PHASE EQUILIBRIA AT HIGH TEMPERATURES IN OXIDE SYSTEMS INVOLVING CHANGES IN OXIDATION STATES

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ABSTRACT. Determination of phase equilibria in oxide systems involving changes in oxidation states requires careful control of atmospheric conditions. The desired $O_2$ partial pressure may be obtained experimentally by using vacuum techniques or by mixing $O_2$ with an inert gas in the range 1 to $10^{-3}$ atm. Under more reducing conditions the desired $O_2$ partial pressure is best obtained by mixing $CO_2$ and $H_2$ in various proportions. The resulting $O_2$ partial pressure is calculated from known equilibrium data.

In the description of phase equilibria in such systems, the $O_2$ partial pressure of the gas phase is an important parameter. Diagrams showing projections of the liquidus surface with liquidus isotherms and fractionation curves should be supplemented by curves showing equilibrium partial pressures of $O_2$ of the gas phase. New criteria for derivation of paths of equilibrium crystallization must be established. Compositions of condensed phases change during crystallization in a manner which is described by straight lines pointing towards the $O$ apex of the model used to represent the system.

Iron oxide containing silicates are the best-known examples of systems where changes in oxidation states are involved. The systems $Fe-O$, $FeO-Fe_2O_3-SiO_2$ and $MgO-FeO-Fe_2O_3-SiO_2$ are used for the purpose of illustrating principles.

INTRODUCTION

A knowledge of equilibrium as well as kinetic relationships is necessary in order to understand and predict chemical reactions. In cases where reaction rates are very low, equilibrium data are of relatively little use for an evaluation of industrial processes, while they still may be of great importance for an understanding of geological processes, where the time factor is less critical. As reaction rates increase, equilibrium data become increasingly important. Although few, if any, industrial processes operate under perfect equilibrium conditions, equilibrium data have their great value in defining limits for the reactions taking place.

It is customary, for classification purposes, to distinguish between homogeneous and heterogeneous equilibria. Actually, a single homogeneous phase can not be isolated; it is not possible in practice to contain or support it without introducing one or more other phases. However, where the main reactions take place within the homogeneous part of the system, such as for instance in a gas phase, the equilibrium may be considered homogeneous. Heterogeneous equilibria, on the other hand, are those in which mass transfer across phase boundaries is an important part of the process. Such equilibria invariably involve condensed phases, either liquid or solid or both. The conditions governing the coexistence of phases at equilibrium can be derived from classical thermodynamics, and are commonly expressed in the law referred to as Gibbs' Phase Rule.

$$P + F = C + 2$$

Here $P$ designates the number of phases existing together at equilibrium, $F$ is the number of degrees of freedom and $C$ the number of components. The dependence of phase relationships on the variables of the system is best il-

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illustrated in the geometrical constructions known as phase diagrams. Among the variables influencing the phase assemblage may be temperature, pressure, chemical composition, electrical field, magnetic field etc. It has been found experimentally that the latter two may usually be ignored. Furthermore, in most cases reactions are carried out at a total pressure of 1 atm., leaving temperature and chemical composition as the main variables. The dependence of phase relationships on these variables is what is usually illustrated in a phase equilibrium diagram.

A very substantial amount of phase equilibrium work on oxide systems has been described in the literature during the last decades. In reviewing these studies one is impressed by the large amount of data available on systems made up from oxides of noble gas type ions, such as for instance \( \text{SiO}_2, \text{Al}_2\text{O}_3, \text{MgO}, \text{CaO} \). The great interest in such oxides is, of course, well founded. These oxides are among the most abundant constituents of the earth's crust, and a knowledge of systems made up from these components is important in geological sciences as well as in technology. There are, however, a large number of other oxides, as well as other compounds, which are equally important, and becoming more so as new materials are developed. Many of these materials involve components made up from ions of transition elements where changes in oxidation states not only are possible but indeed very common. The study of phase equilibria in such systems is somewhat more complicated than the study of the systems just mentioned, because the gas phase plays an important role in the equilibria. The present paper discusses methods for studying and describing such systems.

**METHODS FOR DETERMINING PHASE EQUILIBRIA IN OXIDE SYSTEMS**

*Ordinary Dry Silicate Systems.*—In working out and describing phase equilibria in "ordinary dry" silicate systems it is customary to ignore the vapor phase and treat the equilibria in terms of the condensed phase rule

\[ P + F = C + 1 \]

where \( P \) indicates the number of condensed phases present, while the other symbols have the same meaning as explained before. No serious error is introduced by doing this as long as the vapor pressure of each constituent is low. Such systems are usually studied in an open quench furnace in air atmosphere. As an illustration, consider the system \( \text{CaO}-\text{MgO}-\text{SiO}_2 \), at liquidus temperatures. At equilibrium there is a certain partial pressure of each constituent in the gas phase coexisting with the condensed phases. These partial pressures vary with temperature and composition of the liquid, each assemblage of condensed phases requiring, at equilibrium, a very definite composition of the gas phase. During the time required for equilibrium to be

