.$^{(283)}$ The system is not ternary. The method of projection is identical to that used in Fig. 93.
Fig. 99. Diagram showing phase relations at liquidus temperatures in the system iron oxide-$\text{Al}_2\text{O}_3$-$\text{SiO}_2$ in air, based mainly on data of Muan,$^{(284)}$ with minor changes based on recent data for the system $\text{Al}_2\text{O}_3$-$\text{SiO}_2$.\(^{132,134}\) The system is not ternary. The method of projection is identical to that used in Fig. 94.
Fig. 100. Diagram showing phase relations at liquidus temperatures in the system iron oxide-\( \text{Al}_2\text{O}_3 \)-\( \text{SiO}_2 \) at 1 atm \( \text{O}_2 \) pressure, based mainly on data of Muan,\(^ {279} \) with minor changes based on recent data for the system \( \text{Al}_2\text{O}_3 \)-\( \text{SiO}_2 \).\(^ {132,134} \) The system is not ternary. The method of projection is identical to that used in Fig. 94.
Fig. 101. Diagram showing phase relations at liquidus temperatures in the system iron oxide-Cr$_2$O$_3$-SiO$_2$ in air, after Muan and Sōmiya. Dash-double dot lines are conjugation lines indicating compositions of coexisting spinel and liquid along the cristobalite-spinel boundary curves, as discussed in the text. The system is not ternary. The method of projection is identical to that used in Fig. 94.
**FeO-Fe₂O₃-Cr₂O₃-SiO₂**: Knowledge of phase relations in the system FeO-Fe₂O₃-Cr₂O₃-SiO₂ is very limited as compared with that of the three quaternary systems discussed above. The equilibria at liquidus temperatures have been established only at the oxygen pressure of air (0.21 atm).\(^{285}\) The graphical illustration appears as Fig. 101. The diagram has many features reminiscent of the system MgO-Cr₂O₃-SiO₂ (see Fig. 83). The extensive two-liquid region is intersected by the cristobalite-spinel and spinel-sesquioxide boundary curves. Liquidus (and solidus) temperatures rise very rapidly as Cr₂O₃ is added to iron oxide-silica mixtures in air.

**FeO-Fe₂O₃-TiO₂-SiO₂**: Studies of phase relations in the system iron oxide-titanium oxide-SiO₂, similarly, have been restricted to the level of oxygen pressure prevailing in air (0.21 atm).\(^{286}\) The diagram is reproduced in Fig. 102. The strongly stabilizing effect of TiO₂ on the corundum-type structure of hematite (Fe₂O₃) relative to the

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**Fig. 102.** Diagram showing phase relations at liquidus temperatures in the system iron oxide-TiO₂-SiO₂ in air, after MacChesney and Muan.\(^{286}\) The system is not ternary. The method of projection is identical to that used in Fig. 94.
Fig. 103. Diagram showing phase relations at liquidus temperatures for a part of the system iron oxide-manganese oxide-SiO$_2$ in an atmosphere of CO$_2$ and H$_2$ in ratio 1:1, after Riboud and Muan.$^{(287)}$ The system is not ternary. Compositions of condensed phases have been projected along oxygen reaction lines onto the plane FeO-MnO-SiO$_2$.

spinel-type structure of magnetite (Fe$_3$O$_4$) is reflected in the appearance of hematite as a primary crystalline phase in air (only magnetite and silica are stable crystalline phases in equilibrium with liquid in the system iron oxide-SiO$_2$ in air, Fig. 45b). The two-liquid region is intersected by the cristobalite-rutile boundary curve (compare the system CaO-TiO$_2$-SiO$_2$, Fig. 82).

**Fe-Mn-Si-O**: Phase equilibria in the system iron oxide-manganese oxide-SiO$_2$ at liquidus temperatures have been studied at two levels of oxygen pressure, those prevailing in a gas mixture of CO$_2$ and H$_2$ in ratio 1:1,$^{(287)}$ and that of air (0.21 atm).$^{(288)}$ The diagrams obtained are shown in Figs. 103 and 104, respectively. Extensive solid
Fig. 104. Phase relations at liquidus temperatures in the system iron oxide-manganese oxide-SiO₂ in air, after Muan and Sōmiya. The system is not ternary. Compositions of condensed phases have been projected along oxygen reaction lines onto the plane FeO-Fe₂O₃-Mn₃O₄-SiO₂.

Solution formation among orthosilicate and metasilicate phases is seen to prevail under strongly reducing conditions. Silica (cristobalite or tridymite) and spinel (approximate composition Fe₃O₄-FeMn₂O₄) occupy ~95% of the composition triangle in air, under which conditions the metasilicate phase and particularly the olivine phase appear only within very small areas adjacent to the manganese oxide-SiO₂ join. Liquidus and solidus temperatures are relatively low in most composition areas of the triangles at both levels of oxygen pressure. A large area of existence of two immiscible liquids is present in both cases.

CaO-FeO-Fe₂O₃-P₂O₅: Following the pioneering study of the system CaO-iron oxide-P₂O₅ in contact with metallic iron by Oelsen and Maetz some 20 years ago, a large number of investigators have dealt with various aspects of the phase relations.
existing among the above components. A summary of the present status of our knowledge of the system is shown in Fig. 105, based mainly on recent survey papers by Trömel and co-workers.\(^{290,291}\) Detailed, reliable experimental data are still available only for limited parts of the system, as indicated by solid boundary curves and liquidus isotherms, as opposed to the dashed curves showing inferred relations in parts of the diagram where experimental data are largely lacking. The most striking feature of the diagram is the liquid miscibility gap extending from a point adjacent to the FeO apex toward a composition point close to 3CaO·P\(_2\)O\(_5\). This characteristic of the system is

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**Fig. 105.** Phase relations at liquidus temperatures in the system CaO-iron oxide-P\(_2\)O\(_5\) in contact with metallic iron, based mainly on data summarized by Trömel and co-workers.\(^{290,291}\) Qualitatively inferred boundary curves are shown as dashed curves. The system is not ternary. The method of projection is identical to that used in Fig. 93.
Fig. 106. Phase relations at liquidus temperatures in the system CaO-chromium oxide-SiO$_2$ in air, after Glasser and Osborn.\(^{234}\) The system is not ternary in the area adjacent to the CaO apex, because of the presence of chromium in oxidation states higher than +3.

The key to the success of the Thomas process, as will be explained in the chapter dealing with steelmaking slags.

**CaO-Cr$_2$O$_3$-CrO$_3$-SiO$_2$:** Phase relations in the system CaO-chromium oxide-SiO$_2$ at liquidus temperatures in air are shown in Fig. 106.\(^{233}\) An area comprising compositions of mixtures consisting of two immiscible liquids occupies a large part of the composition triangle. Phases in which chromium is present in oxidation states higher than 3+ occur at subsolidus temperatures in the vicinity of the CaO-Cr$_2$O$_3$ join. Only at temperatures high enough to avoid the latter difficulty is the system ternary when studied in air atmosphere.
MgO-MnO-Mn₂O₃-SiO₂: Phase relations in the system MgO-MnO-Mn₂O₃-SiO₂ in equilibrium with a gas phase consisting of CO₂ and H₂ in ratio 1:1 are shown in Fig. 107. Composition points for condensed phases in this diagram have been projected along oxygen reaction lines onto the plane MgO-MnO-SiO₂, in accordance with principles explained before. The diagram has many features in common with that of the system MgO-iron oxide-SiO₂ in contact with metallic iron (Fig. 93), because the ions Mg²⁺ and Mn²⁺, like Mg²⁺ and Fe²⁺, readily substitute for each other in crystalline oxide structures. A notable difference between the diagrams of Figs. 93 and 107, however, is the shape of the metasilicate fields. Because the metasilicate of iron (FeSiO₃) is not

Fig. 107. Phase relations in the system MgO-manganese oxide-SiO₂ at liquidus temperatures in an atmosphere consisting of CO₂ and H₂ in ratio 1:1, after Glasser and Osborn.
Fig. 108. Phase relations at liquidus temperatures in the system CaO-manganese oxide-SiO₂ in an atmosphere consisting of CO₂ and H₂ in ratio 1.17:1, after Glasser.²⁴⁰

stable at liquidus temperatures, the field in which this structure type is stable in Fig. 93 disappears before it reaches the right side (the join FeO-SiO₂) of the triangle. The metasilicate of manganese (MnSiO₃), on the other hand, is stable, and hence in Fig. 107 the primary phase area of metasilicate extends all the way across the diagram from the left to the right side. However, because MnSiO₃ has a different structure from that of MgSiO₃ at liquidus temperatures, a boundary curve separates the metasilicate field into two primary phase areas in Fig. 107. It is also interesting to note in Fig. 107 that MnSiO₃ melts incongruently to tridymite and liquid, MgSiO₃ melts incongruently to orthosilicate (forsterite) and liquid, and intermediate compositions along the metasilicate join have rhodonite as the primary crystalline phase.

**CaO-MnO-Mn₂O₃-SiO₂**: Phase relations in the system CaO-manganese oxide-SiO₂ have been determined at oxygen pressure levels (CO₂/H₂ = 1.17) similar to those for
the system MgO-manganese oxide-SiO$_2$ discussed above. The liquidus surface delineated under these conditions is seen projected along oxygen reaction lines onto the face CaO-MnO-SiO$_2$ in Fig. 108. The most notable difference between the MgO- and the CaO-containing systems is the more limited solid solubility among the various crystalline phases present in the latter system.

**MnO-Mn$_2$O$_3$-Al$_2$O$_3$-SiO$_2$:** Phase relations in the system manganese oxide-Al$_2$O$_3$-SiO$_2$ have been determined at the low oxygen pressures prevailing when runs are made in a purified nitrogen atmosphere. Under these conditions the system is well represented by the composition triangle MnO-Al$_2$O$_3$-SiO$_2$ as shown in Fig. 109. Liquidus (and solidus) temperatures are low (~1100–1200°C) in major parts of the composition triangle. Hence MnO has a strong fluxing effect on alumina-silica bodies. Implications of this in refractory technology will be discussed in detail in a later chapter of this book.

**Fig. 109.** Phase relations at liquidus temperatures in the system MnO-Al$_2$O$_3$-SiO$_2$, mainly after Snow. Probable locations of boundary curves and liquidus isotherms outside the region studied by Snow are dashed.
C. Systems in Which a Gas Phase Plays No Important Role

When only very stable oxides (e.g., CaO, MgO, SiO₂, etc.) are present as components in a quaternary system, the phase relations existing among condensed phases can be discussed without taking into consideration the gas phase. Total composition of condensed phases may be assumed to remain constant, and paths of crystallization are derived by methods described under idealized conditions for the system MgO-FeO-Fe₂O₃-SiO₂. Although limited parts of many quaternary systems of stable oxides have been studied in detail, there are few systems for which reliable data in the liquidus temperature region are available for the entire composition volume. Probably the most thoroughly investigated system among these is CaO-MgO-Al₂O₃-SiO₂, which is of fundamental importance for an understanding of the chemistry of blast furnace slags. This system will be used as an example in the following to demonstrate some of the methods used in representing and interpreting phase relations in a complex quaternary system of stable oxides. Other systems will be discussed only briefly.

1. THE SYSTEM CaO-MgO-Al₂O₃-SiO₂

   a. Phase relations at liquidus temperatures. A tetrahedron representing the system CaO-MgO-Al₂O₃-SiO₂ is shown in Fig. 110, with one component at each apex and circles representing compositions of the end members of the various stable crystalline phases present in the system. Considering that many of these crystalline phases occur in different modifications, that some of them are partly soluble in each other at liquidus temperatures, and that liquids in a certain composition volume are only partly soluble in each other at liquidus temperatures, it is readily realized that the system is one of immense complexity. Only by a systematic subdivision of the tetrahedron into smaller units is it possible to obtain meaningful data and to present them in an orderly and clear manner.

   Two different methods are commonly used in carrying out this subdivision, as illustrated in Fig. 110. One is to choose planes representing compositions of mixtures having a constant content of one of the components. Such planes are parallel to one of the faces of the tetrahedron used to represent the quaternary system. Plane a in Fig. 110 is an example of such a plane, in which the Al₂O₃ content is constant. The other choice consists in working along planes formed by joining triplets of points representing compositions of end members of crystalline phases present in the system. Ordinarily, compatible compounds are chosen as apices of these triangular planes, so that the resulting system is ternary or partly ternary. Plane b in Fig. 110 is an example of such a plane. Experimentally determined phase relations at liquidus temperatures within each chosen plane are then usually drawn separately in the form of a triangular diagram, with liquidus temperatures indicated by liquidus isotherms, and boundary curves separating the various primary phase areas in accordance with methods described in Chapter 5.

   There is usually a principal difference between the triangular diagrams obtained by the two types of planes mentioned above. This difference is recognized by consideration of the geometrical relations existing within the tetrahedron CaO-MgO-Al₂O₃-SiO₂ (Fig. 110). When the planes are parallel to one of the faces of the tetrahedron, the compositions of the crystalline phases in equilibrium with the liquids are usually not represented by points within the chosen plane. Hence the triangular diagram thus obtained is not ternary, and paths of equilibrium crystallization can be derived accurately only by a consideration of the relations prevailing within the tetrahedron
Fig. 110. Tetrahedron representing the quaternary system CaO-MgO-Al₂O₃-SiO₂, with one component at each apex and circles representing binary and ternary compounds appearing in the system. Planes (a) and (b) indicate alternative ways of choosing mixtures for delineating phase relations at liquidus temperatures, as discussed in the text.

representing the quaternary system. This does not, however, detract from the usefulness and practicality of determining and representing phase relations in a quaternary system by means of a set of planes of this type. This is especially the case if the equilibria at liquidus temperatures only are of primary interest. If no crystalline phase or only a trace of one or more crystalline phases is present, the composition of the liquid is represented by points within the plane, and hence the triangular diagram gives a true representation of the relations prevailing at liquidus temperatures. When, on the other hand, the planes are chosen by joining points representing compositions of compounds within the tetrahedron, the phase relations prevailing in the resulting triangular diagram
are usually simpler. This is because one may choose the planes such that the compounds constituting the apices of the triangular diagram, or solid solutions among these compounds, are the only crystalline phases appearing in equilibrium with liquids within this triangle. In this case the triangular diagram is truly ternary, and paths of equilibrium crystallization can be derived by the methods described previously (see Chapter 5). In many cases, however, even though the plane is chosen according to the second method, the resulting system is only partly ternary. This is because one or more crystalline phases and the liquid in mixtures of certain compositions within a temperature range in the system do not have compositions which can be represented in terms of the three chosen apices of the triangular diagram. The plane sketched in Fig. 110 is a case in point. In this system (CaO·Al₂O₃·2SiO₂·CaO·MgO·2SiO₂·2MgO·SiO₂), spinel

![Diagram](image)

**Fig. 111.** Phase relations at liquidus temperatures in the 5% Al₂O₃ plane of the system CaO-MgO-Al₂O₃-SiO₂, after Osborn, DeVries, Gee, and Kraker. Abbreviations used have the following meanings: Mer = merwinitite, Mon = monticellite.
Fig. 112. Phase relations at liquidus temperatures in the 10% $\text{Al}_2\text{O}_3$ plane of the system CaO-MgO-Al$_2$O$_3$-SiO$_2$, after Osborn, DeVries, Gee, and Kraner. Abbreviations used have the following meanings: Mer = merwinitite, Mon = monticellite.

(MgAl$_2$O$_4$) appears as a phase in some mixtures. Nevertheless, in most of this system, ternary relations exist, and very useful liquidus as well as solidus data have been obtained.

Examples of representation of phase relations in the system CaO-MgO-Al$_2$O$_3$-SiO$_2$ in terms of both types of triangular diagrams are shown in Figs. 111 through 119. The first seven among these (Figs. 111 through 117) represent phase relations at liquidus temperatures in planes of constant Al$_2$O$_3$ contents spaced at 5% intervals between 5% and 35% Al$_2$O$_3$ (the basal plane, CaO-MgO-SiO$_2$ was shown in Fig. 77). The most important feature of these diagrams, from the standpoint of steelmaking, is the presence in each plane of a considerable area within which the liquidus and solidus temperatures are relatively low (≤1500°C). This area is seen to extend into the "basic" parts of the system, where the SiO$_2$ content is as low as 10–30% (depending on the Al$_2$O$_3$ level which the plane represents). These relations will be discussed in detail in a later section dealing with the chemistry of blast furnace slags.
Fig. 113. Phase relations at liquidus temperatures in the 15% $\text{Al}_2\text{O}_3$ plane of the system CaO-MgO-$\text{Al}_2\text{O}_3$-$\text{SiO}_2$, after Osborn, DeVries, Gee, and Kraner.$^{(299)}$ Abbreviations used have the following meanings: PWoll = pseudowollastonite, Mer = merwinitite.
Fig. 114. Phase relations at liquidus temperatures in the 20% $\text{Al}_2\text{O}_3$ plane of the system CaO-MgO-$\text{Al}_2\text{O}_3$-$\text{SiO}_2$, after Osborn, DeVries, Gee, and Kraner. Abbreviation used has the following meaning: Mer = merwinite.
Fig. 115. Phase relations at liquidus temperatures in the 25% Al₂O₃ plane of the system CaO-MgO-Al₂O₃-SiO₂, after Osborn, DeVries, Gee, and Kraner.\textsuperscript{(299)}
Fig. 116. Phase relations at liquidus temperatures in the 30% Al₂O₃ plane of the system CaO-MgO-Al₂O₃-SiO₂, after Osborn, DeVries, Gee, and Kraner. (299)
Fig. 117. Phase relations at liquidus temperatures in the 35% $\text{Al}_2\text{O}_3$ plane of the system $\text{CaO}$-$\text{MgO}$-$\text{Al}_2\text{O}_3$-$\text{SiO}_2$, after Osborn, DeVries, Gee, and Kraner.$^{(299)}$
Combination of the liquidus phase relations within a number of such planes leads to a clear picture of quaternary phase relations within the volume of the CaO-MgO-Al₂O₃-SiO₂ tetrahedron covered by these planes. It is not feasible to show a legible illustration of the quaternary relations by superimposing these planes in a perspective drawing on paper. However, in the laboratory or in the steelplant, when detailed knowledge of phase relations within this system is needed, it is not only feasible but entirely practical to illustrate the relations simply and clearly. This is done in a tetrahedral model of transparent plastic into which transparent planes are inserted at intervals of 5% Al₂O₃. Within each bounding face of the tetrahedron, as well as within each plane of constant Al₂O₃ content, the boundary curves separating the various primary phase areas and liquidus isotherms are shown. The curves in the series of superimposed planes help the observer visualize the surfaces between adjacent primary phase volumes and the variation of liquidus temperatures within the tetrahedral model.

Examples of phase relations according to the second method of choosing planes through the tetrahedral model are given in Figs. 118 and 119. The four planes CaO-MgO-2SiO₂-SiO₂-CaO-Al₂O₃; 2SiO₂, SiO₂-2MgO-SiO₂-CaO-Al₂O₃; 2SiO₂, CaO-MgO-2SiO₂-2MgO-SiO₂-CaO-Al₂O₃; 2SiO₂ (see Fig. 110) are pictured. These planes outline a relatively small tetrahedron within the tetrahedron for the system CaO-MgO-Al₂O₃-SiO₂. Approximate phase relations within each of these planes at liquidus temperatures are illustrated in the composite diagram of Fig. 118. In diagrams (a) and (c) the compositions of all crystalline phases appearing in equilibrium with liquid can be expressed in terms of the components at the apices of the triangular diagrams, and hence these two systems are ternary. In diagrams (b) and (d) a spinel phase appears whose composition is represented by points outside the triangle. Hence these diagrams are not ternary in composition areas where spinel is present as a phase.