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1. The term condensed phases is used here and throughout the remainder of the paper to designate liquid and solid phases as distinguished from a gas phase.
2. Pressure is, of course, an extremely important variable in geological sciences, as evidenced by the large amount of research work presently going on in the field of hydrothermal synthesis at high pressures and elevated temperatures.
attained among condensed phases the equilibrium composition of the gas phase over the charge may or may not be obtained, depending to a large extent on the degree or circulation of air through the furnace. Whether or not this true equilibrium composition of the gas phase over the sample is reached is, however, not important in practice. This is because the vapor pressure of each constituent is so low\(^5\) that the sample may build up, or try to build up, the equilibrium composition of the gas phase without changing appreciably the total composition of the condensed phases. Equilibria among the latter can therefore be studied without controlling the atmosphere, and the phase relationships can be discussed in terms of the condensed phase rule.

**Systems Involving Changes in Oxidation States.**—In cases where elements of changing oxidation states are involved in the equilibria, the situation is usually more complicated. Consider an arbitrary element Me forming two oxides MeO\(_x\) and MeO\(_y\). Here the element Me occurs in two different states of oxidation, Me\(^{x+}\) and Me\(^{y+}\), respectively. Suppose that these oxides are dissolved in a condensed phase in equilibrium with a gas phase. The following reaction is of critical importance:

\[
(MeO_x)_{\text{in soln.}} = (MeO_y)_{\text{in soln.}} + \frac{(x-y)}{2} O_2
\]

It will be seen that a change in O\(_2\) pressure causes a change in the relative proportions Me\(^{x+}\)/Me\(^{y+}\) in the condensed phase, and vice versa. Hence in treating systems involving such components the partial pressure of O\(_2\) must be taken into consideration in addition to the vapor pressures of the components themselves. As long as all these pressures are very low (of the same order of magnitude as for CaO, MgO and SiO\(_2\)), such systems can be studied and described in a manner similar\(^6\) to the treatment of CaO—MgO—SiO\(_2\). The vapor pressures of the oxides themselves as a function of temperature are predetermined. For a large number of important oxides, such as for instance iron oxides, these pressures are very low up to liquidus temperatures. The equilibrium O\(_2\) pressure, however, is a function of the ratio MeO\(_x\)/MeO\(_y\) in the condensed phases, increasing rapidly as this ratio increases. If the MeO\(_x\)/MeO\(_y\) ratio of the condensed phases in a mixture is such that the equilibrium O\(_2\) pressure of the gas phase is low, phase equilibria for this mixture can be studied in a vacuum system or in a purified inert gas atmosphere. The basis for the use of this method is the slow exchange of O\(_2\) between the gas phase and the condensed phases. As an illustration, assume that the MeO\(_x\)/MeO\(_y\) ratio in the liquid phase at the temperature considered is such that the corresponding partial pressure of O\(_2\) is 10\(^{-9}\) atm. Assume furthermore that a completely “perfect” inert gas is used, with no O\(_2\) present in the gas initially. The mixture when heated in a furnace through which this inert gas flows will try to build up the equilibrium O\(_2\) pressure of 10\(^{-9}\) atm. The amount of

\(^5\) The term “ordinary” is used in this paper to designate oxide systems involving only ions of noble gas type, as distinguished from systems containing transition elements. The term “dry” is used to indicate that no water is present, as distinguished from hydrothermal systems.

\(^6\) The vapor pressures of CaO, MgO and SiO\(_2\) at 1400°C in air are approximately (Brewer, 1953): CaO, 10\(^{-19}\) atm.; MgO, 10\(^{-8}\) atm.; SiO\(_2\), 10\(^{-9}\) atm.
oxygen required to build up this low pressure in a moderate volume of gas (the inert gas flows through the furance at a moderate speed) is very small
\[
\left( \frac{10^{-9}}{22.4} \cdot 32 = 1.4 \times 10^{-9} \text{ g oxygen per liter of gas} \right). \text{ Hence the } \text{MeO}_{\alpha}/\text{MeO}_{\gamma} \text{ ratio of the condensed phases is changed very little, and for practical purposes the composition of the condensed phases may be considered constant. If the inert gas is not "perfect", the situation is similar. Assume for the sake of argument that the inert gas (or the vacuum system) contains a small amount of oxygen corresponding to an } O_2 \text{ pressure of } 10^{-7} \text{ atm. In order to establish equilibrium between the gas phase and the condensed phases the latter phases must pick up } O_2 \text{ from the gas phase. However, the difference } 10^{-7} - 10^{-9} \text{ is very small, and again an enormous volume of gas would be required to change significantly the relative amounts } \text{MnO}_{\alpha}/\text{MnO}_{\gamma} \text{ and hence the total composition of the condensed phases (} \sim 1.4 \times 10^{-7} \text{ g oxygen per liter of gas). For all practical purposes, therefore, the total composition of the condensed phases may be considered constant. This is the basis for the method used by Schuhmann, Powell and Michal (1953) in their study of a part of the system } FeO—Fe_2O_3—SiO_2. \text{ They made up mixtures in the low } Fe_2O_3 \text{ part of the system by weighing up the three components } FeO, Fe_2O_3 \text{ and } SiO_2 \text{ in required proportions. The mixtures were heated in platinum containers in an inert gas atmosphere, and the results interpreted on the basis of the assumption that the total composition of the condensed phases did not change during the period of time necessary to attain equilibrium among the condensed phases.}^7

An alternative method for studying such systems under reducing conditions is the one used by Bowen and Schairer (1932) in their investigation of phase equilibria in iron silicates. Their work, which was started 25 years ago, was the pioneering effort in the field and represented the first real breakthrough in experimental studies of iron oxide containing systems. The method consists in examining equilibria among condensed phases in mixtures contained in Fe crucibles in a purified inert gas atmosphere, such as for instance } N_2. \text{ The partial pressure of } O_2 \text{ of the gas phase under these conditions is that corresponding to the equilibria }
\[
Fe_2O_3\text{(in melt)} = 2FeO\text{(in melt)} + \frac{1}{2}O_2\text{(g)}
\]
and
\[
Fe_2O_3\text{(in melt)} + Fe(s) = 3FeO\text{(in melt)}
\]
at any particular temperature. In the binary system } Fe - O \text{ only one degree of freedom exists in the presence of the phases above (liquid, metallic } Fe, \text{ gas), and the } O_2 \text{ pressure is a function of temperature alone. In a ternary system, such as for instance } FeO—Fe_2O_3—SiO_2, \text{ one additional degree of freedom exists with the same phase assemblage, and the equilibrium } O_2 \text{ pressure is a function of temperature as well as the amount of one of the com-

Air atmosphere can not be used for the experimental study of such equilibria. This point will be discussed in more detail below.

These authors were fully aware of the composition changes caused by iron going into the platinum of the container, according to the reaction } 3FeO = Fe + FeO_3. \text{ However, in most instances this reaction was not extensive enough to change the results significantly.}^7
ponents of the liquid phase. If wüstite (FeO)⁸ is one of the phases present, this \( O_2 \) pressure is equal to the equilibrium pressure at which FeO and Fe coexist in equilibrium in the binary system Fe – O, at the temperature in question. (For data on this equilibrium, see papers by Darken and Gurry (1945, 1946). If wüstite is not present as a phase, at temperatures below its melting point (1371°C), this \( O_2 \) pressure is lower than the pressure corresponding to the FeO/Fe equilibrium.

At considerably higher levels of \( O_2 \) pressures, equilibrium may be reached between an \( O_2 \) containing gas phase and the condensed phases within a reasonable period of time. As an example, one liter of \( O_2 \) gas of 1 atm. pressure corresponds to 1.43 g oxygen. Hence a moderate rate of flow of gas through the furnace in this case will supply enough oxygen to change the \( \text{MeO}_x/\text{MeO}_y \) ratio of the condensed phases to the equilibrium value within a reasonable period of time. It is therefore possible in practice to study equilibria in oxide systems, involving a gas phase at 1 atm. \( O_2 \), and in air (corresponding to \( p_{O_2} = 0.21 \) atm.). If the \( O_2 \) pressure of the gas is decreased, either by using a vacuum or by mixing with an inert gas, the volume of gas necessary to bring about the change in composition of condensed phases required for equilibrium increases rapidly (proportional to \( \frac{1}{p_{O_2}} \)). An \( O_2 \) pressure of approximately \( 10^{-3} \) atm. is a practical lower limit for studying the equilibria when oxygen is present only as \( O_2 \) molecules in the gas phase.

It is possible, however, to obtain equilibrium between the gas phase and the condensed phases also below these levels of \( O_2 \) pressures by using indirect methods of creating the desired \( O_2 \) partial pressures. The most convenient way of doing this is to use an oxygen-containing gas which upon heating in the furnace decomposes to another gas species under liberation of \( O_2 \). Gases suitable for this purpose are \( \text{H}_2\text{O} \) and \( \text{CO}_2 \), which decompose upon heating according to the equations:

\[
2\text{H}_2\text{O} = 2\text{H}_2 + \text{O}_2, \quad \text{and} \\
2\text{CO}_2 = 2\text{CO} + \text{O}_2,
\]

respectively.

The equilibrium constant for each of these reactions as a function of temperature is well known. If \( \text{CO}_2 \) or \( \text{H}_2\text{O} \) is used alone, and the total pressure is kept constant, the \( O_2 \) pressure is a function of temperature alone. This means that \( O_2 \) pressure and temperature can not be varied independently if the pure gases are used, and this of course is a serious drawback. If, however, some \( \text{H}_2 \) is mixed with the \( \text{H}_2\text{O} \) or some CO with the \( \text{CO}_2 \), the dissociations of \( \text{H}_2\text{O} \) or \( \text{CO}_2 \) are suppressed to a degree which can be controlled by varying the mixing ratios of the gases. The \( O_2 \) pressure now is a function of temperature as well as \( \text{H}_2\text{O}/\text{H}_2 \) or \( \text{CO}_2/\text{CO} \) mixing ratios. \( O_2 \) pressure and

⁸ Wüstite is a defect structure with a considerable variation in the Fe/O ratio (Darken and Gurry, 1945, 1946). Although the stoichiometric composition FeO cannot be realized in practice, the formula for wüstite is usually written as FeO for the sake of convenience.