Boundary curves in each of these triangular diagrams are the origins of divariant liquidus surfaces extending into the tetrahedron outlined by the planes under discussion, and points of intersection between three boundary curves in each of these planes are starting points for univariant liquidus curves extending into the tetrahedron. The approximate locations of these surfaces and curves and the intersection of the latter at quaternary liquidus invariant points are illustrated in Fig. 119(a), modified after Osborn and Tait. Here the irregular tetrahedron shown within the large tetrahedron in Fig. 110 has been enlarged and redrawn in the form of a regular tetrahedron whose four bounding faces are the triangles which were portrayed in Fig. 118. In the present case it is possible to visualize the geometrical relations prevailing in the interior of this tetrahedron because the phase relations are relatively simple. However, it is frequently exceedingly difficult to do so. For this reason Schairer has proposed a simplified method by which the essential features of phase relations in such a tetrahedron may be illustrated. This method consists in plotting the quaternary liquidus univariant curves in the plane of the paper in a schematic manner without representing the true spatial relationships but with clear indication of the nature of the phases coexisting in equilibrium along each curve and at the intersections of these curves, and a clear indication of liquidus temperatures at invariant points and the direction of change of liquidus temperatures along the univariant curves. The sketch in Fig. 119(b) shows such a simplified “Schairer diagram” for the system CaO·MgO·2SiO₂·SiO₂-CaO·Al₂O₃·2SiO₂·2MgO·SiO₂.

The principles discussed above may be extended to other parts of the system CaO-MgO-Al₂O₃-SiO₂.

b. Phase relations at solidus temperatures. Phase relations at solidus temperatures can be derived for a quaternary system by methods similar to those described for ternary systems. Graphical representation again is the main difficulty in extending the relations
Fig. 118. Sketches showing approximate phase relations at liquidus temperatures in four planes: (a) CaO-MgO-2SiO₂-SiO₂-CaO·Al₂O₃·2SiO₂,(298) (b) SiO₂-2MgO-SiO₂-CaO·Al₂O₃·2SiO₂,(293) (c) CaO-MgO-2SiO₂-2MgO-SiO₂-SiO₂,(257) (d) CaO-MgO-2SiO₂-2MgO-SiO₂-CaO·Al₂O₃·2SiO₂,(298) within the tetrahedron CaO-MgO-Al₂O₃-SiO₂.
Fig. 119. (a) Perspective drawing of regular tetrahedron used to illustrate phase relations at liquidus temperatures in the system CaO-MgO-2SiO₂-2MgO-SiO₂-SiO₂-CaO-Al₂O₃, modified after Osborn and Tait. Heavy lines originating at ternary invariant or ternary piercing points on the four faces of the tetrahedron are quaternary univariant curves representing compositions of liquids coexisting in equilibrium with three crystalline phases. (b) Diagram showing in a simplified manner phase relations within the tetrahedron in (a), as explained in the text. Abbreviations used have the following meanings: F = forsterite, D = diopside, P = protoenstatite, A = anorthite, T = tridymite.

from a ternary to a quaternary system. Only general features of the solidus surfaces will be considered here. The system CaO-MgO-Al₂O₃-SiO₂ will be used as an example, as this seems to be the only quaternary system for which a systematic approach to the delineation of the solidus surface has been carried out.

If no solid solution formation takes place among the crystalline phases present in the system, solidus temperatures are those of quaternary liquidus invariant points, except for compositions lying along binary or ternary joins, where solidus temperatures are then the binary or ternary invariant points. Each volume formed by the points representing compositions of crystalline phases coexisting with liquids of a quaternary invariant point comprises compositions of all mixtures having the temperature of the invariant point as the solidus. It follows that under these conditions, i.e., no solid solutions formed, the solidus temperature changes abruptly from one composition volume to the next.

When there is complete or partial solid solubility among two or more of the crystalline phases, on the other hand, composition volumes are present within which the solidus temperatures change continuously. These relations have their counterparts in ternary systems, as was illustrated and discussed in Chapter 5.

Of particular interest in our present discussion are the solidus relations in our simplified illustration of quaternary phase equilibria by means of selected planes through
Fig. 120. The solidus surface in the 10% Al₂O₃ plane of the system CaO-MgO-Al₂O₃-SiO₂, after Roeder and Osborn. The various designations used are explained in the text.

The tetrahedron representing the system. The solidus surface in each of these planes is the intersection between the chosen plane and the composition volumes within which the solidus temperature is constant or changes continuously with changing composition. These intersections are relatively easy to draw when the planes pass through composition points of compounds in such a manner that phase relations within the plane are truly ternary. In such a case the methods discussed in Chapter 5 are directly applicable. For nonternary parts of such planes, as well as for planes of constant content of one of the components, the relations are derived from considerations of the quaternary relations on the basis of the general principles outlined above.

An example of a solidus surface is shown in Fig. 120, illustrating the 10% Al₂O₃ plane through the system CaO-MgO-Al₂O₃-SiO₂. The various lines outline areas (numbered 1–46) within each of which all mixtures have the solidus temperatures listed in Table 6-1. The crystalline phases present within each of these areas at solidus temperatures are also listed in the table.
### Table 6-1

**SOLIDUS TEMPERATURES, AND PHASES PRESENT IN THE VARIOUS AREAS OUTLINED IN FIG. 120**

<table>
<thead>
<tr>
<th>Number of Area</th>
<th>Solidus Temperature</th>
<th>Crystalline Phases* Present at Solidus Temperature</th>
<th>Number of Area</th>
<th>Solidus Temperature</th>
<th>Crystalline Phases* Present at Solidus Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1300°</td>
<td>An + Cord + Mul + Sil</td>
<td>24</td>
<td>1250°-1357°</td>
<td>Di + Fo(75-83) + Mel(70-100)</td>
</tr>
<tr>
<td>2</td>
<td>1200°</td>
<td>An + Cord + En + Sil</td>
<td>25</td>
<td>1210°-1225°</td>
<td>An + Di + Mel(70-81)</td>
</tr>
<tr>
<td>3</td>
<td>1200°-1222°</td>
<td>An + En(82-100) + Sil</td>
<td>26</td>
<td>1380°-1390°</td>
<td>Mel(37-63) + Mer + Sp</td>
</tr>
<tr>
<td>4</td>
<td>1170°</td>
<td>An + Di(78) + En(82) + Sil</td>
<td>27</td>
<td>1390°-1400°</td>
<td>C$_2$S + Mel(37-100) + Mer</td>
</tr>
<tr>
<td>5</td>
<td>1135°-1200°</td>
<td>An + Di(100-78) + Sil</td>
<td>28</td>
<td>1390°</td>
<td>C$_2$S + Mel(37) + Mer + Sp</td>
</tr>
<tr>
<td>6</td>
<td>1135°</td>
<td>An + Di + Sil + Wo(93)</td>
<td>29</td>
<td>1300°-1360°</td>
<td>C$_2$S + Mel(0-100) + Ra</td>
</tr>
<tr>
<td>7</td>
<td>1150°</td>
<td>An + Pw + Sil + Wo(93)</td>
<td>30</td>
<td>1290°-1350°</td>
<td>Mel(0-100) + Pw + Ra</td>
</tr>
<tr>
<td>8</td>
<td>1220°-1266°</td>
<td>An + Mel(0-81) + Pw</td>
<td>31</td>
<td>1390°-1414°</td>
<td>C$_2$S + Mel(0-37) + Sp</td>
</tr>
<tr>
<td>9</td>
<td>1220°</td>
<td>An + Mel(81) + Pw + Wo(93)</td>
<td>32</td>
<td>1395°</td>
<td>C + C$_3$A + C$_3$S + Per</td>
</tr>
<tr>
<td>10</td>
<td>1210°</td>
<td>An + Di + Mel(81) + Wo(93)</td>
<td>33</td>
<td>1380°</td>
<td>C$_3$A + C$_2$S + C$_3$S + Per</td>
</tr>
<tr>
<td>11</td>
<td>1225°</td>
<td>An + Di + Fo(83) + Mel(70)</td>
<td>34</td>
<td>1295°</td>
<td>C$<em>3$A + C$</em>{12}$A$_7$ + C$_2$S + Per</td>
</tr>
<tr>
<td>12</td>
<td>1200°-1270°</td>
<td>An + Di(78-100) + Fo</td>
<td>35</td>
<td>1300°</td>
<td>CA + C$_1$A$_7$ + C$_2$S + Per</td>
</tr>
<tr>
<td>13</td>
<td>1200°</td>
<td>An + Di(78) + En(82) + Fo</td>
<td>36</td>
<td>1325°</td>
<td>CA + C$_2$S + Per + Sp</td>
</tr>
<tr>
<td>14</td>
<td>1200°-1260°</td>
<td>An + En(82-100) + Fo</td>
<td>37</td>
<td>1410°</td>
<td>C$_2$S + Mer + Per + Sp</td>
</tr>
<tr>
<td>15</td>
<td>1240°</td>
<td>An + Cord + En + Fo</td>
<td>38</td>
<td>1400°</td>
<td>Mer + Mon + Per + Sp</td>
</tr>
<tr>
<td>16</td>
<td>1300°</td>
<td>An + Cord + Fo + Sp</td>
<td>39</td>
<td>1400°</td>
<td>Mon(74-100) + Per + Sp</td>
</tr>
<tr>
<td>17</td>
<td>1285°</td>
<td>An + Fo(80) + Mel(70) + Sp</td>
<td>40</td>
<td>1400°</td>
<td>Fo(74) + Mon(74) + Per + Sp</td>
</tr>
<tr>
<td>18</td>
<td>1285°-1400°</td>
<td>Fo(74-80) + Mel(63-70) + Sp</td>
<td>41</td>
<td>1400°-1540°</td>
<td>Fo(74-100) + Per + Sp</td>
</tr>
<tr>
<td>19</td>
<td>1380°</td>
<td>Fo(75)+ Mel(63) + Mon(75) + Sp</td>
<td>42</td>
<td>1350°</td>
<td>CA + C$_3$S + Geh + Sp</td>
</tr>
<tr>
<td>20</td>
<td>1380°-1400°</td>
<td>Mel(63) + Mon(75-100) + Sp</td>
<td>43</td>
<td>1380°-1436°</td>
<td>Mel(63-100) + Mer + Mon</td>
</tr>
<tr>
<td>21</td>
<td>1375°-1437°</td>
<td>Fo(74-75) + Mel(63-100) + Mon(74-75)</td>
<td>44</td>
<td>?</td>
<td>Mel(63-100) + Mon(75-100)</td>
</tr>
<tr>
<td>22</td>
<td>1380°</td>
<td>Mel(63) + Mer + Mon + Sp</td>
<td>45</td>
<td>1285°-1317°</td>
<td>An + Fo(80-100) + Sp</td>
</tr>
<tr>
<td>23</td>
<td>1475°</td>
<td>An + Cor + Mul + Sp</td>
<td>46</td>
<td>1285°-1360°</td>
<td>An + Mel(0-70) + Sp</td>
</tr>
</tbody>
</table>

*Abbreviations used have the following meanings:

- **Ak** = Akermanite
- **An** = Anorthite
- **Cor** = Corundum
- **Cord** = Cordierite
- **C$_3$A** = 3CaO·Al$_2$O$_3$
- **C$_{12}$A$_7$** = 12CaO·7Al$_2$O$_3$
- **CA** = CaO·Al$_2$O$_3$
- **CA$_2$** = CaO·2Al$_2$O$_3$
- **CA$_6$** = CaO·6Al$_2$O$_3$
- **C** = CaO
- **Di** = Diopside
- **En** = Enstatite
- **Fo** = Forsterite
- **Geh** = Gehlenite
- **Mel** = Melilitc (Given in % akermanite)
- **Per** = Periclase
- **Pw** = Pseudowollastonite
- **Ra** = Rankinite
- **Sil** = Silica
- **Wo(93)** = 93% CaSiO$_3$,
  7% CaMgSi$_2$O$_6$

Parentheses after the compound abbreviation indicates the content (in %) of that species in one of the solid-solution series shown below: Diopside-Enstatite; Akermanite-Gehlenite (Mellilitc); Forsterite-Monticellite. Thus Fo(80-100) means that forsterite ranges in composition from 80% forsterite-20% monticellite to 100% forsterite.
c. Isothermal sections. The construction of isothermal sections through a quaternary system is in principle not more difficult than for a ternary system, although the graphical representation is much more complicated. Hence diagrams showing perspective drawings illustrating isothermal sections for quaternary systems do not appear in the literature. The following general features would apply to such a diagram, and they are most easily visualized by comparison with ternary systems: A certain volume within the tetrahedron representing the system would comprise compositions of mixtures all having liquidus temperatures below that of the isothermal section in question. All these mixtures would consist of only one phase, a homogeneous liquid, at the chosen temperature. The surface outlining this volume represents compositions of liquids which are in equilibrium with one or more crystalline phases. In most areas of this surface, only one crystalline phase will be in equilibrium with the liquid. This crystalline phase may be a pure compound represented by a point, a binary solid solution represented by a line, a ternary solid solution represented by a surface, or even a quaternary solid solution represented by a volume. In any case, the straight lines (conjugation lines) connecting compositions of coexisting liquid and crystalline phases describe a volume within which all mixtures have the same phase assemblage, crystals plus liquid, at the chosen temperatures. Where the surface outlining the all-liquid region is intersected by a divariant surface between two adjacent primary phase volumes in the quaternary system, the curve of intersection represents compositions of liquids which are in equilibrium with two crystalline phases of constant or variable composition. The volume described by the conjugation lines comprises compositions of mixtures all consisting of liquid and the same two crystalline phases. Similarly, the intersection between the surface outlining the all-liquid region and a quaternary univariant line represents composition of a liquid coexisting with three crystalline phases. The volume described by the conjugation lines for this situation comprises mixtures all having the same phase assemblage at the chosen temperature. Finally, if the chosen isothermal temperature happens to coincide with a quaternary liquidus invariant temperature, the intersection between three univariant curves is on the surface of the all-liquid region. This point represents the composition of a liquid which is in equilibrium with four crystalline phases, and the composition volume within which this situation prevails is defined by the conjugation lines.

In addition to the volumes mentioned above, there are in some instances volumes comprising compositions of mixtures in which no liquid is present at the chosen temperature. The phase assemblages within these volumes are determined from a consideration of composition volumes. These are the quaternary analogues of the composition triangles discussed in Chapter 5, and are derived by methods which have been described there.

The situation with regard to isothermal sections for mixtures within the planes presented in Figs. 111 through 118 is as follows: In planes of constant content of one of the components (Al₂O₃ in our present case) (Figs. 111 through 117), the compositions of all crystalline phases are usually represented by points outside the plane, as is the composition of the liquid phase, except at the liquidus temperature of a particular mixture. Meaningful isothermal sections can be sketched for such planes only at temperatures in the vicinity of the liquidus, and the methods used are analogous to those for ternary systems.

In planes defined by points representing compositions of compounds within the quaternary system (Figs. 118 and 119), isothermal planes for areas where the relations are truly ternary are drawn in accordance with methods described in Chapter 5. In areas within these planes where the relations are not ternary, the same reservations with regard to use of isothermal sections are valid as for the planes of constant Al₂O₃ contents.
SYSTEMS WITH MORE THAN FOUR COMPONENTS

A. General Considerations

The graphical representation of phase relations in systems with more than four components is very difficult because of the many composition variables present (see for instance a paper by Roeder and Osborn\textsuperscript{(303)}). No attempt will be made in this book to give a general treatment of such systems. However, it is sometimes possible to show phase relations in a five-component system in a meaningful way by using geometrical methods similar to those applied for four-component systems. This is the case when one of the independent variables is held constant or is forced to follow a set pattern. Good examples of this are iron oxide-containing systems when either the oxygen pressure is kept constant or the equilibria are being investigated in contact with metallic iron. The simplifications possible in this case are in principle analogous to those used in representing phase relations in the quaternary system MgO-FeO-Fe\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} in terms of triangular diagrams and in representing the ternary system FeO-Fe\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} in terms of a diagram with the appearance of a binary system, as shown in previous chapters.

B. Liquidus Relations in Two Selected Systems

The systems CaO-FeO-Fe\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} and CaO-MgO-FeO-Fe\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} will be used as examples in the following. When equilibria in these systems are investigated in contact with metallic iron, the iron present in the oxide phases is almost exclusively in the ferrous state. Hence the equilibrium relations are well represented in terms of the tetrahedra CaO-FeO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} and CaO-MgO-FeO-SiO\textsubscript{2}, respectively.

1. CaO-IRON OXIDE-\textsubscript{Al}2\textsubscript{O}3-SiO\textsubscript{2} IN CONTACT WITH METALLIC IRON

A tetrahedron representing the system is portrayed in Fig. 121, with one component at each apex and circles representing idealized end member compounds. Phase relations have been studied in considerable detail within the volumes outlined by planes joining the FeO apex with pairs of the composition points 2CaO-SiO\textsubscript{2}, CaO-SiO\textsubscript{2}, 2CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}, CaO-Al\textsubscript{2}O\textsubscript{3}-2SiO\textsubscript{2} and SiO\textsubscript{2}\textsuperscript{(301,304)}. The data can be illustrated and evaluated by the same methods used for volumes within the system CaO-MgO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}. The tetrahedron 2CaO-SiO\textsubscript{2}-CaO-SiO\textsubscript{2}-2CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}-FeO is used as an example in Fig. 122. Liquidus phase relations in the interior of the tetrahedron are shown in a perspective drawing in Fig. 122(a) and in the form of a simplified “Schairer type” diagram in Fig. 122(b).
Fig. 121. Tetrahedron representing the system CaO-iron oxide-Al₂O₃-SiO₂ in contact with metallic iron.
Fig. 122. (a) Perspective drawing of regular tetrahedron used to illustrate phase relations at liquidus temperatures in the system 2CaO·SiO₂·FeO·CaO·SiO₂·2CaO·Al₂O₃·SiO₂. Heavy lines originating at invariant or piercing points on the four faces of the tetrahedron are quaternary univariant curves representing compositions of liquids coexisting in equilibrium with three crystalline phases. (b) “Schairer-type” diagram showing in a simplified manner phase relations within the tetrahedron in (a). Abbreviations used have the following meanings: W = wüstite, Ol = olivine, Ra = rankinite, CS = calcium metasilicate (wollastonite or pseudowollastonite), Mel = melilit.
Fig. 123. Tetrahedron representing the system CaO-MgO-iron oxide-SiO$_2$ in contact with metallic iron, showing planes within which phase relations at liquidus temperatures have been studied experimentally.

2. CaO-MgO-IRON OXIDE-SiO$_2$ IN CONTACT WITH METALLIC IRON

Phase relations for a part of the system CaO-MgO-FeO-Fe$_2$O$_3$-SiO$_2$ in contact with metallic iron have been similarly determined.$^{305,306}$ A tetrahedron representing this system is shown in Fig. 123, with one component at each apex and light lines indicating positions of planes which have been studied experimentally. The main features of the liquidus phase relations are shown by means of a "Schairer type" diagram in Fig. 124.
Fig. 124. “Schairer-type” diagram showing essential features of phase relations at liquidus temperatures in the system CaO-MgO-iron oxide-SiO₂ in contact with metallic iron, after Ricker\(^{305}\) as modified by Osborn.\(^{306}\)
A. Introduction

The importance of the slag phase in iron- and steelmaking is evidenced by the maxim "take care of the slag, and the steel will take care of itself." Until relatively recently, the "taking care of the slag" was an art rather than a science. Few fundamental principles of chemistry were applied to this field of technology, and the melter had to rely almost exclusively on his own experience and that handed down to him by his predecessors. The art of steelmaking is now gradually becoming a science of steelmaking, however, as sound chemical and engineering principles are being increasingly used as guides in the processes involved.