⁹ These gases are interchangeable; CO may be mixed with \( \text{H}_2\text{O} \) and \( \text{H}_2 \) with \( \text{CO}_2 \). The interdependence of the equilibrium ratios \( \text{H}_2\text{O}/\text{H}_2 \), \( \text{CO}_2/\text{CO} \), \( \text{CO}_2/\text{H}_2 \) and \( \text{H}_2\text{O}/\text{CO} \) at a certain \( O_2 \) pressure is expressed by the equilibrium constant for the “water gas equation” \( \text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O} \).
temperature can therefore be varied independently. The advantage of using mixed gas atmospheres rather than vacuum or inert gas is the presence of oxygen not only as \( \text{O}_2 \) but in bound form (\( \text{H}_2\text{O} \) or \( \text{CO}_2 \)) as well. At temperatures high enough to make the gas reactions rapid, a mechanism is available by which the \( \text{O}_2 \) exchange between the gas phase and the condensed phases can take place within a reasonable period of time in spite of the low partial pressure of \( \text{O}_2 \). As soon as \( \text{O}_2 \) is removed from the gas phase by reaction with the condensed phases, the equilibrium amount is restored by the decompositions \( 2\text{H}_2\text{O} = 2\text{H}_2\text{O} + \text{O}_2 \) or \( 2\text{CO}_2 = 2\text{CO} + \text{O}_2 \), whatever the case may be. It is emphasized that such methods for equilibrium studies can be used only at temperatures sufficiently high to make the gas reactions rapid.

**Representations of Phase Relationships**

*The System Fe – \( \text{O}_2 \).*—Systems containing iron oxides as components have been studied more thoroughly than any other oxide systems in which changes in oxidation states are involved. These will be used as examples in the following.

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**Fig. 1.** Diagram showing stability relationships among the phases hematite (\( \text{Fe}_2\text{O}_3 \)), magnetite (\( \text{FeO.} \text{Fe}_2\text{O}_3 \)), wüstite (\( \text{FeO} \)), metallic iron (\( \text{Fe} \)), liquid oxide and liquid iron as a function of temperature (in °C) and \( \text{O}_2 \) pressure (in atm.). Heavy solid lines are boundary curves separating the various phase areas labelled in the diagram. Light dashed-double dot lines are lines of equal \( p_{\text{H}_2}/p_{\text{H}_2} \) ratios of the gas phase at 1 atm. total pressure.
A thorough understanding of phase equilibria in the system Fe–O is essential as a background for discussing more complicated multicomponent iron silicates. The most recent and complete reports on the system are the excellent papers in 1945 and 1946 by Darken and Gurry (1945, 1946). These authors summarize results of earlier work in addition to providing a large amount of new data. The following discussion is based on data contained in their papers as well as data available in a recent compilation of thermodynamic constants by Coughlin (1954).

The importance of controlling the $O_2$ pressure was emphasized in the last section. The diagram shown in figure 1 is intended to bring out this point more clearly and in a quantitative way for the Fe–O system. In this plot phase equilibrium relationships among metallic iron (Fe), wüstitte (FeO), magnetite (FeO$_2$Fe$_2$O$_3$), hematite (Fe$_3$O$_4$), liquid iron and liquid oxide are illustrated as a function of temperature (°C) and partial pressure of $O_2$. The diagram has been constructed from data explained in detail later in connection with figure 2. The following rules should be observed when using the diagram in figure 1. In an area where one condensed phase exists in equilibrium with a gas, the system possesses 2 degrees of freedom. Hence, in a field such as for instance that of wüstitte both temperature as well as $O_2$ pressure may be changed without causing any phase changes. Along a bound-

![Diagram](image)

**Fig. 2.** Diagram presented in order to illustrate stability relationships among iron oxides and metallic iron as a function of temperature (in °C) and ratios of $H_2O/H_2$ of the gas phase in equilibrium with the condensed phases. Heavy solid lines are boundary curves separating the various phase areas labelled in the diagram. Light dash-dot lines are $O_2$ isobars. The heavy dash-cross line shows equilibrium ratios $p_{H_2O}/p_{H_2}$ of pure water vapor as a function of temperature at a total pressure of 1 atm.
ary curve, however, where 2 condensed phases coexist in equilibrium with a gas phase, the system has only 1 degree of freedom. Hence, if temperature is chosen, the \( O_2 \) pressure is fixed and vice versa. It will be noticed that the \( O_2 \) pressures of the gas phase in equilibrium with the various condensed phases in the system vary over a very large range, as temperatures vary between room temperature and liquidus temperatures. This of course is directly related to the large heat effects associated with each of the reactions represented by the boundary curves: 

\[
\frac{\ln p_{O_2}}{dT} = \frac{\Delta H^o}{RT^2}, \quad \text{where} \quad \Delta H^o \text{ is the heat of reaction per mole of } O_2 \text{ for each reaction, such as for instance: } 6Fe_2O_3 = 4Fe_3O_4 + O_2. \]