One such important guide in slag chemistry is the wealth of information contained in phase equilibrium diagrams for oxide systems. The present chapter deals with the use of such diagrams as a means of optimizing compositions of slags in various iron- and steelmaking processes. For the purpose of our discussion the slags are conveniently divided into two general groups. One comprises the type of slag encountered in the iron-making process in a blast furnace. At the low oxygen pressures prevailing in this furnace, only oxides which are thermodynamically very stable are present in the slag phase. The most important constituents are CaO, MgO, Al₂O₃, and SiO₂, and the phase relations are well understood from a consideration of the quaternary system CaO-MgO-Al₂O₃-SiO₂. The other group encompasses slags from various steelmaking processes which are carried out at considerably higher oxygen pressures than those of the blast furnace. Under these conditions oxides of lesser stabilities are present as constituents of the slag phase, in addition to the very stable oxides. Hence it is more difficult to systematize the discussion with reference to phase diagrams with a small number of components. Many simplifications and assumptions are necessary in order to discuss the chemistry of such slags.

B. Iron Blast Furnace Slags

1. GENERAL CONSIDERATIONS

The following slag characteristics are important for maximum efficiency in operation of a blast furnace:

1. The slag should be completely liquid at steelmaking temperatures.
2. The slag should be such that uncontrollable variation in its composition is tolerated without a troublesome slag developing.
3. The slag should have high sulfur-removing capacity.
4. The slag should have favorable flow and diffusion characteristics (low viscosity).
2. PHASE RELATIONS AT LIQUIDUS TEMPERATURES IN THE SYSTEM CaO-MgO-Al₂O₃-SiO₂

An excellent starting point for an evaluation of optimum slag composition in terms of the above criteria is afforded by phase equilibria at liquidus temperatures in the system CaO-MgO-Al₂O₃-SiO₂. Graphical representations of such equilibria have been presented in Chapter 6, and the following discussion is made with reference to diagrams shown there (Figs. 110 through 119).

The primary phase volumes present in the tetrahedron of Fig. 110 are lime (CaO), periclase (MgO), silica (SiO₂), spinel (MgAl₂O₄), pseudowollastonite (α-CaSiO₃), wollastonite (β-CaSiO₃), dicalcium silicate (Ca₂SiO₄), tricalcium silicate (Ca₃SiO₅), forsterite (Mg₂SiO₄), melilitite solid solutions (Ca₂MgSi₂O₇-Ca₂Al₂SiO₇), pyroxene solid solutions (MgSiO₃-CaMgSi₂O₆), monticellite (CaMgSiO₄), merwinite (Ca₂MgSi₂O₈), cordierite (Mg₂Al₄Si₂O₁₈), anorthite (Ca₂Al₂Si₂O₈), and sapphire (Mg₄Al₆Si₄O₁₆). Liquidus temperatures within each of these primary phase volumes vary with compositions in a manner which is visualized by inspection of the liquidus isotherms in each plane of constant Al₂O₃ content (see Figs. 111 through 117). For the purpose of the present discussion we will select one of these planes, 10% Al₂O₃, as an example for a more detailed discussion. It is seen (Fig. 112) that the liquidus surface is very steep and liquidus temperatures in general are high in the primary phase areas of periclase, lime, tri- and dicalcium silicate, forsterite, and silica (cristobalite and tridymite), whereas the liquidus surface is relatively flat and liquidus temperatures are relatively low in the primary phase areas of pseudowollastonite, wollastonite, pyroxene, melilitite, merwinite, and monticellite.

The performance of slags within this plane in terms of the four criteria listed above at a temperature of 1500°C* will be considered in the following.

First, mixtures within the area bounded by the 1500°C liquidus isotherm in Fig. 112 are all liquid at the temperature under consideration and hence meet requirement (1). For the sake of clarity, this area has been crosshatched in the simplified diagram of the 10% Al₂O₃ plane shown in Fig. 125.

The second requirement, that of latitude with respect to possible uncontrollable composition changes, makes it desirable to avoid close approach to composition areas where a crystalline phase starts to separate out, viz., the outline of the shaded area.

The situation with respect to the third requirement, that of high sulfur-removing capacity may be evaluated approximately from thermodynamic data for pure oxide and sulfide components. Standard free energies of formation of oxides and sulfides of a number of elements were presented in Fig. 3, and differences (ΔΔG°) between the free energies of formation of sulfides and oxides were presented in Fig. 6. Although the behavior of these substances in a liquid slag will depend also on their free energies of solution, the latter contributions constitute second-order effects, and it may be inferred that the less positive these (ΔΔG°)-values are, the stronger is the sulfur-removing capacity of that oxide constituent of the slag. It is seen that K₂O and Na₂O are the best desulfurizers. However, because of their high vapor pressures and severe rate of attack on refractories, these oxides are not practical components of slags except as additions after tapping. The sulfur-removing capacity of the practical slag components increases in the order SiO₂ < Al₂O₃ < MgO < CaO. Clearly, low SiO₂ (and Al₂O₃) content and high CaO (and MgO) content are desired in order to achieve the best possible sulfur retention by the slag. The critical question is: For the given alumina content of 10%, what is the lowest possible silica content? From the diagram

* Slag temperatures in the basic iron blast furnace are usually about 1500°C. The temperature of 1500°C is chosen for purpose of illustration. The reasoning involved and the nature of the conclusions reached are similar if a somewhat different temperature is chosen.
Fig. 125. Simplified diagram showing phase relations in the 10% Al₂O₃ plane through the system CaO-MgO-Al₂O₃-SiO₂. The projected liquidus surface is shown only at temperatures above 1500°C. The crosshatched area defined by the 1500°C liquidus isotherm comprises compositions of mixtures which are all liquid at 1500°C. Abbreviations used have the following meanings: Crist = cristobalite, Mer = merwinite.

in Fig. 125 it is seen that the minimum silica content within the all-liquid region is that of point a (≈32% SiO₂, 44% CaO, 14% MgO), representing a liquid in equilibrium with merwinite and periclase. Attempts to decrease the SiO₂ content below this value, at 1500°C, would only result in precipitation of merwinite and/or periclase crystals without changing the SiO₂ content of the liquid significantly.* Hence a liquid of com-

* The phases merwinite and periclase contain no Al₂O₃, and the remaining liquid will increase its Al₂O₃ content as these two crystalline phases separate out. The liquid composition will change along a divariant liquidus surface in the quaternary system, and the composition change is characterized by virtually constant SiO₂ and increasing Al₂O₃ content of the liquid. Hence the sulfur-removing capacity of the liquid will decrease as crystallization proceeds, and at the same time the amount of liquid will decrease.
position represented by point a is inferred to have the highest sulfur-removing capacity at the chosen level of Al₂O₃ content.

A test of these inferred general relations is provided by the data of Holbrook and Joseph (307) and of Holbrook (308). Lines of equal sulfur distribution ratios between slag and metal ("isodesulfurization lines") at 1500°C according to the data of the above authors are shown superimposed on the 1500°C isothermal section in Fig. 126. In a general way there is good agreement between the two sets of data. The point of maximum desulfurization, according to Holbrook and Joseph and to Holbrook, is located somewhat closer to the CaO-MgO join (lower SiO₂ content) than is inferred from the liquidus data. This slight discrepancy is probably explained, at least in part, by the presence of FeO and S in the experiments of Holbrook and Joseph and of Holbrook.

The fourth requirement listed, that of low viscosity, very conveniently is fulfilled when the third requirement is fulfilled. The viscosity of an alumino-silicate liquid is primarily a function of the degree of polymerization of silicon-aluminum-oxygen tetrahedra. The "basic" oxides CaO and MgO help to break the links among the tetrahedra in these polymerized structures, and promote the tendency for formation of isolated tetrahedra. Hence the viscosity of the liquids decreases with increasing contents of CaO and MgO. For a given Al₂O₃ content, therefore, the viscosity of the liquid phase will be lower the lower the SiO₂ content is. There is a limit for this tendency, however. At very low SiO₂ contents (below that of point a in Fig. 125) the viscosity starts to increase with decreasing SiO₂ content because increasing amounts of crystals are
suspended in the liquid. The minimum viscosity therefore is reached for the liquid represented by the point of lowest silica content a within the all-liquid area. More accurate viscosity data than are available at the present time\(^{(309)}\) will probably show that the points of maximum desulfurization and minimum viscosity do not exactly coincide, but without much doubt they will be close together.

Optimum slag compositions for a temperature of 1500°C, as derived on the basis of the criteria discussed above, are presented in Table 8–1 for the 10% \(\text{Al}_2\text{O}_3\) plane as well as for other planes of constant \(\text{Al}_2\text{O}_3\) content in the system \(\text{CaO-MgO-Al}_2\text{O}_3-\text{SiO}_2\).\(^{(299)}\)

<table>
<thead>
<tr>
<th>(\text{Al}_2\text{O}_3)</th>
<th>(\text{CaO})</th>
<th>(\text{MgO})</th>
<th>(\text{SiO}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>43</td>
<td>16</td>
<td>36</td>
</tr>
<tr>
<td>10</td>
<td>44</td>
<td>14</td>
<td>32</td>
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<tr>
<td>15</td>
<td>44</td>
<td>12.5</td>
<td>28.5</td>
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<td>20</td>
<td>45</td>
<td>11</td>
<td>24</td>
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<tr>
<td>25</td>
<td>48</td>
<td>8</td>
<td>19</td>
</tr>
<tr>
<td>(57)*</td>
<td>(6)*</td>
<td>(12)*</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>56</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>35</td>
<td>54</td>
<td>4</td>
<td>7</td>
</tr>
</tbody>
</table>

* These numbers represent an alternative optimum slag composition which is more favorable than the other with respect to sulfur retention but does not have as large latitude with respect to composition changes.\(^{(289)}\)

If the area of optimum slag composition within each \(\text{Al}_2\text{O}_3\) plane is considered to be a circle, the juxtaposition of these circles, one on top of the other, will form a cylindrical volume extending upward from the bottom and tilting to the left within the tetrahedron representing the system \(\text{CaO-MgO-Al}_2\text{O}_3-\text{SiO}_2\), as illustrated in Fig. 127. The average value of the weight percent ratio \((\text{CaO} + \text{MgO})/(\text{Al}_2\text{O}_3 + \text{SiO}_2)\) for mixtures within this volume is 1.41. This may be used as a convenient guide in controlling compositions of blast furnace slags. The splitting of the cylindrical volume into two branches at the highest \(\text{Al}_2\text{O}_3\) contents is in accordance with the alternative optimum compositions listed in Table 8–1.

The above discussion was concerned only with the optimum relative proportions of \(\text{CaO}, \text{MgO}, \) and \(\text{SiO}_2\) at chosen constant \(\text{Al}_2\text{O}_3\) content. The following question remains to be answered: Is there an optimum \(\text{Al}_2\text{O}_3\) content for \(\text{CaO-MgO-Al}_2\text{O}_3-\text{SiO}_2\) slags in a blast furnace? Or, in other words, is the optimum composition area in one \(\text{Al}_2\text{O}_3\) plane equivalent to those of other planes? The data of Holbrook and Joseph\(^{(307)}\) and of Holbrook\(^{(308)}\) indicate that for slags of optimum composition with respect to \(\text{CaO}, \text{MgO}, \) and \(\text{SiO}_2\) proportions, the sulfur-removing capacity of the slag is a maximum at an \(\text{Al}_2\text{O}_3\) content of approximately 10%. Their study did not, however, extend to sufficiently low \(\text{SiO}_2\) contents at the lowest \(\text{MgO}\) levels to prove that this inference is valid. Indications are that it matters little what the \(\text{Al}_2\text{O}_3\) content of the slag is, within reasonable limits (0–30%), so long as the ratio \((\text{CaO} + \text{MgO})/(\text{Al}_2\text{O}_3 + \text{SiO}_2)\) is maintained at approximately the optimum value of 1.41.
3. EFFECT OF TITANIUM OXIDE ON LIQUIDUS RELATIONS IN THE SYSTEM CaO-MgO-Al₂O₃-SiO₂

In addition to the main constituents CaO, MgO, Al₂O₃, and SiO₂, blast furnace slags commonly contain lesser amounts of other components, for instance FeO, TiO₂, MnO, and S. The presence of these additional components will usually have only a second-order effect on the equilibria prevailing among the four main components discussed in the preceding section.

The role of TiO₂ in blast furnace slags has been the subject of considerable guessing, and some data bearing on the role of this oxide are of special interest. Liquidus temperatures in an air atmosphere have been delineated for mixtures of constant Al₂O₃ plus TiO₂ contents in the system CaO-MgO-Al₂O₃-TiO₂-SiO₂. In these circumstances the equilibria are conveniently illustrated by means of triangular diagrams, by extending to a five-component system the ideas presented in detail in a previous section dealing with the quaternary system CaO-MgO-Al₂O₃-SiO₂. As an example, the phase relations in mixtures containing 10% Al₂O₃ and 5% TiO₂ are shown in Fig. 128. If this diagram is compared with the 15% Al₂O₃ plane in the system CaO-MgO-Al₂O₃-SiO₂ (see Fig. 113), the comparison in effect shows the change in phase relations at liquidus temperature caused by a substitution of 5% TiO₂ for 5% Al₂O₃.

Fig. 127. Perspective drawing of the tetrahedron representing the system CaO-MgO-Al₂O₃-SiO₂, showing as cylindrical volumes the optimum compositions of blast furnace slag. Diagram based on work of Osborn, DeVries, Gee, and Kraner.
Fig. 128. Phase relations at liquidus temperatures at constant $\text{Al}_2\text{O}_3$ plus $\text{TiO}_2$ content of 15% in the system $\text{CaO-MgO-Al}_2\text{O}_3$-$\text{TiO}_2$-$\text{SiO}_2$, after Osborn and Gee.\(^{(310)}\)

permit a more direct comparison, the liquidus isotherms with and without $\text{TiO}_2$ are superimposed on each other in the diagram of Fig. 129. It is seen that the phase relations are very similar with and without $\text{TiO}_2$, except that spinel no longer has a primary phase area on the liquidus surface when 5% $\text{TiO}_2$ is present. Liquidus temperatures are in general slightly lowered when $\text{TiO}_2$ replaces part of the $\text{Al}_2\text{O}_3$. However, in the area chosen as optimum compositions for slags in the 15% $\text{Al}_2\text{O}_3$ plane in the system
Fig. 129. Diagram showing a comparison of liquidus isotherms in the 15% \( \text{Al}_2\text{O}_3 \) plane through the system \( \text{CaO-MgO-Al}_2\text{O}_3-\text{SiO}_2 \) (solid curves) after Osborn, DeVries, Gee, and Kraner,\(^{299}\) and when 5% \( \text{TiO}_2 \) replaces one-third of the \( \text{Al}_2\text{O}_3 \) (dashed lines), after Osborn and Gee.\(^{310}\)

\( \text{CaO-MgO-Al}_2\text{O}_3-\text{SiO}_2 \) at 1500°C the two sets of liquidus isotherms shown in Fig. 129 almost coincide. Hence the substitution of 5% \( \text{TiO}_2 \) for \( \text{Al}_2\text{O}_3 \) does not change significantly the relative proportions of the other constituents, \( \text{CaO}, \text{MgO}, \) and \( \text{SiO}_2 \), which constitute the optimum composition of the slag. In other words, the phase relations within the quaternary system \( \text{CaO-MgO-Al}_2\text{O}_3-\text{SiO}_2 \) as illustrated by a series of constant \( \text{Al}_2\text{O}_3 \) planes in Figs. 111 through 117 may also be used to select the optimum slag composition when \( \text{TiO}_2 \) is present as a component, provided the \( \text{Al}_2\text{O}_3 \) plane selected is that corresponding to the sum of the \( \text{Al}_2\text{O}_3 \) and \( \text{TiO}_2 \) contents of the slag. Because \( \text{Al}_2\text{O}_3 \) and \( \text{SiO}_2 \) are approximately complementary in their functions as constituents of \( \text{CaO-MgO-Al}_2\text{O}_3-\text{SiO}_2 \) slags, so are \( \text{TiO}_2 \) and \( \text{SiO}_2 \) at relatively high oxygen pressures. It appears on the basis of the above that the observed “gumminess” of many \( \text{TiO}_2 \)-containing slags must be attributed to factors other than the effect of \( \text{TiO}_2 \) on liquidus temperatures of the slags.

The main effect of the components \( \text{FeO}, \text{MnO}, \) and \( \text{S} \) present in blast furnace slags is thought to be a slight lowering of liquidus temperatures and hence an expansion of the areas of existence of one homogeneous liquid phase.
Fig. 130. Solidus surface of a part of the 10% $\text{Al}_2\text{O}_3$ plane through the system CaO-MgO-$\text{Al}_2\text{O}_3$-$\text{SiO}_2$, after Roeder and Osborn. Abbreviations used have the following meanings: Per = periclase, Sp = spinel, Fo = forsterite, $\text{C}_2\text{S} = \text{Ca}_2\text{SiO}_4$, Wo = wollastonite, Di = diopside, Mer = merwinite, Mon = monticellite, Mel = melilitite, An = anorthite, Sil = silica. Solid triangle shows optimum compositions of blast furnace slags in the 10% $\text{Al}_2\text{O}_3$ plane.
4. PHASE RELATIONS AT SOLIDUS TEMPERATURES IN THE SYSTEM CaO-MgO-Al₂O₃-SiO₂

The preceding discussion was concerned exclusively with phase relations prevailing in the liquidus temperature region and applied specifically to the properties of the slag phase as it existed at the high temperature of the blast furnace during the heat. Attention will now be directed toward another and related problem: To what extent can phase equilibrium data be used to predict and explain what happens to the constitution and behavior of the slag as it is being tapped and cooled? The type of diagram which is most useful for illuminating this problem is the solidus surface. The 10% Al₂O₃ plane through the system CaO-MgO-Al₂O₃-SiO₂ was used as an example of such a surface and presented in Fig. 120. An enlargement showing the part of this plane which is of particular interest in blast furnace technology is presented in Fig. 130. The phase assemblages present in the various areas, each of which is designated by an identifying number, are found in Table 6-1 on page 141. The following features of this solidus surface are especially noteworthy for judging freezing behavior of slags. First, it is seen that the solidus surface in the common composition ranges of blast furnace slags is highly complex, consisting of many small areas within each of which a different phase assemblage is present at solidus temperature. Within some of these areas the solidus temperature is constant, within others it is variable, in accordance with relations explained in Chapter 6.

The manner in which a slag will solidify upon cooling depends to a large extent on the temperature range over which crystals and liquid coexist or, in other words, the sharpness of crystallization. These relations can be derived by a comparison of Figs. 112 and 130. A clearer illustration is afforded by the diagram presented in Fig. 131, showing curves of equal differences between liquidus and solidus temperature as a

![Diagram showing lines of equal differences between liquidus and solidus temperatures in the 10% Al₂O₃ plane through the system CaO-MgO-Al₂O₃-SiO₂, after Roeder and Osborn.](image)

Fig. 131. Diagram showing lines of equal differences between liquidus and solidus temperatures in the 10% Al₂O₃ plane through the system CaO-MgO-Al₂O₃-SiO₂, after Roeder and Osborn. Solid triangle shows optimum compositions of blast furnace slags in the 10% Al₂O₃ plane.
function of composition within the 10% Al₂O₃ plane. The optimum composition of blast furnace slags at this Al₂O₃ content, as derived previously, is marked with a solid triangle. It is seen that this triangle is located in an area where liquidus and solidus temperatures differ by less than 200°C. Hence slags of optimum composition will usually freeze completely over a temperature range of <200°C, assuming that equilibrium conditions prevail.