Oxygen pressures at the lowest temperatures shown in figure 1 are so low as to have little or no physical meaning. Physically more meaningful are ratios \( p_{H_2O}/p_{H_2} \) or \( p_{CO_2}/p_{CO} \) of the gas phase in equilibrium with the various oxides. Lines representing equilibrium values of \( p_{H_2O}/p_{H_2} \) ratios are plotted as dash double dot lines in figure 1. It is seen that these lines fall close to and are nearly parallel to the boundary curves separating the various phase areas. More "spread out" and readable diagrams are obtained by plotting \( p_{CO_2}/p_{CO} \) and \( p_{CO_2}/p_{CO} \) ratios of the gas phase in equilibrium with the various condensed phases as a function of temperature, as shown in figures 2 and 3, respectively. The diagram in figure 2 has been constructed from the following data: The boundary curve along which metallic

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Fig. 3. Diagram illustrating stability relationships among iron oxides and metallic iron as a function of temperature and ratios of \( CO_2/CO \) of the gas phase in equilibrium with the condensed phases. Heavy solid lines and light dash-dot lines have the same meanings as in last diagram. The heavy dash-double cross line indicates ratios \( p_{CO_2}/p_{CO} \) in equilibrium with carbon (graphite) as a function of temperature at a total pressure of 1 atm.
iron and wüstite or liquid oxide coexist in equilibrium with gas (curve II), as well as part of the curve where magnetite, wüstite and gas exist together in equilibrium (curve III), have been plotted from data obtained by direct measurements of \( \text{H}_2\text{O}/\text{H}_2 \) ratios of the gas in equilibrium with these phases, as reported in the literature. The lower temperature part of curve II (600-1000°C) was constructed from the data of Emmetts and Shultz (1930), while the upper region (1200-1515°C) was plotted from the data of Chipman and Marshall (1940). The low temperature part of curve III (600-800°C) was drawn on the basis of the data of Emmetts and Shultz (1930). The upper part of this curve (1096-1388°C) was constructed on the basis of data reported by Darken and Gurry (1946). These authors used \( \text{CO}_2/\text{CO} \) and \( \text{CO}_2/\text{H}_2 \) gas mixtures rather than \( \text{H}_2\text{O}/\text{H}_2 \) to study the equilibrium described by this line. Their data have been converted to values of \( \text{H}_2\text{O}/\text{H}_2 \) ratios by use of the equilibrium data for the reactions

\[
2\text{CO}_2 = 2\text{CO} + \text{O}_2 \\
2\text{H}_2\text{O} = 2\text{H}_2 + \text{O}_2
\]

as tabulated in a recent publication by Coughlin (1954). The liquidus curve \( V \), as well as that part of the hematite-magnetite boundary curve IV falling between 1100 and 1450°C, likewise, have been constructed from the data of Darken and Gurry (1946) by conversion to \( \text{H}_2\text{O}/\text{H}_2 \) ratios as described above. No experimental data are available for the boundary curve magnetite-metallic iron (curve I) and the hematite-magnetite boundary curve below 1100°C (curve IV). These parts of the curves have been constructed on the basis of calculated values obtained from the standard free energy data tabulated by Coughlin (1954). For checking purpose, curves were also constructed from calculated values in regions where direct measurements have been made (curves II, III, part of curve IV). The calculated curves are in good agreement with the experimental curves except for the magnetite-wüstite boundary (curve III). The discrepancy in the latter case is not surprising. The data listed in the tables of Coughlin refer to wüstite of composition \( \text{Fe}_0.94\text{O} \), while the wüstite in equilibrium with magnetite varies in composition in the range \( \text{Fe}_0.65\text{O} \) to \( \text{Fe}_0.82\text{O} \) (see phase diagram of Darken and Gurry (1945, 1946)). Light dashed lines show partial pressures of \( \text{O}_2 \). The heavy dash-cross line in the upper part of the diagram gives equilibrium values of \( \text{pO}_2/\text{pH}_2 \) of pure water as a function of temperature. The position of this curve relative to the boundary curves shows the stability ranges of the various iron oxides in pure water vapor. It will be noticed that at temperatures below approximately 1070°C hematite is the stable phase in equilibrium with water vapor. At temperatures between 1070°C and 1595°C magnetite is the equilibrium phase in a water vapor atmosphere, and above 1595°C a liquid oxide phase is stable under these conditions. It should be pointed out that neither wüstite nor metallic iron are equilibrium phases in water vapor at any temperature at a total pressure of 1 atm. In order to study equilibria in regions of the diagram falling below this dissociation curve for pure \( \text{H}_2\text{O} \) it is necessary to mix \( \text{H}_2 \) (or some other reducing agent) with the \( \text{H}_2\text{O} \) in amounts that may be calculated from the diagram in figure 2. One important relationship should be
made clear at this point: The values of $\text{H}_2\text{O}/\text{H}_2$ ratios plotted in figure 2 are the *equilibrium* ratios at any particular temperature. In order to study experimentally equilibria among the iron oxide phases it is usually necessary to mix the two gases in fixed proportions at room temperature and heat this gas mixture to whatever temperature is desired for the study of the equilibria among the condensed phases. These two ratios (original mixing ratio at room temperature and equilibrium ratio at the elevated temperature) are not the same. They are related to each other in the following way: Let $p_{\text{H}_2\text{O}(t)}$ and $p_{\text{H}_2(t)}$ be the partial pressures of $\text{H}_2\text{O}$ and $\text{H}_2$, respectively, in the starting gas mixture at room temperature. Upon heating, $\text{H}_2\text{O}$ decomposes according to the equation