Important inferences regarding the mineral constitution of solidified blast furnace slags may be made from the type of diagram shown in Fig. 130. For instance, the main crystalline phases present when optimum slags in the 10% Al₂O₃ plane are cooled to room temperature are likely to be dicalcium silicate, melilite, merwinite, monticellite, periclase, and spinel. Minor constituents of the slag, such as FeO, MnO, TiO₂, and S probably will not change these relations appreciably.

It is also suggested that important inferences regarding the textures of solidified slags may be made from the diagrams presented above, because the temperature range of coexistence of liquid and crystals during cooling undoubtedly has an important bearing on the size and shapes of crystals formed and on the proportion of the slag which will appear as a glassy phase in the final product.

C. Steelmaking Slags

1. PHOSPHATE SLAGS

Probably the most spectacular and interesting example of use of phase diagrams to illuminate steelmaking slag problems is that of the basic Bessemer process, commonly referred to as the Thomas process. The slags developed during blowing in these vessels consist mainly of CaO, iron oxide, and P₂O₅, with lesser amounts of SiO₂ and MnO commonly present.

a. Equilibria in the system CaO-Iron Oxide-P₂O₅. As a first approximation, one may discuss the chemistry of phosphate slags in terms of the three major constituents, CaO, iron oxide, and P₂O₅. The diagram for this system in contact with metallic iron was shown in Fig. 105. The feature of main interest in applying this diagram to slag problems is the liquid immiscibility area which dominates the central part of the system. The temperature interval of 1500–1600°C is of particular interest, and isothermal sections at 1500, 1550, and 1600°C are shown in Fig. 132, in order to illustrate phase relations as clearly as possible. In each of these isothermal sections there are two areas of coexistence of two immiscible liquids, which are separated by composition areas in which crystalline phases are present in the phase assemblages. In the present discussion we will be mainly concerned with the lower of these two-liquid regions, that closest to the FeO-CaO join in each of the diagrams. Light straight lines traversing this two-liquid region are conjugation lines connecting points representing compositions of liquid phases coexisting in equilibrium, at the temperature of the diagram. The location and direction of these conjugation lines are of paramount importance for an understanding of the phosphorus-removing capacity of slags within the system.

Although the mechanism of removal of phosphorus from metal is not thoroughly understood, the process is thought to consist of two main steps. The first is oxidation of P to P₂O₅, and this is followed by the combination of the P₂O₅ formed with basic constituents of the slag, mainly CaO. The simultaneous presence of FeO and CaO of high chemical potentials is essential for these reactions to proceed. Slags within the system CaO-FeO-P₂O₅ possess these properties, as is shown by the following reasoning. One of the liquids in Fig. 128 has high FeO content, and therefore possesses a high capacity for transferring oxygen from the gas phase to the metal. The other liquid
Fig. 132. Isothermal sections at 1550, 1600, 1650, and 1700°C through the system CaO-iron oxide-P_2O_5 in contact with metallic iron, based mainly on data summarized by Trömel and co-workers\(^{290,291}\) (compare Fig. 105). Abbreviations used have the following meanings: C_4P = Ca_4P_2O_9, C_3P = Ca_3P_2O_8, L = liquid(s).

has high CaO content and therefore has a high capacity for reacting with P_2O_5 once the phosphorus has been oxidized. Since the chemical potential of each species is identical in the two phases coexisting in equilibrium, liquids of high CaO content in the area adjacent to the miscibility gap on the left have the unique property of having very high oxygen transfer capacity while simultaneously being almost saturated with respect to CaO (see boundary curve separating the liquid area from that of lime + liquid in Fig. 132).

In practice, Thomas slags usually have compositions represented by an area located between the liquid miscibility gap and the CaO saturation curve of the system CaO-FeO-P_2O_5 at steelmaking temperatures,\(^{131}\) as indicated by the shaded area in
Fig. 133. The main trends in the composition changes of the slag during blowing in the converter have been discussed by Fischer and Straube\(^{(312)}\) as well as by Knüppel, Oeters, and Gruss.\(^{(313)}\)

The dramatic effect of slag composition on distribution of phosphorus and oxygen between slag and metal phases is shown in Fig. 134, reproduced from Trömel, Fix, and Fritze.\(^{(291)}\) Their data were obtained under two different experimental conditions, those of slags saturated with 3CaO·P\(_2\)O\(_5\) and with 4CaO·P\(_2\)O\(_5\) plus CaO, respectively. The results show that very low phosphorus contents of the metal may be obtained whether the slag is saturated with 3CaO·P\(_2\)O\(_5\) or with 4CaO·P\(_2\)O\(_5\) plus CaO, or for any liquid whose composition is in the area between these two saturation curves. The oxygen content of the metal, on the other hand, is strongly dependent on whether the slag is saturated with 3CaO·P\(_2\)O\(_5\) or with 4CaO·P\(_2\)O\(_5\) plus CaO. It is seen that approach to the latter saturation is desirable in order to simultaneously reduce the oxygen and the phosphorus contents of the metal.

Although lowering of temperature causes a decrease in phosphorus as well as oxygen content of the metal phase, the effect seems to be smaller than has been commonly assumed in the past.

A parameter which may have an important bearing on these equilibria in the slag phase is the oxygen pressure of the system. Whenever a slag phase during blowing in a converter is in contact with an oxidizing gas phase as well as a metal phase, considerable oxygen pressure gradients will exist in the slag. Turkdogan and Bills claim\(^{(314)}\) that the liquid miscibility gap in the system CaO-FeO-P\(_2\)O\(_5\) gradually decreases in size as the oxygen pressure is increased from that of equilibrium with metallic iron, and that at a certain critical oxygen pressure the miscibility gap probably disappears completely. His inference has recently been refuted, however, by Olette\(^{(315)}\) who finds that the extent of the miscibility gap in the system CaO-iron oxide-P\(_2\)O\(_5\) does not vary significantly with varying oxygen pressures.

b. Effects of various additions on equilibria in the system CaO-iron oxide-P\(_2\)O\(_5\).

Actual slags used in the Thomas process almost invariably contain some SiO\(_2\) and MnO, and often some MgO, in addition to the three main constituents CaO, iron oxide, and P\(_2\)O\(_5\). Although phase relations in most parts of the resulting multicomponent system are unknown, the bounding ternary systems and selected joins through the system have been studied in detail. Phase diagrams for the systems CaO-iron oxide-SiO\(_2\) and CaO-iron oxide-P\(_2\)O\(_5\) in contact with metallic iron were shown in Figs. 95 and 105 respectively, and the joins 3CaO·P\(_2\)O\(_5\)-2CaO-SiO\(_2\)\(^{(316,317)}\) and 3CaO·P\(_2\)O\(_5\)-SiO\(_2\)\(^{(318)}\) are portrayed in Figs. 135 and 136, respectively. In addition, information is available on the effects of SiO\(_2\) and MnO on the main area of interest, that of liquid immiscibility. Oelsen and Maetz in 1948\(^{(319)}\) showed that the liquid miscibility gap decreases as the SiO\(_2\) content increases, and they estimated that the liquid miscibility gap will disappear when the SiO\(_2\) content exceeds 15\%, as illustrated in the sketch of Fig. 137. Trömel and Fritze\(^{(320)}\) have studied the effects of SiO\(_2\) additions on P distribution between slag and metal.

Quantitative data for the effects of additions of MgO or MnO on phase relations in the system CaO-FeO-P\(_2\)O\(_5\) are not available, in spite of their importance in defining optimum compositions and limiting phosphorus-removing capacity of Thomas slags. Oelsen and Maetz\(^{(319)}\) showed, however, that no liquid miscibility gaps exist in the systems MgO-FeO-P\(_2\)O\(_5\) and MnO-FeO-P\(_2\)O\(_5\). Bookey\(^{(321,322)}\) determined free energies of formation of magnesium and calcium phosphates and concluded from the much lower stabilities of the former that magnesia plays a negligible role, compared with lime, in dephosphorization.
Fig. 133. Sketch showing as shaded elongated area approximate compositions of common Thomas slags, after Rellermeyer and Kootz. \(^{(311)}\)

Fig. 134. Diagram showing effect of slag composition and temperature on P and O contents of metal phase in equilibrium with slag, after Trömel, Fix, and Fritze.\(^{(290)}\) The abbreviation Misc. denotes miscibility gap.
Fig. 135. Proposed phase diagrams for the join 2CaO·SiO₂–3CaO·P₂O₅ through the system CaO·P₂O₅–SiO₂, after Trömel, Harkort, and Hotop (316) in (a) and after Bredig (317) in (b). Abbreviations used have the following meanings: C₂S = Ca₂SiO₄, C₃P = Ca₃P₂O₈, L = liquid. Letters K, R, and S are used to designate three different solid solution phases between Ca₂SiO₄ and Ca₃P₂O₈, in accordance with the terminology of Trömel, Harkort, and Hotop.

Fig. 136. Phase diagram for the join 3CaO·P₂O₅·SiO₂ through the system CaO·P₂O₅·SiO₂, after St. Pierre. (318)
Liquid miscibility gaps similar to that present in CaO-FeO-P₂O₅ also exist in the systems SrO-FeO-P₂O₅, BaO-FeO-P₂O₅, Li₂O-FeO-P₂O₅, and K₂O-FeO-P₂O₅. These systems have not been studied in detail, however, because the components are of very doubtful potential use in practical steelmaking processes, either because of lack of availability in large quantities, or because of their high vapor pressures at steelmaking temperatures, or both. However, one alkali oxide-iron oxide-phosphate system, Na₂O-FeO-P₂O₅, has been the subject of more detailed experimental study. The feature of main interest in the present discussion is the large area of equilibrium existence of two immiscible liquid phases, as shown in Fig. 138. In fact, the miscibility gap in this system is more extensive than in CaO-FeO-P₂O₅, and the stability of sodium orthophosphate seems to exceed that of calcium orthophosphate. Attempts to use additions of Na₂O (in the form of Na₂CO₃) to enhance the phosphorus-removing capacity of Thomas slags have not been very successful, however, because of serious vaporization problems with the alkali oxide. Further attempts to clarify the conditions for possible use of sodium phosphate slags have been made by Turkdogan and Maddocks, who studied parts of the system Na₂O-P₂O₅-SiO₂.

In spite of the large number of investigations of phosphate slags which have been made during the past 20 years, it appears that good possibilities still exist for further optimizing compositions of these slags to yield lower phosphorus contents of the metal phase than those presently attainable. The quantitative evaluation of these possibilities will require a knowledge of equilibrium relations existing in the enormously complex oxide system resulting when MnO, SiO₂, and alkali oxides are added to the system CaO-FeO-P₂O₅.

Although the present book is devoted to the subject of equilibria among oxide phases, it is logical at this point to consider the effect of a nonoxidic but ionic substance, CaF₂, on the equilibria just discussed. Calcium fluoride is often added to steelmaking slags.
Fig. 138. Diagram showing extent of liquid miscibility gap in the system Na₂O-iron oxide-P₂O₅ in contact with metallic iron, after Oelsen and Wiemer.\(^{(323)}\)

Fig. 139. Phase diagram for the system "FeO"-CaF₂, after Körber and Oelsen.\(^{(327)}\)
as a fluxing agent. Its function in a Thomas slag is qualitatively understood from a consideration of phase relations existing in the two systems obtained by combining CaF$_2$ with iron oxide and tri-calcium phosphate, respectively. The pronounced dissimilarity between CaF$_2$ and FeO melts is expressed by an extensive liquid miscibility gap existing in this system.\(^{(327)}\) as shown in Fig. 139. In contrast to this, complete miscibility exists in the system CaF$_2$-3CaO-P$_2$O$_5$.\(^{(323)}\) (Fig. 140). These relations suggest that CaF$_2$ additions to Thomas slags will promote the separation of a liquid even richer in FeO and hence with higher oxygen transfer potential than that present in the system CaO-FeO-P$_2$O$_5$. That this is actually the case has been shown by Olsen. However, the citric acid solubility of the cooled slag is lowered when CaF$_2$ additions are used. Since the economic success of the Thomas process depends on the use of the cooled slag as fertilizer, the application of CaF$_2$ to enhance the dephosphorizing capacity of the slag is not a practical solution.

### 2. BASIC OPEN-HEARTH AND BASIC OXYGEN CONVERTER SLAGS

Basic open-hearth and basic oxygen converter slags in general contain the same oxide constituents as Thomas slags. The relative amounts of the various oxides are usually quite different, however. Whereas slags in the Thomas process usually contain \(\sim 20\%\) P$_2$O$_5$ and only \(\sim 5\%\) SiO$_2$, the slags under consideration in the present section contain only 2–4% P$_2$O$_5$ but as much as 15–20% SiO$_2$. Common composition ranges of these slags are listed in Table 8–2.

Knowledge of phase relations in the highly complex multicomponent system made up by the components listed in this table is desirable for an evaluation of reactions taking place in these slags. Such knowledge is not available, and even if we had the
necessary data, it would be exceedingly difficult to illustrate phase relations in such a complex system. However, important inferences regarding the chemistry of these slags may be made from a consideration of phase equilibria in simpler systems.

As a first approximation consider the system CaO-iron oxide-SiO₂. The 1600°C isothermal sections through this system at two different levels of oxygen pressure, those in contact with metallic iron and that of air, are shown in Fig. 141(a) and (b), drawn on the basis of diagrams presented in Figs. 95 and 96. The crosshatched area in each diagram in Fig. 141 comprises compositions of mixtures which are all liquid at 1600°C. A comparison of the two diagrams shows that the extent of the all-liquid area is approximately the same at the two vastly different oxygen pressures prevailing in these diagrams. Although data are lacking for oxygen pressures intermediate between those of diagrams (a) and (b) in Fig. 141, it appears safe to assume that the positions of the outlines of the all-liquid area do not vary significantly over the range of oxygen pressures usually prevailing in the slag phase of steelmaking furnaces (1–10⁻⁸ atm). For maximum desulfurization and dephosphorization capacity of the slags, it is important to obtain homogeneous liquids with the lowest possible SiO₂ contents which are simultaneously as close as possible to being saturated with CaO at steelmaking temperatures. Hence the regions of the diagrams separating the all-liquid area from those where liquids coexist in equilibrium with either CaO or the calcium-silicates (Ca₉SiO₅ and Ca₉SiO₄) are particularly important in steelmaking technology. This area is indicated with solid circles in Fig. 141.

Inferences regarding the effects of MgO, MnO, Al₂O₃, P₂O₅, and CaF₂ on the extent of the all-liquid area of Fig. 141 may be made on the basis of available phase equilibrium data for the systems obtained when one or more of the above components are added to CaO-iron oxide or CaO-SiO₂ mixtures (see Figs. 18, 65, 66). With MgO as a possible exception, all the above components will probably lower the liquidus surface of the system CaO-iron oxide-SiO₂ and hence increase the area comprising mixtures which are all liquid at a chosen temperature. In addition to this effect of lowering the liquidus surface, CaF₂ probably also has other important functions, such as lowering viscosity and hastening dissolution of limestone lumps coated with dicalcium silicate, as well as raising the FeO activity of the melt because of the strong unmixing tendency in the system FeO-CaF₂ (compare previous discussion of Thomas slags).

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>AMOUNTS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>30–55</td>
</tr>
<tr>
<td>MgO</td>
<td>3–12</td>
</tr>
<tr>
<td>MnO</td>
<td>4–15</td>
</tr>
<tr>
<td>FeO</td>
<td>5–40</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1–10</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0–4</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0–2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>5–25</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1–4</td>
</tr>
<tr>
<td>S</td>
<td>0.05–0.30</td>
</tr>
<tr>
<td>CaF₂</td>
<td>0–2</td>
</tr>
</tbody>
</table>
Fig. 141. The 1600°C isothermal sections through the system CaO-iron oxide-SiO₂ at two different levels of oxygen pressures, those prevailing in contact with metallic iron in (a) and that of air in (b). Abbreviations used have the following meanings: 
\[ \text{C}_3\text{S} = \text{Ca}_3\text{SiO}_5, \text{C}_2\text{S} = \text{Ca}_2\text{SiO}_4, L = \text{liquid}. \]

3. ACID SLAGS

Common composition ranges of acid open-hearth and acid electric furnace slags are listed in Table 8-3.

The main constituents are SiO₂, FeO, and MnO, with lesser amounts of CaO and Al₂O₃ commonly present. Phase relations in the five-component systems (or six, counting the two iron oxides FeO and Fe₂O₃) made up from these oxides are not known. However, the system iron oxide-manganese oxide-SiO₂ under reducing conditions, as shown in Fig. 103, constitutes a good starting point. The 1600°C isothermal section through this system is illustrated in Fig. 142. Acid slags have compositions approaching those of the SiO₂ saturation curve (a-a') constituting the upper limit of the area of homogeneous liquids. With CaO and FeO contents being relatively low in these slags,

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>AMOUNTS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>1– 8</td>
</tr>
<tr>
<td>MnO</td>
<td>10–20</td>
</tr>
<tr>
<td>FeO</td>
<td>20–40</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1– 5</td>
</tr>
<tr>
<td>SiO₂</td>
<td>45–55</td>
</tr>
</tbody>
</table>

Table 8-3

COMPOSITION RANGES OF COMMON ACID SLAGS
Fig. 142. The 1600°C isothermal section through the system iron oxide-manganese oxide-
SiO₂ in an atmosphere consisting of CO₂ and H₂ in ratio 1:1, after Riboud and
Muan²⁰² (compare Fig. 103).

their dephosphorization and desulfurization capacities are low, and pig iron of rela-
tively high purity is required for successful use of the acid processes. The effects of small
additions of Al₂O₃ or CaO to mixtures within this ternary system can be estimated
from available data on phase equilibria in the systems CaO-FeO-SiO₂ and FeO-Al₂O₃-
SiO₂ in contact with metallic iron, and CaO-MnO-SiO₂ and MnO-Al₂O₃-SiO₂ under
reducing conditions (see Figs. 95, 98, 108, and 109, respectively). Addition of Al₂O₃
to the FeO-MnO-SiO₂ slags lowers the liquidus surface, whereas CaO addition may
either lower or raise the liquidus surface.
OXIDE INCLUSIONS

A. Introduction

The problem of inclusions in steel is enormously complicated because of the large number of components usually present and the lack of equilibrium conditions usually prevailing during formation and subsequent reactions of the inclusions. It is therefore important, even more so than in other areas of iron- and steelmaking, to exercise utmost caution in the application of phase equilibrium diagrams to inclusion problems. With these limitations, however, phase equilibrium diagrams are useful as a guide in evaluating the nature and behavior of inclusions in the various kinds of steel.

It is practical for our purpose to classify nonmetallic inclusions in steels into two main groups. One group comprises what is commonly referred to as exogenous inclusions, consisting largely of material which has been eroded away from refractories. These exogenous inclusions usually consist of oxide phases which have stable existence in the refractory phases from which they originate, but they do not even approach equilibrium with the metal phase in which they are entrapped. Consequently, the composition, constitution, and properties of this type of inclusion can be predicted from phase equilibrium data presented in the succeeding chapter on refractories.

The second main group comprises the so-called endogenous inclusions which form within the steel during its deoxidation and subsequent cooling. For this type of inclusion a sufficiently close approach to equilibrium may be expected to prevail so that the appropriate phase diagrams of oxide phases in contact with metallic iron become useful guides for evaluation of the reactions which take place. It is to these endogenous inclusions that the remainder of the present chapter will be devoted.

There are two main areas of the problem of endogenous inclusions in which phase diagrams may be used advantageously. One concerns the phase assemblages which are likely to result on formation of the inclusions during solidification of the steel ingot. The other concerns the behavior of the inclusions during subsequent annealing and rolling of the steel ingot.