$$2\text{H}_2\text{O} = 2\text{H}_2 + \text{O}_2$$

At equilibrium we have the relationship

$$K = \frac{p_{\text{O}_2(\text{eq.})} \cdot p_{\text{H}_2(\text{eq.})}}{p_{\text{H}_2\text{O}(\text{eq.})^2}}$$

where $p_{\text{O}_2(\text{eq.})}$ etc. are the partial pressures of the gases at equilibrium at the high temperature, and $K$ is the equilibrium constant at the same temperature. Let us call $p_{\text{H}_2(\text{eq.})} = x$. Then we have the following relationships:

$$p_{\text{O}_2(\text{eq.})} = x$$
$$p_{\text{H}_2(\text{eq.})} = (1-x) \cdot p_{\text{H}_2(t)} + 2x$$
$$p_{\text{H}_2\text{O}(\text{eq.})} = (1-x) \cdot p_{\text{H}_2\text{O}(t)} - 2x$$

Hence:

$$K = \frac{x \cdot (1-x) \cdot p_{\text{H}_2(t)} + 2x}{(1-x) \cdot p_{\text{H}_2\text{O}(t)} - 2x}^2$$

and

$$\frac{p_{\text{H}_2\text{O}(\text{eq.})}}{p_{\text{H}_2(\text{eq.})}} = \frac{(1-x) \cdot p_{\text{H}_2\text{O}(t)} - 2x}{(1-x) \cdot p_{\text{H}_2(t)} + 2x}$$

If $x << p_{\text{H}_2\text{O}(t)}$ and $x << p_{\text{H}_2(t)}$ we have

$$\frac{p_{\text{H}_2\text{O}(\text{eq.})}}{p_{\text{H}_2(\text{eq.})}} \approx \frac{p_{\text{H}_2\text{O}(t)}}{p_{\text{H}_2(t)}}$$

and likewise

$$K \approx \frac{x \cdot p_{\text{H}_2(t)^2}}{p_{\text{H}_2\text{O}(t)^2}}$$

or $x \approx Kr^2$, where $r =$ mixing ratio

$$\frac{p_{\text{H}_2\text{O}(t)}}{p_{\text{H}_2(t)}}$$

These approximations are valid in all regions of the diagram in figure 2 except in close proximity of the line for dissociation of pure water. For pure water the following relationships hold:
\[ p_{O_2(\text{eq.})} = x \]
\[ p_{H_2(\text{eq.})} = 2x \]
\[ p_{H_2O(\text{eq.})} = 1 - 3x \]
\[ K = \frac{x \cdot (2x)^3}{(1 - 3x)^3}, \text{ or } K = \frac{4x^3}{(1 - 3x)^2} \]

At moderate or low temperatures, where \( K \) is small, \( x < < 1 \), and the following approximation is valid:

\[ K \approx 4x^3; \quad x \approx \left( \frac{K}{4} \right)^{1/3} \]

Hence

\[ \frac{p_{H_2O(\text{eq.})}}{p_{H_2(\text{eq.})}} \approx \left( \frac{p_{O_2}}{K} \right)^{1/2} \approx \left( \frac{\left( \frac{K}{4} \right)^{1/3}}{K} \right)^{1/2} \approx \frac{1}{1.25 \cdot K^{1/3}} \]

In order to study equilibria above the dissociation curve for pure water (fig. 2), on the other hand, it is necessary to mix \( O_2 \) with the \( H_2O \). At moderate or low temperatures, where the dissociation of water is small, this amounts to practically the same as mixing \( O_2 \) with an inert gas; the partial pressure of \( O_2 \) in the mixture is practically the same as the proportion of \( O_2 \) mixed with the gas.