B. Inferred Liquid Immiscibility Relations Bearing on Oxide Inclusions

Insufficient experimental data are available to describe quantitatively the phase relations existing in the proximity of the iron apex of ternary iron-metal-oxygen systems of importance in considerations of inclusion equilibria. However, it is interesting to speculate on the possible role of liquid immiscibility in determining sequences of phase appearance during formation of inclusions and the resulting shape of the oxide phase formed. The system Fe-Mn-O will be used as an example. An inferred projection of
the liquidus surface for this system was sketched in Fig. 61. It was inferred (see page 79) that the boundary curve between metallic iron (with some manganese in solid solution) and manganowüstitite (FeO-MnO) must traverse the two-liquid area of the ternary system. At the situation represented by this straight line there exist in equilibrium two crystalline phases (iron and manganowüstitite) and two liquid phases (one metallic, with composition close to Fe, the other oxidic, with composition close to the FeO-MnO join). The possible significance of this division of the two-liquid region into two separate areas in which the primary crystalline phases differ in nature (one a metal, one an oxide phase) will be illustrated in the following by inferring paths of equilibrium crystallization for two selected mixtures.

Take as an example first a mixture A which is unsaturated with oxygen and contains a relatively small amount of Mn (Fig. 143). As a metal phase of composition close to the Fe apex starts to separate out at the liquidus temperature, the liquid composition first changes along the curve $A-a_1$. A second, oxidic liquid $a_1'$ separates out at temperature $t_{a_1}$, and solid metal coexists with two liquids $a_1-a_2$ and $a_1'-a_2'$ over a narrow temperature range $t_{a_1}-t_{a_2}'$. The liquid metal phase is completely consumed at $a_2'$, and solid metal is in equilibrium with a liquid oxide phase changing in composition from $a_2'$ to $a_3$ as the temperature decreases from $t_{a_2}$ to $t_{a_3}$. Manganowüstitite starts to separate out together with metal at point $a_3$, and the composition of the remaining oxide liquid changes along the ferromanganese-manganowüstitite boundary curve from $a_3$ to $a_4$ upon further cooling of the mixture. The final product of crystallization is a mixture of metallic iron containing some manganese, and manganowüstitite.

Consider next a mixture B which is also unsaturated with respect to oxygen but which contains more manganese than the mixture considered above. Metal of composition close to Fe starts to separate out at the liquidus temperature, and the liquid composition changes from B to $b_1$ as the temperature decreases. Manganowüstitite

![Fig. 143](image-url) Fig. 143. Sketch showing inferred paths of equilibrium crystallization of selected mixtures close to the Fe apex of the system Fe-Mn-O. The diagram has been distorted in order to show the relations as clearly as possible (compare Fig. 61).
crystals start to separate out at \( b_1 \), and the metallic liquid changes composition along the iron-manganowüstite boundary curve adjacent to the Fe-Mn join of the triangular diagram. The liquid phase disappears when its composition is such that the conjugation line connecting the two points representing compositions of the two crystalline phases existing in equilibrium with the liquid passes through the point representing total composition of the original liquid metal. In the sketch of Fig. 143, this situation is assumed to prevail when the liquid composition has reached point \( b_2 \).

The most important difference between the two crystallization paths, so far as the nature of resulting inclusions is concerned, is the time of appearance and the nature of the oxide phase. In the first case, where the Mn content is low, the oxide separates out as a liquid phase while a large proportion of the metal is still liquid. The oxide inclusions formed are likely to be spherical in shape. In the second case, however, when the Mn content is much higher, the oxide phase is separated out in the form of manganowüstite crystals. It is inferred that the oxide inclusions thus formed will tend to be more irregularly shaped than in the case previously discussed.

C. Behavior of Oxide Inclusions During Heating and Rolling of Steel

1. GENERAL CONSIDERATIONS

During heating and rolling, steel ingots are usually exposed to temperatures in the range of 1000–1300°C. If the temperature is below the solidus of the oxide inclusions, it may be expected that changes in size, shape, and distribution of inclusions from those existing in the as-cast ingot will be relatively minor. However, if partial or complete melting of the inclusions takes place, the oxide material will readily flow during the rolling process and assume a distribution and shape entirely different from those present in the ingot. Phase equilibrium diagrams for combinations of common inclusion constituents at oxygen pressures equal to or approaching those existing in contact with a metal phase therefore constitute a very important source of information for judging the behavior to be expected from the inclusions during these operations.

The most important deoxidizers are Mn, Al, and Si; less common are Ca, Ti, and Zr. Other elements reacting with oxygen when present in steel include Cr, V, and B. The most pertinent phase diagrams for evaluating oxide inclusion behavior are thus those for the systems iron oxide-MnO, iron oxide-Al2O3, iron oxide-SiO2, iron oxide-TiO2, iron oxide-ZrO2, iron oxide-Cr2O3, iron oxide-oxvanadium oxide, iron oxide-B2O3, iron oxide-MnO-SiO2, iron oxide-Al2O3-SiO2, iron oxide-TiO2-SiO2, iron oxide-ZrO2-SiO2, CaO-iron oxide-SiO2, iron oxide-Cr2O3-SiO2, iron oxide-oxvanadium oxide-SiO2, and iron oxide-B2O3-SiO2, all in equilibrium with metallic iron. Several of these diagrams have been presented in the first part of this book, and some of these will be discussed further in the following. For the remaining systems there is no reliable information available at the present time.

2. EQUILIBRIA WHEN ONLY ONE DEOXIDIZING ELEMENT IS USED IN PLAIN CARBON STEEL

Mn: The product of deoxidation with Mn is a solid solution which may be represented by the approximate formula \((Fe, Mn)O\). Sloman and Evans\(^{(320)}\) found that the solid solutions formed have compositions varying continuously between the two end members. This is in accordance with the most recent laboratory data on FeO-MnO solid solutions\(^{(198, 202)}\) and the phase diagram for the system FeO-MnO as shown in Fig. 60. Solidus temperatures are above 1370°C for the entire composition range, and no appreciable change in appearance of the inclusions during rolling is expected. The shape
of the oxide inclusions as they are formed during cooling of the steel, however, depends on the MnO-FeO ratio of the crystals. Those containing a high proportion of FeO are usually spherical, whereas the outlines become increasingly irregular as the MnO content increases. These appearances are probably related to the position of the two-liquid region relative to the metal-metal oxide boundary curve in the system Fe-Mn-O, as discussed in a previous section (see Figs. 61 and 143).

**Al**: If aluminum alone is used as a deoxidizer in a plain carbon steel, the oxide phases formed are one or more of those occurring as stable phases in the system FeO-Al₂O₃ in contact with metallic iron. As can be seen from the diagram of Fig. 59, wüstite, hercynite, and corundum are the only phases present. As the amount of deoxidizer increases, wüstite plus hercynite, hercynite, hercynite plus corundum, or corundum alone appear as inclusions, in that sequence. Because the lowest solidus temperature is ~1350°C, the inclusions are not likely to undergo drastic changes during rolling of the steel.

**Si**: Examination of the products resulting from deoxidation with silicon has confirmed the occurrence of one or more of the three crystalline phases (counting all modifications of SiO₂ as one phase) present in the system iron oxide-SiO₂ in contact with metallic iron (Fig. 45a). These phases are, in order of increasing silicon content of the steel: wüstite, fayalite, and silica. Solidus temperatures are approximately 1180°C for most mixtures within this system. Hence partial or complete melting, with accompanying change in appearance of the inclusions, may be expected to take place during rolling of the steel.

**Ti**: Phase relations among oxides formed when Ti is used as a deoxidizer in steel are very complicated, because both titanium and iron occur in various oxidation states.

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**Fig. 144.** Sketch showing probable extensions of composition joins to the titanium oxide side of the FeO-TiO₂ join in the system Fe-Ti-O, as discussed in the text.
in the crystalline oxide phases. Phase equilibria in the system iron oxide-TiO₂ in contact with metallic iron are useful as a first guide for judging the phases likely to be present (Fig. 55a). They are, in order of increasing titanium oxide content (increasing amount of Ti used as deoxidizer): wüstite ("FeO"), ulvospinel (2FeO·TiO₂), ilmenite (FeO·TiO₂), pseudobrookite (FeO·2TiO₂), and rutile (TiO₂). In addition to these phases, Ti₃O₅ (anasovite), Ti₂O₃ and, rarely, TiO have been reported to be present in inclusions separated from steels deoxidized with Ti. The probable relations between these latter phases and those appearing in the system iron oxide-TiO₂ in contact with metallic iron (Fig. 55a) are illustrated in the sketch of Fig. 144. The sesquioxide (ilmenite) and pseudobrookite solid solution series presumably extend beyond the composition points FeO·2TiO₂ and FeO·TiO₂ toward Ti₃O₅ and Ti₂O₃, respectively. Members of the solid solution series FeO·2TiO₂-Ti₃O₅ and FeO·TiO₂-Ti₂O₃ probably appear as inclusion phases in contact with Fe-Ti alloys of varying compositions in the vicinity of the Fe apex of the diagram.

Zr: No intermediate compounds are formed between FeO and ZrO₂, and a mixture of the two phases wüstite and zirconia will result as Zr is used as a deoxidizer in plain carbon steels (Fig. 72).

Cr: Several investigations have been made of phases appearing when Cr, Fe, and O react to form oxide inclusions in steel. Unfortunately, the observations made by the various investigators are conflicting in many important aspects. A thorough test of the inferences made is difficult because equilibrium data for the system Fe-Cr-O are scarce. All observers of Fe-Cr-O inclusions seem to agree that wüstite, iron chromite, and Cr₂O₃ appear as phases, either singly or in pairs. In addition, a tetragonal phase with composition intermediate between FeO-Cr₂O₃ and Cr₂O₄, as well as the end member compound Cr₃O₄, have been reported. It is not known with certainty whether the latter two phases are truly stable. Recent work on the 1300°C isothermal section through the system Fe-Cr-O has shown that only wüstite, iron chromite with spinel type structure, and Cr₂O₃ have stable existence in equilibrium with a metal phase of almost pure Fe at this temperature. The relations are illustrated in the diagram of Fig. 58.

B: Deoxidation equilibria involving boron are very poorly known. Data are lacking on thermodynamic properties of Fe-B alloys as well as on B₂O₃-containing oxide systems, notably iron oxide-B₂O₃ and iron oxide-B₂O₃-SiO₂. Attempts to calculate and to determine experimentally the deoxidation constants of boron have been made by Gurry and by Derge respectively. The data obtained by the two investigators are in poor mutual agreement.

3. EQUILIBRIA WHEN TWO DEOXIDIZING ELEMENTS ARE USED

Mn-Si: Deoxidation products resulting when Mn-Si alloys are used as deoxidizing agents are well represented in terms of the ternary system FeO-MnO-SiO₂. The diagram shown in Fig. 103 is a projection of the liquidus surface of this system and thus illustrates the highest temperature of existence of a crystalline phase, as a function of composition of the mixture. Perhaps a more significant piece of information for evaluating inclusion behavior is the lowest temperature of existence of a liquid phase, the solidus temperature, as a function of composition of the mixture. This relation is illustrated by the projection of the solidus surface shown in Fig. 145. The diagram is typical for a system in which no ternary compounds are formed and in which extensive solid solubility exists between the binary end members of the various stable structures. Only for a very limited part of the system, the composition triangle a-b-SiO₂, is the
Fig. 145. Projection of the solidus surface for the system iron oxide-manganese oxide-SiO$_2$ in an atmosphere consisting of CO$_2$ and H$_2$ in ratio 1:1. The diagram was constructed on the basis of Fig. 103.

solidus temperature constant (1185°C). This is the triangle formed by the points representing compositions of the three crystalline phases (olivine solid solution, pyroxenoid solid solution, tridymite) which coexist in equilibrium with liquid at the only ternary invariant situation present in the system. The rest of the diagram is made up of composition areas within which solidus temperatures vary continuously with varying Mn/Fe ratios of the crystalline phases coexisting within each of these areas. As is evidenced by the diagram of Fig. 145, solidus temperatures are within such a range that some liquid may be expected to form during heating and rolling of steel containing as inclusions phases within the system FeO-MnO-SiO$_2$.

**Al-Si:** The use of Al-Si alloys as deoxidizing agents gives oxide phases whose compositions may be adequately represented by the system iron oxide-Al$_2$O$_3$-SiO$_2$ in contact with metallic iron. A projection of the solidus surface for this system is shown in Fig. 146, constructed from the diagram in Fig. 98 by methods explained in a previous section. This solidus surface is typical of those obtaining when a ternary phase is formed and there is little mutual solubility among the crystalline phases. It is seen that the triangle is divided into a number of smaller triangles within each of which all mixtures have the same solidus temperature. Between these composition triangles are small areas in which solidus temperatures vary with varying compositions of one or both crystalline phase(s) coexisting in equilibrium within each of these areas. In general, solidus temperatures are seen to be low (1083–1210°C) for all mixtures within this system, except those of composition in the proximity of the Al$_2$O$_3$ apex of the diagram. Hence inclusions of compositions within this system are likely to be at least partly melted during rolling of steel.
Fig. 146. Projection of the solidus surface of the system iron oxide-Al₂O₃-SiO₂ in contact with metallic iron, constructed from the diagram shown in Fig. 98.

4. EQUILIBRIA IN MULTICOMPONENT INCLUSION SYSTEMS

a. General considerations. Quite often, the number of components present in oxide inclusions is so high that an evaluation of phase relations on the basis of relatively simple phase diagrams is impossible. The complexity of the inclusions may be caused primarily by the complexity of the deoxidizer used, or the complexity of the steel serving as "host" for the inclusions, or both. Obviously, in alloy steels the number of combination possibilities among all elements coming from both sources above is very high. A systematic treatment of all these possible combinations is not possible at present because of lack of pertinent data, and would not be practical even if such data were available. Instead, a few examples will be presented to show some of the complexities involved and general considerations used in applying phase equilibrium data to such problems.

b. Deoxidation with Ca alloys. Calcium has a unique position among deoxidizing elements. Its vapor pressure is so high at steelmaking temperatures that a large proportion of the element is lost to the gas phase. The amount of this loss depends on the deoxidizing alloy used and the method by which the deoxidation is carried out. Sims and Briggs (342) believe that Ca takes no appreciable part in deoxidation processes, whereas Plöckinger and Rank (343) as well as Koch (344) ascribe a considerable deoxidizing role to Ca. The latter authors point out that whereas the inclusions usually are low in CaO, the oxide phases rising to the top of the metal bath as a slag contain appreciable amounts of CaO. Typical compositions of oxide inclusions and slags formed
for selected Ca-containing deoxidizers are indicated by the data of Table 9–1. The first three examples given in the table comprise heats in which CaSi alloys containing 1–2% Al and ~5–15% Fe are used as deoxidizers. In this case the oxide inclusions are well represented by composition points within the system CaO–FeO–Al₂O₃–SiO₂ (see Figs. 121, 122). The fourth example listed in Table 9–1 pertains to a heat in which a CaTiSi alloy containing 2% Al and ~17% Fe is used as deoxidizer. Compositions of oxide inclusions formed in this case may be represented as a first approximation by points within the system Al₂O₃–SiO₂–TiO₂ (see Fig. 85). A more precise estimate of the solidus and liquidus temperatures may be obtained by judging the effect of ~1% FeO and ~3% CaO on the diagram in Fig. 85.

### Deoxidation with Mn-Al-Si alloys

Koeh, Wentrup, and Reif have investigated oxide inclusions when Mn-Al-Si alloys were used as deoxidizers. Compositions could be satisfactorily represented as a first approximation in terms of the quaternary system FeO–MnO–Al₂O₃–SiO₂. When the Mn content of the deoxidizer was low, the FeO content of the inclusions was frequently sufficiently low that the phases appearing could be predicted on the basis of equilibria in the ternary system MnO–Al₂O₃–SiO₂ (see Fig. 109). In addition to the above components, the inclusions were sometimes found to contain appreciable amounts of Cr₂O₃ (up to 20%) even though the Cr content of the metal phase did not exceed 0.05%.

### Deoxidation with Fe-Si and Al in Mn-Cr steels

Oxide inclusions formed in manganese-chromium steels have been studied in considerable detail by Plöckinger. The constitution and behavior of the oxide inclusions and slags may be predicted as a first approximation from phase relations existing in the system Al₂O₃–Cr₂O₃–SiO₂ (Fig. 82), and from inferences regarding the effects of small additions of FeO (and MnO or V₂O₃) upon these equilibria.
A. Introduction

The area of iron- and steelmaking in which phase equilibrium data on oxide systems find their most important and extensive use is that of refractory linings of furnaces and of auxiliary equipment.

The oxide phases commonly making up these refractory bodies undergo compositional and structural changes during use, or they react with each other and with materials added to the refractory body during use. The complex reactions which take place in such multicomponent and multiphase bodies are best described and explained in terms of the vast amount of equilibrium data which are contained in phase diagrams for common oxide systems.

The phase equilibrium data presented in preceding sections of this book have usually been represented in terms of projections of the liquidus surface. This surface always constitutes a good starting point for applying phase equilibrium data to various technological problems. In the case of refractory technology, one is usually more interested in solidus than in liquidus temperatures, however. The former can usually be derived, at least approximately, from the liquidus surface, provided an estimate can be made of interrelations of compositions of liquid and crystalline phases coexisting in equilibrium. Methods for constructing solidus surface diagrams from the liquidus surface have been described in Chapters 4 and 5. In the discussion of equilibria among oxide phases present in steelplant refractories, which follows below, the relations are discussed sometimes with reference to the liquidus surface diagram, sometimes with reference to a solidus surface diagram, and sometimes with reference to an isothermal section. As a general rule it may be assumed that the liquidus surface will serve as an adequate reference for the discussion. Only when points of particular importance or complexity are to be emphasized is resort made to a solidus surface or an isothermal section drawn with a specific purpose in mind.

Enormous quantities of refractories are consumed by the steel industry. Only oxides which are abundantly present in the earth's crust and hence are available at a reasonable cost may be considered as potential raw materials for refractories in steelmaking. The oxides which singly or in combination are of greatest importance as refractory materials are, in order of decreasing availability, SiO₂, Al₂O₃, iron oxide, CaO, MgO, Cr₂O₃, TiO₂. The phase relations existing in the enormously complex system formed by these oxide components provide a key to an understanding of the chemistry of steelplant refractories.

*As noted in the Preface, major parts of this chapter have been reproduced in essentially the same form as they appeared in Chapter 18 of Electric Furnace Steelmaking, (347) by kind permission of the AIME and Interscience Publishers.
In order to systematize the discussion of phase equilibrium data in the following, the refractories will be classified into four main groups: silica, alumina-silica, chrome, and magnesia. Within the last group are included magnesite (magnesia), forsterite, and dolomite.

**B. Silica Brick**

1. **GENERAL CONSIDERATIONS**

Silica brick used in steelmaking furnaces almost invariably contain several percent of oxides other than their main constituent, SiO₂. Some of these “foreign” oxides come from impurities present in the raw materials used. Alumina and alkalies are the most important among these impurities, but iron oxide and titania are also common. Other “foreign” oxides are intentionally added during manufacture of the brick. The most common among these additives is lime (about 2–4%), but iron oxide and titania may also be used. Finally, the refractory bodies are being contaminated during use. A large number of oxide constituents may be added to the refractory in this way. Particularly important are iron oxides transported through the atmosphere, and iron oxides and lime added by the splashing of slags.

The properties of silica brick as manufactured and in service will be briefly evaluated in the following by a consideration of phase relations prevailing in SiO₂ itself and in systems obtained by combining SiO₂ with one or more other oxide components.

A diagram showing simplified versions of stability relations among the various SiO₂ modifications was presented in Fig. 9. Although many of the complexities of the phase relations are left out, the diagram suggests that control of the appearance of the various crystalline modifications may be of paramount importance in developing a sound silica brick. This is suggested even more strongly by the curves shown in Fig. 147, illustrating specific volumes of the various SiO₂ modifications as a function of temperature.\(^{(62)}\)

![Graph showing specific volumes of various modifications of SiO₂ as a function of temperature](image)

*Fig. 147.* Curves showing specific volumes of various modifications of SiO₂ as a function of temperature, after Sosman.\(^{(62)}\)
Diagrams showing the effects of one oxide component on the refractoriness of a body composed predominantly of SiO$_2$ were presented in Figs. 18 through 24. These diagrams can be used to judge the upper temperature limit of use of silica bodies if liquid development is the main cause of failure. Clearly, alumina and alkalies are particularly harmful (Figs. 19 through 21). Liquidus and solidus temperatures are drastically lowered by relatively small additions of these components. On the other hand, the oxides of the divalent cations, CaO, MgO, FeO, and MnO have only a small tendency to promote liquid formation when added to silica (Figs. 18, 22, 45a, 53a). The most significant feature of the diagrams for these systems is the area of two immiscible liquids adjacent to the SiO$_2$ end, with the associated extension of high liquidus temperatures out to 30 or more percent of the divalent oxide. As a consequence of this feature, the amount of liquid present in a mixture of composition close to SiO$_2$ remains small in amount even at 1700°C. Addition of a few percent of these divalent oxides to SiO$_2$ does not therefore cause a large decrease in the refractoriness of a silica body, in marked contrast to the effect of alumina and alkalies. Similar liquid miscibility gaps are present in the systems iron oxide-SiO$_2$ in air (Fig. 45b) and 3CaO·P$_2$O$_5$·SiO$_2$ (Fig. 136). Liquid miscibility gaps also exist in the systems Cr$_2$O$_3$·SiO$_2$ and TiO$_2$·SiO$_2$ (Figs. 23 and 24, respectively). The latter two systems are distinguished from the former, however, by the appearance of the two-liquid region on the low-SiO$_2$ side of the eutectic instead of on the high-SiO$_2$ side.

2. SILICA BRICK AS MANUFACTURED

a. Raw materials and their conversion. The usual starting materials for silica refractories are quartz, either as very fine-grained chaledony or as the more coarsely crystalline quartz in sandstones and in quartzites, plus a few percent of lime. A “green” silica brick, composed of quartz, lime, and a temporary organic binder, is fired by raising the temperature very slowly to about 1450°C, holding at this temperature for a few hours, and then cooling very slowly. The brick must be fired below the maximum temperature of stability of tridymite (1470°C), but at a temperature as close to this as feasible in order to obtain a high rate of conversion of the silica grains to tridymite.

It seems necessary to convert most of the SiO$_2$ to tridymite in order to obtain high strength, and in addition it is desirable because of the smaller volume change accompanying the tridymite crystallographic inversions, as compared with cristobalite (Fig. 147), with a consequent lesser tendency toward cracking of a brick on rapid heating or cooling. The quartz starting material first inverts to high quartz, and then to cristobalite, with expansion of the grains as indicated in Fig. 147. At this stage the grain shapes have changed but little, and on cooling the brick has low strength. Even if the brick is heated to a sufficiently high temperature to develop appreciable liquid but the SiO$_2$ is still cristobalite, e.g., to 1500°C, the calcium silicate bond present on cooling does not suffice to prevent the brick from being punky and weak. It apparently is on conversion of the cristobalite to tridymite that high strength develops, as tridymite crystals grow across grain boundaries. A liquid phase in which SiO$_2$ as cristobalite can dissolve and crystallize out as tridymite is undoubtedly necessary for the rapid formation of tridymite as required in production. Because of this, one may judge on comparing Figs. 18 and 22 why CaO is used in silica brick manufacture rather than MgO, and why iron oxide is sometimes added as well. The CaSiO$_3$·SiO$_2$ eutectic is below 1470°C, whereas the MgSiO$_3$·SiO$_2$ eutectic is above this temperature. Adding iron oxide will increase the amount of liquid present below 1470° in lime-silica mixtures. A silica brick with MgO addition is more refractory than one with CaO addition because of the greater extent of the two-liquid region, and furthermore, MgO is preferable to CaO in the brick in resisting fluxing by iron oxide in use. However, MgO additions are not
preferred because of the low rate of tridymite formation and consequent low strength with ordinary production schedules.

One may take CaO along with SiO₂ as two constituents of a silica brick and judge the effect of certain other substances by examining ternary systems. The effects of adding Al₂O₃, TiO₂ or Cr₂O₃ will be briefly discussed.

b. Effect of Al₂O₃ on refractoriness of silica brick. Phase relations in the system CaO-Al₂O₃-SiO₂ (see Fig. 80) have been the basis for developing the present improved brick known as “superduty.” Application of this diagram to silica-brick chemistry was discussed first by Greig and in more detail later by Harvey and Birch and by Kraner. The predictions derived from Greig's diagram have been borne out by plant experience. Unlike most refractories, silica brick is used in certain important applications right up to the point of failure by melting. Therefore a constituent which causes a lowering of the temperature at which the brick erodes rapidly by melting will in these applications cause a corresponding lowering of the maximum temperature of usefulness of the brick. The cristobalite liquidus region of the diagram in Fig. 80 is the key to an understanding of the combined effect of lime and alumina on a silica brick. The two-liquid region present in the system CaO-SiO₂ diminishes rapidly as Al₂O₃ is added, and appears only as a small area adjacent to the CaO-SiO₂ join in Fig. 80. Isotherms on the cristobalite liquidus surface in the vicinity of the two-liquid area have approximately the same course as the outline of the two-liquid area. The effect of this situation on the amounts of liquid which form under equilibrium conditions in SiO₂ bodies containing small amounts of CaO and Al₂O₃ is illustrated in Fig. 148, showing curves of constant amounts of liquid as a function of composition at 1660°C. It is

![Diagram showing lines of equal percentage of liquid phase present under equilibrium conditions at 1660°C for mixtures adjacent to the SiO₂ apex of the system CaO-Al₂O₃-SiO₂. Diagram constructed from Fig. 80.](image-url)
clearly seen that a decrease in alumina content from 0.7 to 0.3%, for instance, makes a significant difference in percent of liquid present when the silica refractories are being used at this temperature (1660°C). It is also seen that when alumina is present in the brick (for instance ~0.5%), addition of 2 or 3% of lime actually increases refractoriness of the brick slightly.

**c. Effect of TiO₂ on refractoriness of silica brick.** The effect of titania as a constituent of silica brick containing lime can be judged from Figs. 24 and 82, and more explicitly from Fig. 149. The latter figure shows an enlarged picture of the 1660°C isothermal section through the SiO₂-rich part of the system CaO-TiO₂-SiO₂. Titania added to pure silica lowers the refractoriness of the latter drastically. This was mentioned earlier (page 40) with reference to Fig. 24, and also appears from the isothermal section in Fig. 149, showing that a mixture of 99% SiO₂ and 1% TiO₂ (point x) will be ~25% liquid (ratio x-SiO₂/x'-SiO₂ · 100%) at 1660°C. With 2% lime present in addition to 1% TiO₂ (point y), the situation is more favorable, however, because of the extension of the two-liquid region as CaO is added to SiO₂-TiO₂ mixtures. Under these conditions only ~8% liquid (ratio y-SiO₂/y'-SiO₂) is present in the refractory body at 1660°C. If superior physical properties, for instance lower porosity, can be obtained for a silica brick by the presence of a small amount of TiO₂, then as long as an appropriate amount of lime (or iron oxide or magnesia) is also present, the small decrease in refractoriness may be acceptable.

**d. Effect of Cr₂O₃ on refractoriness of silica brick.** Chromium oxide is becoming increasingly important as a constituent of steelplant refractories. Although silica refractories at present do not usually contain chromium oxide, they may in the future.
Moreover, silica brick is commonly placed against refractories containing large amounts of chromium oxide. Hence reactions of silica brick and chromium oxide at high temperatures need to be understood. The nature of these reactions can be judged by an examination of the phase diagram for the system CaO-Cr₂O₃-SiO₂ (Fig. 106). An enlarged and somewhat distorted picture of the area adjacent to the SiO₂ apex is shown in Fig. 150. It will be noticed that the field of cristobalite is compressed into a narrow band along the CaO-SiO₂ side line, and that the isothermal boundary curve along which cristobalite, chromium oxide, and two liquids are in equilibrium (1705°C) is virtually at the same temperature as the cristobalite two-liquid isotherm in the binary system CaO-SiO₂ (1707°C). Take as an example a mixture x consisting of 97% SiO₂, 2% CaO, and 1% Cr₂O₃. At temperatures below 1705°C the compositions of liquids developed in this mixture are represented by points along the cristobalite-Cr₂O₃ boundary curve a-b. The liquidus isotherms in the cristobalite primary phase area between this boundary curve and the CaO-SiO₂ side of the triangle extend into the triangle in a direction such that the distance from the SiO₂ apex to points along an isotherm remain about constant. Hence the amount of liquid formed in a high-silica mixture at a chosen temperature below 1705°C is practically the same whether Cr₂O₃ is present or not. Similarly, the temperature of essentially complete melting of the refractory is that of the invariant situation where cristobalite and Cr₂O₃ coexist in equilibrium with two liquids (1705°C). Since this temperature is practically the same as that of the appearance of the two-liquid region in the system CaO-SiO₂, Cr₂O₃ may be added to a superduty silica brick without significantly increasing or decreasing its resistance to melting. Therefore if a gain is possible for other reasons by additions of Cr₂O₃, this may be done without sacrificing refractoriness.
If Cr₂O₃ is added to a silica brick, tridymite does not form as readily, with a resultant decrease in strength. Low strength is particularly noteworthy in a chrome-silica brick composition developed for basic open-hearth roof use. This brick contains several percent each of Cr₂O₃ and MgO. In the system MgO-Cr₂O₃-SiO₂ (Fig. 83), the compound MgO-Cr₂O₃ coexists in equilibrium with cristobalite, Cr₂O₃, and liquid at 1710°C. A high-silica mixture in this system does not therefore develop any liquid until this temperature is reached if the ratio of Cr₂O₃ to MgO is equal to or greater than that in the compound MgO-Cr₂O₃. Although somewhat more refractory than the ordinary superduty silica brick, the principal advantage is not in this characteristic but in the greater resistance to iron-oxide fluxing at steelmaking temperatures.

3. SILICA BRICK IN SERVICE

In the preceding discussion emphasis was placed on reactions which occur in heating silica brick, as manufactured, to high temperatures. In the principal uses of these brick, paramount importance attaches to their resistance to melting. The initial brick must therefore be as refractory as possible. In addition, the brick must be able to resist the fluxing action of other oxides which come in contact with the hot face of the brick during use.

a. Reactions with iron oxides. In many high-temperature applications of silica brick, iron oxide is the chief fluxing material. As iron oxide penetrates the hot face of the brick, lime and alumina in the brick tend to migrate back from the hot face, leaving a surface composed almost entirely of iron oxide and silica. The phases which form in this hot face can be estimated from the system FeO-Fe₂O₃-SiO₂ (Figs. 38, 39, 41), and the fluxing action of iron oxide as a function of temperature and oxygen pressure of the gas phase can be evaluated on this basis. The most important features of the phase relations, for our present discussion, are the sweep of the two-liquid region across the diagram and the position of the oxygen isobars relative to this miscibility gap. Four levels of oxygen pressures will be used as examples, air (0.21 atm), 10⁻², 10⁻⁵, and 10⁻⁹ atm. As a help in visualizing the relations, Fig. 151 shows isobaric sections through the ternary system at these four oxygen pressures. At each pressure the lowest temperature of liquid formation (solidus temperature) is that of intersection between the appropriate oxygen isobar and the boundary curve along which SiO₂ is one of the crystalline phases present. It is seen (Fig. 151) that this temperature decreases from 1455°C at the highest oxygen pressure (air = 0.21 atm) to a minimum of 1140°C when the oxygen pressure is 10⁻⁹ atm. At any of the chosen levels of oxygen pressure, an increase in temperature above the solidus causes only a small increase in the amount of liquid, so long as the temperature is below that of two-liquid formation. This situation is brought about by the very steep slope of the SiO₂ liquidus surface. An important characteristic of the diagrams is the successive shift of the SiO₂ liquidus curve toward higher SiO₂ contents as the oxygen pressure is decreased. For instance, in air the SiO₂ content of the liquid in equilibrium with silica at 1500°C is ~20%, whereas at 10⁻⁹ atm and the same temperature it is ~43%. Hence the fluxing of silica brick by iron oxide is much more severe at low than at high oxygen pressures.

The maximum temperature to which a silica brick in contact with iron oxide can be used without complete failure of the body is that of the liquidus within the two-liquid region. This temperature is seen to increase as the oxygen pressure decreases, from 1665°C in air to 1700°C at pO₂ = 10⁻⁹ atm. Hence an open-hearth furnace with a silica roof can be operated for shorter times at higher temperatures when strongly reducing conditions are maintained under the roof than under more oxidizing conditions.
Fig. 151. Isobaric sections through the system FeO-Fe₂O₃-SiO₂ presented to show effect of oxygen pressure on refractoriness of silica brick in contact with iron oxides. Diagram constructed on the basis of Figs. 38 and 41. Arrows show directions of change of boundary curves with decreasing oxygen pressures.

The effect of Cr₂O₃ additions to silica brick in increasing the resistance to iron-oxide fluxing may be estimated from Fig. 101. It will be noted that the crystalline phase in equilibrium with cristobalite and liquid is an iron-chromium spinel solid solution rather than magnetite. As indicated by the conjugation lines, the composition of this spinel in equilibrium with cristobalite is about 19% Cr₂O₃ at 1600°C and 31% Cr₂O₃ at 1700°C. As iron oxide is added to a silica-chrome body, part of it is thus absorbed by the chromium oxide as this spinel phase forms. From the geometrical relations drawn in Fig. 101 it can be readily seen that Cr₂O₃ additions greatly increase the resistance of a silica body to fluxing by iron oxide. The following table, derived from the relations shown in Fig. 101, shows the approximate amounts of liquid present in a silica body containing 0, 5, and 10% Cr₂O₃, as iron oxide is added in amounts of 10, 20, and 30%. The profound effect of Cr₂O₃ on liquid development in silica-iron oxide mixtures is evident.

<table>
<thead>
<tr>
<th>% Iron Oxide</th>
<th>% Liquid at 1650°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0% Cr₂O₃</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>30</td>
<td>45</td>
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b. Fluxing by other oxides. Just as silica brick has good resistance to the fluxing action of iron oxide, so it has a similarly good resistance to fluxing by other oxides which have similar liquid immiscibility relations with silica, for instance CaO, MgO,
and MnO. As discussed earlier, chromium oxide has practically no effect on liquid formation in silica brick (see Fig. 23). “Neutral” refractories such as chrome-magnesite brick may be placed in juxtaposition to silica brick with little expectation of fluxing difficulties, especially if the alumina content of the materials is low.

Alumina and alkalies, unlike the oxides just discussed, have a strong fluxing action on silica brick, as can be deduced from the diagrams of Figs. 19 through 21.

C. Alumina-Silica Refractories

1. GENERAL CONSIDERATIONS

The term alumina-silica refractories will be used as designation for a group of refractories whose compositions can be expressed as a first approximation by the binary system Al₂O₃-SiO₂.

The constitution of these refractories can be judged as a function of chemical composition and temperature from the diagram shown in Fig. 19. On being fired the refractory is composed of mullite and silica if the Al₂O₃ content is less than 72% Al₂O₃, and of mullite and corundum if the percentage of Al₂O₃ is higher. In the former, liquid will develop on heating to the temperature of the cristobalite-mullite eutectic (~1590°C), while in the mullite-corundum bodies liquid appears only at temperatures above that of the mullite-corundum eutectic (~1840°C).

2. FLUXING BY VARIOUS OXIDES

a. Alkali oxides. Where high refractoriness is a requirement of the body, high-purity materials must be used, especially with regard to alkali content. The lowered refractoriness caused by the presence of potash in alumina-silica mixtures is graphically illustrated by the phase diagram for the system K₂O-Al₂O₃-SiO₂, shown in Fig. 75. The ternary eutectic labelled A has a temperature of only 985°C. Liquid will develop at this low temperature in all bodies having compositions within the composition triangle 3Al₂O₃·2SiO₂-K₂O-Al₂O₃·6SiO₂·5SiO₂. Not only is the temperature of liquid formation low, but the liquid at point A contains relatively little K₂O (~10%). Hence small amounts of K₂O added to mullite-silica bodies cause large amounts of liquid to form. Clearly, potash, a common constituent of clays, must be kept at a minimum for good refractoriness.

b. Iron oxide. Iron oxide is another substance present in small amounts in clays used for refractories. The effect on refractoriness is not nearly so great as that of potash and the other alkalies, but nevertheless it is serious. In order to evaluate reactions in bodies composed of Al₂O₃, SiO₂, and iron oxide, the oxygen pressure of the atmosphere surrounding the refractory must be taken into account. Two levels of oxygen pressures, those in contact with metallic iron and that of air, will be used as examples to demonstrate the relations involved. As a visual aid in this discussion, the solidus surfaces for the system iron oxide-Al₂O₃-SiO₂ in contact with metallic iron and in air are shown in Fig. 152(a) and (b) respectively. Under strongly reducing conditions, (a), a liquid will develop at as low a temperature as 1210°C when a fireclay brick consisting initially of mullite and tridymite (or cristobalite) absorbs a small amount of iron oxide. If, however, the brick is higher in Al₂O₃ and originally consists of mullite and corundum, a liquid will not form until a temperature of 1380°C is reached, even after a considerable amount of iron oxide has been absorbed by the brick. In air, (b), the lowest temperatures of liquid formation for brick of the same compositions as above are considerably higher. Upon the addition of iron oxide a fireclay brick develops a liquid phase only after a temperature of 1380°C or higher is reached, while a high-alumina brick with
absorbed iron oxide withstands temperatures at least as high as 1460°C before a liquid starts forming.

An important difference between the two diagrams (a) and (b) in Fig. 152 is related to the manner in which iron ions can be accommodated in the structures of the crystalline phases present. Two of the crystalline phases present in alumina-silica refractories, mullite and corundum, can accommodate iron ions in their lattices, but only in the ferric state (Fe³⁺). Under strongly reducing conditions, where the iron in the oxide phases is present almost exclusively as Fe²⁺, a substitution of this element in the crystalline phases cannot take place. Hence even small amounts of iron oxide absorbed cause a liquid to develop at temperatures above 1210 or 1380°C, depending on the Al₂O₃/SiO₂ ratio of the original brick, (a). In air, on the other hand, a substantial proportion of the iron is present as Fe³⁺. Hence moderate amounts of iron oxides can be absorbed by an alumina-silica refractory in air without formation of a liquid phase even at temperatures above those of the three-phase triangles labeled 1380 and 1460°C in (b). Composition triangles in which liquid is one of the phases present therefore extend all the way over to the Al₂O₃-SiO₂ side in diagram (a), whereas the analogous areas in diagram (b) terminate before reaching the Al₂O₃-SiO₂ side.

Iron oxide may also act as a catalyst causing the deposition of carbon from carbon monoxide atmospheres, with consequent disintegration of the refractory. High-temperature firing to bring all or most of the iron oxide into a liquid phase is a means of minimizing this difficulty. Temperatures required for this “hard firing” are of the order of 200°C less in atmospheres of very low oxygen pressure than in air, as can be seen by a comparison of diagrams (a) and (b) in Fig. 152.