It will be observed that some of the boundary curves in figure 2 have a positive slope, some have a negative slope, and one (the Fe—wüstite and Fe—liquid oxide boundary) is practically vertical. The latter case illustrates a situation in which the ratio \( p_{n_{FeO}}/p_{n_{Fe}} \) of the gas in equilibrium with the two condensed phases remains essentially constant over a large temperature interval (1000-1600°C). The reason for this is that the heat of reduction of iron oxide to Fe is balanced by an almost identical heat effect of opposite sign, the oxidation of \( H_2 \) to \( H_2O \):

\[ \text{FeO} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O} \]

Therefore, \( \Delta H^0 \) for this reaction is very small, and the equilibrium constant (ratio \( H_2O/H_2 \)) is almost independent of temperature. Curves with positive slope (for example the Fe—Fe₃O₄ boundary curve) result when the heat of reduction of the oxide to the next lower oxide or to metallic iron is larger than the heat of oxidation of \( H_2 \) taking part in the reaction. Conversely, the negative slope of the hematite-magnetite boundary curve illustrates an example of an overall exothermic reaction.

The diagram in figure 3 shows equilibrium ratios \( p_{CO_2}/p_{CO} \) of the gas phase in stable equilibrium with condensed phases in the system Fe—O, as a function of temperature. The diagram has been constructed from the same data as explained in connection with figure 2. It will be observed that the two diagrams in figures 2 and 3 are almost identical. The reason for this is that the dissociation constants of \( H_2O \) and \( CO_2 \) are closely similar, the former being slightly higher at temperatures above 800°C, the latter being slightly
higher at lower temperatures. The various lines have the same meanings as in
the last diagram (fig. 2) with $p_{CO_2}/p_{CO}$ ratios replacing the $p_{H_2O}/p_{H_2}$ ratios.
An additional line of great importance in the present case is the dash-double
cross line illustrating $p_{CO_2}/p_{CO}$ ratios in equilibrium with graphite according
to the equation

$$2CO_{(g)} = C_{(c)} + CO_2_{(g)}$$

This line indicates limiting ratios of $p_{CO_2}/p_{CO}$ at various temperatures. If,
at a chosen temperature, $CO_2/CO$ ratios of the gas phase are decreased from
a value represented by a point in the upper part of the diagram, graphite
starts depositing, with $CO_2/CO$ ratio remaining constant, when the latter ratio
reaches a value corresponding to the point on the dash-cross curve for this
temperature. The reaction $2CO_{(g)} = C_{(c)} + CO_2_{(g)}$ is strongly exothermic,
as evidenced by the steep negative slope of the dash-cross curve in figure 3.
In order to obtain a gas with low $CO_2/CO$ ratios, it is therefore necessary to
go to high temperatures. It will be noticed that the dash-double cross line
intersects the Fe$_3$O$_4$—FeO and the FeO—Fe boundary curves at approximately
660 and 720°C, respectively. These are the lowest temperatures at which
wüstite and metallic iron, respectively, can exist in equilibrium with C - O
gases. This relationship of course is of fundamental importance for an understand-
ing of the blast furnace process, and has some important implications in
certain fields of geochemistry. During the last couple of years geochemists
have taken a great deal of interest in equilibrium relationships of carbonates
at high $CO_2$ pressures. (See for instance papers by Harker and Tuttle, 1956;
Harker and Hutta, 1956). One of the carbonates of great interest in geo-
chemistry is siderite (FeCO$_3$). The graph in figure 3, although constructed
for a total pressure of 1 atm., may be used to judge the possibility of studying
experimentally the reaction

$$FeCO_3_{(c)} = FeO_{(c)} + CO_2_{(g)}$$

It is evident from the diagram that a considerable proportion, the exact
amount depending on temperature, of CO must be mixed with the $CO_2$ in
order to prevent oxidation of FeO to Fe$_3$O$_4$. (See curve III in fig. 3). The
disproportionation of CO to $CO_2$ and C, represented by the dash-double cross
curve, however, puts a limit on the $CO/CO_2$ ratios that can be reached. The
intersection between this curve and curve III at 660°C defines a limiting tem-
perature below which FeO can not exist as an equilibrium phase in the
presence of C and O at a total pressure of 1 atm. Higher pressures will cause
a shift in the dash-double cross curve towards the right, while the boundary
curve III may be expected to be comparatively little affected by an increase
in pressure. The lowest temperature at which siderite may be decomposed to
give wüstite as an equilibrium phase, therefore, is higher than 660°C at high-
er pressures. The metastable equilibrium FeCO$_3$ = FeO + $CO_2$ may be
calculated, below these temperatures, from experimental equilibrium data on
the reaction $3FeCO_3 = Fe_3O_4 + CO + 2CO_2$, if such become available,
combined with thermodynamic data referred to above (Darken and Gurry,
1945, 1946; Coughlin, 1954).
Fig. 4. Diagram to show phase equilibrium relationships in the system Fe—O, mainly after Darken and Gurry (1945, 1946). Heavy solid lines are boundary curves separating phase areas labelled in the diagram and light dash-dot lines are $O_2$ isobars (in atm.). Dashed curves in upper right part of the system are inferred boundary curves in a region where experimental data are lacking ($p_{O_2}>1$ atm.).