**c. Reactions with other types of brick.** Because of the relatively low temperature of the cristobalite-mullite eutectic in the Al₂O₃ system (see Fig. 19), the two types of materials, silica and high-alumina refractories, are incompatible if resistance to high temperatures is required.
Fig. 153. The 1500°C isothermal section for a part of the system MgO-Al₂O₃-SiO₂, presented for the purpose of showing the effect of MgO on liquid formation in Al₂O₃-SiO₂ brick. Diagram constructed on the basis of Fig. 81.

In some applications it may happen that alumina-silica materials come in contact with “basic” brick. Even though magnesia by itself is very refractory, it has a serious fluxing effect on alumina-silica bodies, as is illustrated by phase relations in the system MgO-Al₂O₃-SiO₂ (Fig. 81). Not only are liquidus temperatures in the region of cordierite low (down to 1355°C), but also the percentage of magnesia in the liquid phase is relatively low. Hence a small amount of added magnesia causes a large amount of liquid to form. An example of a quantitative evaluation is illustrated in Fig. 153, where it is assumed that 3% MgO is added to a “superduty” fireclay brick A of composition 42% Al₂O₃, 58% SiO₂ at 1500°C. It is seen that this mixture will be ~60% liquid ($A'\cdot3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2/a\cdot3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2\cdot100\%$) at this temperature.

Unlike magnesia, chromium oxide has in general a “neutral” effect on liquid formation, just as it had on silica brick. It will be noted from Fig. 84 that only a very slight lowering of liquidus temperatures occurs on addition of Cr₂O₃ to high-silica mixtures, and that liquidus temperatures even increase for high-alumina mixtures.

**d. Reactions with slags.** Resistance of alumina-silica refractories to the attack of steelplant slags is in general poor. In terms of phase equilibrium diagrams, this is true because relatively low liquidus and solidus temperatures prevail close to the Al₂O₃-SiO₂ join in such systems as CaO-Al₂O₃-SiO₂ (Fig. 80), MgO-Al₂O₃-SiO₂ (Fig. 81), FeO-Al₂O₃-SiO₂ (Figs. 98 and 152), iron oxide-Al₂O₃-SiO₂ in air (Figs. 99 and 152), and MnO-Al₂O₃-SiO₂ (Fig. 109). Small amounts of each of the slag-forming oxides CaO, MgO, FeO, Fe₂O₃, and MnO cause relatively large amounts of liquid to form in contact with alumina-silica mixtures.
3. REACTIONS WITH FERRO-MANGANESE ALLOYS

Alumina-silica refractories may also be severely damaged by reaction with a metal phase. A good example of this is the reaction between ferro-manganese metal and an alumina-silica body.\(^{351}\) Data are available in the literature to estimate the extent of such reactions, even though the investigations were not originally aimed at predicting or explaining refractory behavior. Körber and Oelsen\(^{352}\) studied the reaction between Fe-Mn alloys of various compositions and silica of a simple slag phase. Their experiments were carried out in silica crucibles, hence the slags were saturated with silica. The results, therefore, apply equally well to the reaction between a metal phase of the same compositions as above and a refractory in which SiO\(_2\) is one of the crystalline phases present. The most significant data obtained by Körber and Oelsen are summarized in Fig. 154, showing equilibrium Si content of the metal phase as a function of the Fe/Mn ratio of the metal. It is seen that a very appreciable amount of Si is extracted from SiO\(_2\) by its reaction with the metal phase, the amount increasing rapidly with increasing Mn content of the metal, up to a limiting amount of about 18% Si when no Fe is present. The amount of Si going into the metal phase decreases with increasing C content,\(^{353}\) as illustrated in Fig. 155.

A refractory-metal reaction of this nature is conveniently described in terms of phase equilibria in the system MnO-Al\(_2\)O\(_3\)-SiO\(_2\) (Fig. 109). As a basis for discussion, consider an alumina-silica brick of original composition 55% SiO\(_2\), 45% Al\(_2\)O\(_3\) reacting with ferromanganese metal, at a constant temperature of 1500°C.* The course of reaction is followed most easily on the 1500°C isothermal section through the MnO-Al\(_2\)O\(_3\)-SiO\(_2\) system, as illustrated in Fig. 156(a). Point A in this diagram represents the starting composition of the brick, and the phases present are mullite and tridymite (compare Fig. 19). As MnO forms by reaction of SiO\(_2\) with Mn according to the equation

\[2\text{Mn} + \text{SiO}_2 = 2\text{MnO} + \text{Si},\]

the brick composition changes along the straight line A-B in Fig. 156(a). The phase changes occurring during this process can be read directly off the diagram by following the A-B line as it traverses the various triangles representing phase assemblages as designated in the figure. As the reaction starts, compositions of the oxide phase changes from the Al\(_2\)O\(_3\)-SiO\(_2\) join into the triangle tridymite + mullite + liquid. The amount of liquid increases as more MnO is absorbed, but the composition of the liquid stays constant at a as long as the mixture remains within this same composition triangle. Because this liquid contains a high percentage of silica, its viscosity is relatively high, and its presence may not severely damage the brick. As the point representing total composition of the brick moves into the triangle mullite + liquid, and successively through the mullite + corundum + liquid to the corundum + liquid composition triangles, the SiO\(_2\) content of the liquid decreases rapidly, and at the same time the relative amount of liquid increases. The system will reach a state of equilibrium when the SiO\(_2\) potential of the slag formed balances the Si potential of the metal phase. The mixture at 1500°C will then consist of corundum and liquid. Long before this final equilibrium state has been reached, however, the brick has been severely or completely damaged by the melting resulting from metal-refractory reaction.

The phases actually found in mixtures in this system after cooling to room temperature depend on the rate of cooling and the rate of crystallization of the various possible crystalline phases. Probable phase assemblages present if perfect equilibrium prevails during cooling are illustrated in Fig. 156(b), which shows an inferred isothermal

\* The reasoning involved is identical and the main features of the phase relations are very similar if somewhat different temperatures are chosen.
Fig. 154. Distribution of manganese and silicon between ferromanganese metal and an MnO-FeO-SiO₂ slag saturated with SiO₂, at 1600°C. The diagram on the left shows equilibrium amounts of silicon of the metal phase as a function of manganese content of the metal. The diagram on the right shows compositions of slags in equilibrium with the metal phase and SiO₂. Straight dashed lines between the two diagrams connect compositions of conjugate metal and slag phases (after Körber and Oelsen(352)).

Fig. 155. Influence of carbon on the distribution of manganese and silicon between ferromanganese metal and an MnO-FeO-SiO₂ slag saturated with SiO₂, at 1600°C, after Körber and Oelsen(353).
section through the system at room temperature. The expected crystalline phases present in the final products are corundum, spessartite, galaxite, and manganosite. However, because of the nonequilibrium conditions usually existing in practice, large or smaller amounts of glass may be expected to be present in the final product at the expense of one or more of the above crystalline phases.

"Post-mortem" examinations of the damaged hearths of ferromanganese blast furnaces have shown compositions of oxide phases as marked by the two circles I and II in Fig. 156. These circles are close to the line A-B, and it appears that the metal-refractory reaction described above accounts well for the actual observations made in practice.

![Diagram](image_url)

**Fig. 156.** (a) The 1500°C isothermal section through the system MnO-Al₂O₃-SiO₂. Mixtures located within the area enclosed by the heavy line a-b-c-d-e-f are all liquid at 1500°C. Light straight lines outline triangles within each of which all mixtures at 1500°C consist of the phases designated for that area in the diagram. Point A represents the approximate starting composition of clay brick, and the line A-B is the deduced path along which the total composition of the brick changes as a result of reactions discussed in the text. The circles marked I and II indicate the regions of actual compositions of brick after reaction with ferromanganese, as discussed in the text. (b) The inferred room-temperature isothermal section through the system MnO-Al₂O₃-SiO₂. Abbreviations used have the following meanings: G = galaxite, S = spessartite, T = tephroite, R = rhodonite, MC = manganese cordierite, Cor = corundum, M = mullite, Crist = cristobalite, Qtz = quartz, L = liquid.
D. Chrome Refractories

1. GENERAL CONSIDERATIONS

During the past 25 years the use of chrome ore as a refractory material for the steel industry has greatly expanded. The ore has good resistance to slag attack, and with magnesia added, the chrome-based materials have good refractoriness. Chrome ore has the added advantage of being "neutral," a property which has long been recognized. Limitations on its use are prescribed by the relatively high cost, by failure tendencies under conditions of fluctuating temperature and/or oxygen pressure, and by poor resistance to attack by iron oxide under some conditions.

The mineralogy and chemistry of chromite have been discussed for instance by Fisher, \(^{(355)}\) by Stevens, \(^{(356)}\) and by Heiligman and Mikami. \(^{(357)}\) Extensive investigations of chrome ore and of chrome-based refractories are described in a 1946 report of the British Iron and Steel Institute. \(^{(358)}\) Excellent summaries of present knowledge of certain aspects of the refractories are given by Rigby \(^{(359)}\) and by Chesters. \(^{(360)}\)

The dominant phase in chrome ore is a complex oxide solid solution with spinel-type structure. This is accompanied by a silicate gangue which usually comprises from about 4 to 10% of the ore. The spinel phase in chrome ore used for refractories may be considered as essentially a mixture of the four end members MgO-Al\(_2\)O\(_3\), MgO-Cr\(_2\)O\(_3\), FeO-Cr\(_2\)O\(_3\), and FeO-Al\(_2\)O\(_3\), and so may be conveniently plotted as shown in Fig. 157. Average analyses \(^{(361)}\) of Philippine, Transvaal (South African), and Rhodesian

![Diagram](image-url)

**Fig. 157.** Tetrahedron representing the system MgO-FeO-Al\(_2\)O\(_3\)-Cr\(_2\)O\(_3\), showing position of the spinel plane. Chrome ores lie essentially on this composition plane. Chrome ores recalculated to 100% of MgO, FeO, Al\(_2\)O\(_3\), and Cr\(_2\)O\(_3\) are plotted on a mole-% basis in the upper right-hand sketch, where average analyses \(^{(361)}\) are plotted of Philippine (P), Transvaal (T), and Rhodesian (R) ores.
ores are plotted on a mole percent basis on the spinel plane drawn as a reciprocal salt
net in the sketch in the upper right. It is common to refer to Philippine ore as high in
alumina and Transvaal ore as high in iron oxide. As suggested by this plot, it may
be more meaningful to refer to the former as high in MgO-Al₂O₃ and the latter as high
in FeO-Cr₂O₃, whereas the composition of Rhodesian ore as plotted is high in
MgO-Cr₂O₃ as compared with the other two. Inasmuch as refractoriness as well as
resistance to fluxing by iron oxide and calcium silicates are no doubt greatest for
MgO-Cr₂O₃, least for FeO-Al₂O₃, and intermediate for MgO-Al₂O₃ and FeO-Cr₂O₃,
the Rhodesian ore composition of Fig. 157 should be the most refractory in steelplant
use, while Philippine and Transvaal compositions are about equivalent.

Chrome ore refractoriness is not high as compared with that of other materials used
in steel furnaces. This is primarily because the gangue material ordinarily has a magnesia:silica mole ratio of less than 2:1 and contains in addition other minor constituents
which all together give a mixture having a relatively low temperature of liquid develop-
ment. For most refractory uses MgO is added to the chrome ore, giving a body with
good refractoriness while still retaining in large measure the desirable properties of
chrome ore.

2. EQUILIBRIA IN A "SIMPLIFIED CHROME ORE."
THE SYSTEM MgO-Cr₂O₃-SiO₂

Reactions with a very important bearing on performance of chromite refractories
are demonstrated by a consideration of phase equilibria in the system MgO-Cr₂O₃-
SiO₂. The liquidus surface for this system was shown in Fig. 83 and the solidus surface
is shown in Fig. 158. For purposes of illustration in using these diagrams, a simplified

![Diagram](image-url)

Fig. 158. The solidus surface for the system MgO-Cr₂O₃-SiO₂, constructed from the dia-
gram presented in Fig. 83. Abbreviations used have the following meanings:
P = periclase, PC = picrochromite, F = forsterite, PE = protoenstatite, Crist =
cristobalite. Numbers represent solidus temperatures (°C) for mixtures within a
triangle or along a join.
“chrome ore” may be considered composed of the spinel picrochromite (MgO-Cr₂O₃), admixed with a small amount of serpentine which when dehydrated lies at the composition point 3MgO-2SiO₂. The point representing the composition of this simplified ore thus lies in the compatibility triangle forsterite-picrochromite-protoenstatite. It will be noted from the diagram of Fig. 158 that on heating this mixture the first liquid will appear at 1550°C. Now if MgO is added in sufficient quantity that the total composition moves into the periclase-picrochromite-forsterite compatibility triangle, the first liquid will not appear until the temperature is 1850°C. A very great temperature advantage from the standpoint of first liquid formation is thus gained by adding a moderate amount of MgO. Inasmuch as the temperature of failure under load is no doubt correlatable to a large extent with the amount of liquid present, the temperature of this type of failure is correspondingly increased for this simplified MgO-Cr₂O₃-SiO₂ “chrome ore.”

3. EQUILIBRIA AMONG OTHER CONSTITUENTS OF CHROME REFRACTORIES

In an actual chrome ore containing iron oxide and alumina in addition to MgO, Cr₂O₃, and SiO₂, the temperatures of liquid formation are much lower than 1550°C and 1850°C for the two cases, but the principle of adding MgO to produce substantially the three-phase mixture of periclase, spinel, and forsterite is the same. The spinel phase contains iron oxide and alumina in addition to MgO and Cr₂O₃, and the periclase and forsterite contain iron oxide.

Phase diagrams involving other spinel end members are helpful in estimating courses of reactions in chromite refractories. Solidus and liquidus temperatures are very low in the system FeO-Al₂O₃-SiO₂ (down to 1083°C, Fig. 98), and only a little higher in the system iron oxide-Al₂O₃-SiO₂ in air (Fig. 99). Hence FeO, Fe₂O₃, and Al₂O₃ as oxide constituents of chromite lower refractoriness. Of the five oxide components of the chromite spinel phase, only MgO and Cr₂O₃ resist to a high degree the fluxing action of calcium silicates, as may be judged from a study of Figs. 77, 80, 95, 96, and 106. Fluxing by iron oxide is again resisted very well by MgO and Cr₂O₃, as suggested by the diagrams of Figs. 93, 94, and 101, but not by Al₂O₃ (Figs. 98 and 99). In short, although our phase equilibrium data are still rather meager, it is evident that MgO and Cr₂O₃ impart great refractoriness and resistance to fluxing by calcium silicate slag and by iron oxide. Alumina and iron oxide, on the other hand, are constituents in chrome ore which in general have the opposite effect.

4. SOLID STATE PHASE CHANGES IN CHROME REFRACTORIES

Failure of chrome refractories is not entirely brought about by liquid formation. In some services, such as roofs and walls of steel furnaces, layers of the order of an inch in thickness may spall or peel off, and in other instances disintegration occurs. The peeling off of layers is a complex and incompletely understood phenomenon. The “bursting expansion” accompanying iron oxide absorption by the spinel grains of a chrome body seems to play a role in this peeling type of failure. When iron oxide goes into solid solution in the spinel, swelling occurs as the porosity is increased. Rigby\(^{(359)}\) believes that this growth is related to different diffusion rates among the ions as they must move and adjust positions during the iron oxide absorption by the spinel. Bursting expansion may be minimized by composition adjustments in the direction of decreasing the Cr₂O₃ content and increasing the Al₂O₃ and SiO₂ contents of the body. Berry, Allen, and Snow\(^{(362)}\) believe that an important factor in the peeling of chromemagnesia brick used in open-hearth furnaces may be growth of periclase crystals as
iron oxide is absorbed. Possibly other factors play important roles in peeling, e.g., changing stresses with temperature changes, alternate melting and crystallization with temperature changes, and thermal shock.

Disintegration may occur as a result of phase changes brought about by changes in partial pressure of oxygen or in temperature. These phase changes are in response to a shift in valence of iron and hence a shift in the oxide composition of the body. Simple illustrations of this type of reaction are afforded by the examples shown in Fig. 159. While the compositions of chrome refractories in general are much more complex, the principles are demonstrated here in terms of the system Fe-Cr-Al-O. The diagrams (a) and (b) in Fig. 159 are isothermal sections at 1380°C, (a), and 1500°C, (b), at a constant oxygen partial pressure, that of air. At 1380°C, (a), only the hexagonal α-R₂O₃ structure and the monoclinic phase Fe₂O₃·Al₂O₃ are present. As temperature is increased to 1500°C, (b), a considerable area of stable existence of a phase with spinel structure has made its appearance in the diagram. This change in phase assemblage of a mixture will be accompanied by a volume change.

5. CHROME-MAGNESIA REFRACTORIES

With large additions of magnesia to chrome ore, the widely used chrome-magnesite and magnesite-chrome refractories come into being. These compositions lie in the very high-temperature part of the tetrahedron of Fig. 157 on a line extending from a point in the spinel plane, representing chrome ore, to the MgO apex. Chemically bonded, fired, and electrocast brick are all used.

These brick after firing are constituted essentially of three phases: a periclase phase containing appreciable iron oxide, a magnesia-rich chrome spinel, and forsterite (and/or
monticellite). Advantages over the straight chrome ore are much greater refractoriness and less tendency toward bursting as iron oxide is absorbed. The brick, however, will spall, peel, or disintegrate, as discussed above, where the environment is conducive to such effects.

E. Magnesia Refractories

Under the term "magnesia refractories" will be grouped the magnesite, dolomite, and forsterite types.

1. MAGNESITE REFRACTORIES

a. General considerations. The term "magnesite refractories," although somewhat a misnomer, nevertheless continues to be applied to bodies composed dominantly of magnesia, whatever the origin of the magnesia may be. Magnesite, MgCO₃, is being displaced by sea water and dolomite as the chief sources of magnesia. In a process which has proven economically feasible, calcined dolomite is caused to react with sea water, resulting in the extraction of nearly all of the magnesium from both, separating as magnesium hydroxide. Either the Mg(OH)₂ or magnesite when heated to a high temperature gives a dense, relatively unreactive, coarsely crystalline material called "dead-burned" magnesia, the magnesia used in magnesite refractories.

Equilibrium curves for the decomposition of MgCO₃ and Mg(OH)₂ were presented in Fig. 2. These curves show as a function of gas pressure the minimum temperature at which decomposition of the carbonate or hydroxide will take place upon heating. Inasmuch as both CO₂ and H₂O have significant partial pressures in air, reactions between these gas species and MgO may take place in the pressure-temperature region to the left of the curves during burning-in or shutdown of steelmaking furnaces. The reaction with CO₂ is ordinarily not a serious problem, but hydration of MgO may occur readily, and the accompanying expansion can cause cracking and disintegration of a refractory. Hydration is deterred by decreasing porosity and increasing grain size through high-temperature heating to give the "dead-burned" magnesia. Constant awareness of the fact that hydration can take place is the best assurance that it will not.

Magnesite refractories in common use are far from 100% MgO. None of the impurities are desirable from the standpoint of resistance to attack by slag and gas, and the same is true of the pores in the refractory. In view of the unlimited supply of magnesia readily available to man, along with its unique set of properties as a steel plant refractory, higher purity and denser magnesia refractories will undoubtedly be developed.

b. Reactions with iron oxides. Magnesia not only has a high melting temperature (~2800°C) but also it is very resistant to attack by iron oxide or calcium silicate slags. In the case of iron oxide, magnesia can absorb it in large quantities and still develop little or no liquid phase at steelmaking temperatures. If the oxygen pressure is low, as for example equal to that existing when the refractory is in equilibrium with metallic iron, the applicable phase diagram is that shown in Fig. 62(a). The periclase-type structure persists as iron oxide is absorbed, and liquidus and solidus temperatures decrease slowly. At a much higher oxygen pressure, as for example that of air, phase equilibrium relations are shown by a different type of diagram (Fig. 62b). With air as atmosphere, magnesia-iron oxide mixtures are even more refractory than at low oxygen pressure. At very high temperatures large amounts of iron oxide go into solution in periclase even though the atmosphere is air, but on cooling a second phase, magnesioferrite spinel (MgFe₂O₄), separates.

In the examples used above, the phase relations in the system MgO-iron oxide were considered at selected, constant levels of oxygen pressure of the gas phase. In practical
operations, the oxygen pressure usually varies continuously both with respect to time and with respect to location in the furnace. The effect of such variations on phase relations in the system MgO-iron oxide are implicitly represented by the diagrams in Figs. 63 and 64, showing selected isothermal sections and the liquidus surface, respectively. These diagrams were derived from data obtained by studying mixtures of MgO, FeO, and Fe$_2$O$_3$ contained in sealed tubes such that the total compositions of condensed phases remained approximately constant. By this experimental method the oxygen pressure inside the tube is determined in each run by the FeO/Fe$_2$O$_3$ ratio of the oxide material which was sealed into the tube, and the temperature of the run. Although numerical values for these oxygen pressures are not determined by this method of study, it is sufficient for our present purpose to recognize that the oxygen pressures increase from very low values in the left part (MgO-FeO side) of the system to very high values in the right part (MgO-Fe$_2$O$_3$ side).

It is seen that only the three crystalline oxide phases, magnesiowüstite (periclase type), magnesioferrite (spinel type), and hematite (corundum type) appear in equilibrium with liquids in the system. Magnesiowüstite is the primary crystalline phase, regardless of magnesium oxide to iron oxide ratio, under strongly reducing conditions (left side of diagram), whereas spinel and subsequently hematite appear as primary crystalline phases as the oxygen pressure increases. There is one important difference to be noted in the use of the two diagrams in Figs. 63 and 64. In Fig. 64 the oxygen pressure of the gas phase increases continuously from left to right. In Fig. 63, however, one of the existing degrees of freedom of the three-component system has been expended in choosing the constant temperature of the section. Hence, in an area where three condensed phases are in equilibrium with gas, the composition of each phase and the oxygen pressure of the gas phase are fixed for each mixture within that area ($P + F = C + 2 = 5; F = 5 - 4 - 1 = 0$). An example of such a situation is the area within which all mixtures at 1700°C consist of magnesiowüstite, magnesioferrite, and liquid (together with gas).

The 1700°C isothermal section through the system MgO-FeO-Fe$_2$O$_3$ as shown in Fig. 160 will be used as an example to derive qualitatively the effect of oxygen pressure on liquid formation and crystalline phase equilibria in magnesium oxide-iron oxide mixtures. Note first that as the oxygen pressure of the gas phase varies, the total composition of any magnesium oxide-iron oxide mixture varies along a straight line ("oxygen reaction line") pointing to the O apex of the triangle representing the system Mg-Fe-O, of which MgO-FeO-Fe$_2$O$_3$ is a part. Using mixture A (26% MgO, 74% iron oxide calculated as Fe$_2$O$_3$) as an example, it is seen that the effect of changing oxygen pressure on liquid formation in magnesium oxide-iron oxide mixtures of high iron content is small so long as the oxygen pressure is relatively low. This follows from the almost parallel courses of the boundary curve between the areas labeled MW and MW + L and those of the oxygen reaction lines. As the oxygen pressure increases from that of A, at 1700°C the amount of liquid present increases slightly until the condition represented by the triangle labeled MW + MF + L is reached. At the oxygen pressure of this isobaric, isothermal invariant situation, magnesioferrite separates out and the liquid phase disappears at constant oxygen pressure (and constant temperature). When the oxygen pressure increases above this level, the mixture is made up entirely of two crystalline phases, magnesiowüstite and magnesioferrite. This relatively moderate effect of changing oxygen pressures on liquid formation as iron oxide attacks magnesite brick is in sharp contrast to the profound effect of the same parameter when silica brick is attacked by iron oxide (compare pages 183 and 184).

Mixture B is used as an example to show the effects of changing oxygen pressure on interconversions among crystalline phases. Originally this mixture consists of one phase only, a magnesiowüstite solid solution of composition B. As the oxygen pressure
increases, the total composition changes along the oxygen reaction line, and the magnesiowüstite phase becomes increasingly rich in Fe$_2$O$_3$. When the composition has reached point B', magnesioferrite with spinel structure starts to separate out, and as oxygen pressure increases further, the two phases magnesiowüstite and magnesioferrite coexist in equilibrium. Both phases increase their MgO content as oxygen pressure increases, particularly the magnesiowüstite phase. At the same time the amount of the magnesioferrite phase increases and that of magnesiowüstite decreases rapidly. Hence iron oxide is transferred from a magnesiowüstite phase to a spinel phase as oxygen pressure increases, and conversely as the oxygen pressure decreases. These changes in proportions of the two phases may cause severe stresses and lead to disruption of the body.

**c. Inferred reactions with iron oxide and Cr$_2$O$_3$.** Actual magnesite refractories used in steelmaking furnaces are much more complicated than the systems discussed so far, because a larger number of additional oxide components are usually present in the brick. Extension into multicomponent systems of the principles discussed so far may serve as a valuable guide to the reactions taking place in the refractories in service. As an example of such a multicomponent system, the phase relations to be expected when Cr$_2$O$_3$ is added as a fourth component to the system MgO-FeO-Fe$_2$O$_3$ will be considered. This component, Cr$_2$O$_3$, is particularly interesting, not only because it is a dominant constituent of chromite refractories, but also because its effect on the relative stabilities
of the three structure types (periclase-, spinel-, corundum-) of iron oxide is opposite that of MgO (compare Figs. 57 and 62). Although experimental data on the system MgO-FeO-Fe₂O₃-Cr₂O₃ are scarce at the present time, it is possible to infer approximate phase relations on the basis of known equilibria for the bounding ternary systems and general knowledge of crystal chemistry. An example of such equilibria is shown in Fig. 161, which illustrates the inferred liquidus surface for the 40% Cr₂O₃ plane in the system MgO-FeO-Fe₂O₃-Cr₂O₃. The most important effects of the Cr₂O₃ addition are seen from a comparison of this diagram with that for MgO-FeO-Fe₂O₃ (Fig. 64), as follows: The primary phase area of magnesiowüstite solid solution has decreased and the areas of magnesioferrite and sesquioxide have increased considerably as a result of the Cr₂O₃ addition. Similarly, liquidus temperatures have increased drastically for mixtures of high iron oxide content. Thus the effect of Cr₂O₃ in increasing solidus and liquidus temperatures as well as in stabilizing phases containing iron predominantly in the Fe³⁺ state is clearly evident in the complex quaternary system MgO-FeO-Fe₂O₃-Cr₂O₃, just as it was in the simpler system of iron oxide and chromium oxide alone (Fig. 57).

**d. Reactions with iron oxide and SiO₂.** Phase equilibria in the quaternary system MgO-FeO-Fe₂O₃-SiO₂ are useful in evaluating reactions where silica as well as iron oxide are constituents of the magnesite refractory. A perspective sketch of a tetrahedron representing this system was shown in Fig. 88. The base of the tetrahedron, corresponding to strongly reducing conditions, is the system MgO-FeO-SiO₂, shown
Fig. 162. Sketches showing the approximate 1650°C isothermal section through the system MgO-iron oxide-SiO$_2$ at two different levels of oxygen pressures: those of contact with metallic iron in (a) and that of air in (b). The diagrams were constructed from Figs. 93 and 94, respectively, with reasonable assumptions regarding directions of conjugation lines. Abbreviations used have the following meanings: MW = magnesiowüstite, MF = magnesioferrite, Ol = olivine, Crist = cristobalite, L = liquid.

in Fig. 93. As oxygen partial pressure increases, compositions of mixtures change in a manner which may be described as a rotation of a surface around the MgO-SiO$_2$ join in the direction from the MgO-FeO-SiO$_2$ basal plane toward the MgO-Fe$_2$O$_3$-SiO$_2$ face of the tetrahedron. The diagram in Fig. 94 applies where the atmosphere is air, and is shown in perspective within the tetrahedron of Fig. 88 as the plane MgO-FeO-Fe$_2$O$_3$-SiO$_2$. From the liquidus surface and reasonable assumptions regarding locations of conjugation lines, approximate isothermal sections through the system at 1650°C at the two levels of oxygen pressures may be constructed, as shown in Fig. 162(a) and (b). These diagrams will be used to evaluate approximate courses of the phase changes taking place as a magnesite body reacts with iron oxide and with iron silicate liquids.

A magnesite refractory has a composition represented by a point near the MgO apex, for instance A in Fig. 162. As iron oxide is absorbed, the composition point moves toward the iron-oxide apex of the triangle representing the system. We will assume in this example that the amount of iron oxide absorbed is small enough that no liquid phase is formed. At very low oxygen partial pressures (Fig. 162a), the body is composed of magnesiowüstite crystals plus a small amount of olivine. The latter is a solid solution of Mg$_2$SiO$_4$ and Fe$_2$SiO$_4$, with its composition therefore represented by a point on the orthosilicate join from 2MgO-SiO$_2$ toward 2FeO-SiO$_2$. With air as atmosphere, the magnesiowüstite crystals are higher in ferric iron, the olivine crystals are virtually pure Mg$_2$SiO$_4$, and a spinel phase, magnesioferrite, is present when large amounts of iron oxide have been absorbed. Thus with silica present an additional phase change occurs during the “breathing” process: the forsterite-fayalite solid-solution crystals change to
a mixture of magnesioferrite and essentially pure forsterite as oxygen partial pressure increases, the reaction reversing as it decreases.

Without question, magnesia-iron oxide-silica refractories should be maintained at constant oxygen pressure and at constant temperature as far as possible in order to minimize phase changes in the body which in turn produce volume changes.

The extraordinary resistance of high-magnesia bodies to fluxing by iron silicate liquids can also be visualized in Fig. 162. Take as an example pure periclase crystals at a temperature of 1650°C to which is added a liquid of fayalite composition (2FeO-SiO₂) in an atmosphere of very low oxygen pressure. Diagram (a) applies to this case. As the liquid is added, olivine crystals will grow and the periclase crystals will become magnesiowüstite solid solutions, with the liquid being soaked up and disappearing. Finally, when a weight of fayalite liquid roughly equal to that of the original periclase has been added, the first trace of liquid will persist. Continuing to increase the fayalite addition at 1650°C causes an increasing amount of liquid to be present in the body. When the amount of fayalite added is approximately 50% higher than that of the original periclase, the mixture will be about two-thirds liquid and one-third magnesiowüstite crystals. Olivine crystals will have disappeared. Between the stage of first appearance of liquid and the stage of predominance of liquid, the magnesiowüstite crystals will no doubt appear singly or in clusters surrounded by liquid. This type of fluxing or chemical attack thus finally disintegrates the magnesia refractory by developing sufficient liquid that the crystals are separated. Erosion of magnesia refractories by iron silicate slags can thus proceed slowly by liquid formation in the refractory at the slag contact after absorption of slag by the refractory finally reaches its saturation point.

This saturation point of a magnesia refractory acting like a blotter for iron-silicate slags is a function of oxygen partial pressure as well as temperature. In the above example the case of very low oxygen partial pressure was taken. At higher oxygen partial pressures an even greater addition of iron silicate is possible before liquid saturation is reached. Referring to Fig. 162(b), which applies to air atmosphere, it is seen that magnesia can soak up approximately twice its weight of iron-silicate liquid before becoming saturated.

e. Reaction with various silicate liquids. Resistance of magnesite refractories to chemical attack by calcium-silicate slags is excellent. Indeed, MgO is fluxed less by high-lime mixtures than is Cr₂O₃. Whereas in the system lime-chromium oxide-silica (Fig. 106) relatively low liquidus temperatures probably prevail in the lime corner because of the presence of chromium in valence states higher than 3+, very high liquidus and solidus temperatures are maintained throughout the low-silica part of the CaO-MgO-SiO₂ system (Figs. 77 and 78).

Even the combined attack of lime, iron oxide, and silica in the form of a high-temperature liquid is resisted to a high degree by magnesia. These reactions are brought out by an inspection of phase equilibria in the system CaO-MgO-FeO-SiO₂ in contact with metallic iron (Figs. 123 and 124). Consider a magnesite refractory as having a composition within the tetrahedron at a point close to the MgO apex. The slag reacting with this crystalline body has a composition within the tetrahedron at a point close to the opposite face, the system CaO-FeO-SiO₂. In this quaternary system are seven liquidus invariant points. Six have temperatures of 1200°C or less, the seventh approximately 1450°C.(305) The MgO contents of the liquids range from 2 to 17%. A lime-iron oxide-silica slag at very low oxygen partial pressures reacting with magnesia will form a liquid at the temperature of and of about the composition of one of these invariant points. Although the temperatures of these invariants are low, so also is the MgO content of the liquid. A great amount of the slag is therefore required in order to dissolve a
certain amount of magnesia or, in other words, magnesia is only sparsely soluble in these slags. In moving within the tetrahedron from one of these invariant points toward MgO, liquidus temperatures rise rapidly. At steelmaking temperatures, the solubility of magnesia in liquids in this system is still relatively small, which accounts for the slag resistance of magnesia.

2. DOLOMITE REFRACTORIES

a. General considerations. Like the magnesite refractories above, dolomite refractories carry the name of the source material. Siliceous dolomite is calcined to drive off CO₂ and convert the mixture approximately to its equilibrium phase assemblage. A typical dolomite refractory has a composition close to a point on the 3CaO-SiO₂-MgO join in the system CaO-MgO-SiO₂ (Fig. 77), consisting therefore of tricalcium silicate and periclase with a small amount of either lime or dicalcium silicate. The presence of either one of the latter phases presents a stabilization problem, for lime hydrates very readily and dicalcium silicate dusts, and either reaction may cause disintegration. Furthermore, both tricalcium silicate and periclase hydrate with ease, although not as rapidly as CaO. The free CaO is best eliminated by maintaining sufficient SiO₂ to keep the composition on the SiO₂ side of the 3CaO-SiO₂-MgO join, or by adding iron oxide to produce dicalcium ferrite. Temporary resistance to hydration is attained by coating the calcined grains with organic material.

b. Stabilization of dicalcium silicate. The high-temperature forms of dicalcium silicate can be stabilized, and the dusting phenomenon thus avoided, by adding to the refractory minor amounts of various “inhibitors.” Chromium oxide, B₂O₃, and P₂O₅, as well as several other oxides, have been found to be effective in inhibiting the inversion to the γ-form, and one of these is usually present in a “stabilized” refractory containing dicalcium silicate. The inhibiting effect probably occurs because of substitution of Cr⁵⁺, B³⁺, or P⁵⁺ ions for Si⁴⁺ ions in the high-temperature structures to a greater extent than in γ-Ca₂SiO₄. Inversion from α’- or β-Ca₂SiO₄, containing these ions, to the γ-form could occur therefore only with expulsion of the foreign ions from the structure, a process apparently not readily accomplished. Hence the high form is stabilized. In a strongly reducing atmosphere the effectiveness of chromium oxide as an inhibitor decreases as the chromium ion is reduced to Cr³⁺, a larger ion which does not readily substitute for Si⁴⁺.²³⁴

c. Reactions with iron oxide. Lime itself is not a good refractory material against iron oxide. This is apparent from the phase diagrams for the system CaO-iron oxide in contact with metallic iron and in air [Fig. 65(a) and (b), respectively]. Similarly, lime is fluxed severely by iron oxide in the presence of SiO₂, as shown by the low liquidus and solidus temperatures prevailing in major parts of the system CaO-iron oxide-SiO₂ in contact with metallic iron (Fig. 95) and in air (Fig. 96).

Our knowledge of phase relations in the system CaO-MgO-iron oxide are very deficient at present. Only the 1500°C isothermal sections for the system at two levels of oxygen pressure, those prevailing in contact with metallic iron and that of air, have been studied in detail.²³⁷ The diagrams are shown in Fig. 163(a) and (b), respectively. The most significant features of the diagrams, from the standpoint of the present discussion, is the large difference in the extent of the areas where no liquid phase is present at the two levels of oxygen pressures. Under strongly reducing conditions, (a), a CaO-MgO mixture of composition A can take up approximately 22% iron oxide without a liquid phase developing at 1500°C. In air, (b), however, only 3% iron oxide can be taken up before a liquid phase develops at the same temperature. Hence, maintaining strongly reducing conditions within a dolomite refractory body exposed to iron-oxide attack is desirable
Fig. 163. The 1500°C isothermal sections through the system CaO-MgO-iron oxide (a) in atmospheres of CO₂/H₂ = 1, and (b) in air, based on data of Johnson and Muan. Abbreviations used have the following meanings: MW = magnesio-wüstite, MF = magnesioferrite, L = liquid.

in order to preserve high refractoriness. It is believed that the tar bonding used in dolomite brick for oxygen steelmaking vessels serves this purpose. In addition, however, the tar probably plays another important role in the chemistry involved during use of such brick. The carbon resulting from the tar causes a deposition of metallic iron from the oxide phases within the refractory, thus acting like an automatic safety valve limiting the amount of iron oxide to a value below that which is necessary to form a liquid phase.

Although data on solidus temperatures for mixtures in the system CaO-MgO-iron oxide-SiO₂ close to the CaO-MgO-iron oxide face are not available at the present time, it is probable that a situation similar to that described above also prevails when SiO₂ is present in the brick. Larger amounts of iron oxide are probably tolerated before a liquid develops under strongly reducing conditions than under oxidizing conditions, because Fe^{2+} can be accommodated more readily than Fe^{3+} in the crystalline phases which are present. The carbon present in the brick again probably serves the dual purpose of keeping essentially all iron in the oxide phases in the ferrous state and in addition causes precipitation of metallic iron and thus limits the amount of iron oxide present in the refractory.

3. FORSTERITE REFRACTORIES

Forsterite refractories are high-magnesia, low-lime bodies made from natural magnesian olivine, usually with addition of magnesia. The olivine starting material has a composition close to the join Mg₂SiO₄-Fe₂SiO₄ of the system MgO-FeO-SiO₂ (see Fig. 93) and contains about 10 to 15% of the Fe₂SiO₄ component. The composition of the dunite source rock, however, lies on the SiO₂ side of the olivine join as a consequence
of the presence of a small amount of higher silica minerals. On ordinary firing of the olivine by itself, the iron oxidizes, forming a separate magnesioferrite phase in equilibrium with nearly pure Mg₂SiO₄, releasing silica in the process to form pyroxene. This is demonstrated by the isothermal sections of the system MgO-iron oxide-SiO₂ presented in Fig. 162. Magnesia is ordinarily added in sufficient amounts, however, that during firing the excess silica over the orthosilicate ratio is converted to forsterite, and there remains in addition a separate magnesiowüstite phase. This material is thus a magnesite type of refractory containing several percent of iron oxide and more than the usual amount of silica.

Because of the iron content, forsterite refractories are subject to disintegration where severe and prolonged conditions of fluctuating temperatures and/or oxygen pressure obtain. This is the same problem as discussed above in connection with magnesite refractories containing iron oxide. This tendency to disintegrate can be minimized by addition of alumina at the expense of refractoriness. The chief effect of alumina probably is in its entering the magnesioferrite structure during firing, where it temporarily blocks the conversion of spinel to magnesiowüstite under conditions of lower oxygen pressure. Forsterite brick containing alumina also have greater strength, and this stronger bonding together of the crystals is a deterrent to disintegration.
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