The diagrams presented in figures 2 and 3 have one serious drawback: They do not show compositions of condensed phases. It is of course possible to draw a phase diagram for the system Fe—O showing compositions of condensed phases. This indeed has been done: the most complete diagram is that presented by Darken and Gurry (1945). They plot the diagram in the usual way with temperatures (in °C) along the vertical axis and composition (expressed in weight % O) along the horizontal axis. Their diagram also has one serious drawback, however: It does not show compositions of the gas phase in equilibrium with the condensed phases. The diagram presented in figure 4 of the present paper is intended to illustrate phase equilibria in the system Fe—O in a manner which eliminates the drawbacks mentioned above. The diagram is essentially a reproduction from Darken and Gurry (1946), the axes being temperature and composition. In addition to the boundary
curves shown in their diagram a family of curves representing equal values of partial pressures of \( O_2 \) of the gas phase in equilibrium with the condensed phases is shown in figure 4. It would be possible, similarly, to construct a family of curves representing equal \( p_{H_2} / p_{H_2O} \) or \( p_{CO_2} / p_{CO} \) ratios of the equilibrium gas phase.

The relationships among the various types of representations should be kept clearly in mind in the use of the diagrams in figures 2-4. In figures 2 and 3 each area corresponds to a situation where one condensed phase, as labelled in the diagram, exists in equilibrium with a gas. Boundary curves in the same two diagrams represent situations where two condensed phases and a gas coexist in equilibrium. In figure 4, on the other hand, areas in the diagram may represent situations where either one or two condensed phases coexist in equilibrium with a gas phase. These observations are not conflicting. In figures 2 and 3 there is no axis to represent compositions of the condensed phases. The two condensed phases of different compositions existing in equilibrium along a boundary curve are therefore recorded in these diagrams by one point, namely that point representing the combination of temperature and \( H_2O/H_2 \) (or \( CO_2/CO \)) ratio at which these phases exist in equilibrium. In fig. 4, however, the axes have been chosen so that compositions of condensed phases are shown. Because the compositions of the condensed phases in equilibrium are different, the two phases are represented by separate points in this diagram. It is as if the boundary curves in figures 2 and 3 were “pulled out” to form areas in figure 4. In figures 2 and 3 adjacent phase areas are separated by boundary curves. In figure 4, correspondingly, each one-phase area (one condensed phase) must be limited on either side by an area where two condensed phases coexist in equilibrium with a gas phase. Because the system possesses two degrees of freedom when one condensed phase exists in equilibrium with a gas, both temperature as well as \( O_2 \) pressure or \( H_2O/H_2 \) (or \( CO_2/CO \)) ratio may vary in one-phase areas in figures 2-4. Therefore the lines representing \( O_2 \) isobars in figure 4 run diagonally across such areas. In a two-phase area (two condensed phases), on the other hand, only one degree of freedom exists and \( p_O2 \) as well as \( H_2O/H_2 \) (or \( CO_2/CO \)) ratios in the gas phase are fixed if the temperature is chosen. The \( O_2 \) isobaric lines therefore must be horizontal lines parallel to the composition axis in a two-phase region.

Ternary and Quaternary Iron Silicates.—The methods used for describing phase equilibrium relationships in the binary system \( Fe-O \) can be extended into the more complicated ternary and quaternary systems. As an illustration of the former, consider the system \( FeO-Fe_2O_3-SiO_2 \), which is part of the ternary system \( Fe-Si-O \). In the following we will focus our attention on the liquidus temperature region. In figure 5 is shown the usual plot of the projected liquidus surface with boundary curves and liquidus isotherms (Muan, 1955). When one crystalline and one liquid phase coexist with a gas phase, the system possesses two degrees of freedom. If temperature and liquid composition are chosen, \( O_2 \) pressures are fixed. It is therefore possible to draw a set of curves representing equal partial pressures of \( O_2 \)
Fig. 5. Phase equilibrium diagram at liquidus temperatures for the system FeO—Fe₂O₃—SiO₂ after Muan (1955). Light lines are liquidus isotherms at 100°C intervals, and heavy lines are boundary curves, with arrows pointing in directions of falling temperatures. The tridymite-cristobalite boundary curve is dashed. Medium lines with stippling on one side indicate limit of two liquid region.

(O₂ isobars) of the gas phase in equilibrium with condensed phases along the liquidus surface. These lines are extensions into the triangle representing the FeO—Fe₂O₃—SiO₂ system of points of intersection between O₂ isobars and the liquidus curve in the Fe—O system (fig. 4). An example of such lines is illustrated in figure 6 (Muan, 1955). Similarly, one may draw lines representing equal $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ (or $p_{\text{CO}_2}/p_{\text{CO}}$) ratios for points along the liquidus surface. Figure 7 gives an illustration of this for the system FeO—Fe₂O₃—SiO₂ (Muan, 1955). It will be noticed that the lines of equal $p_{\text{CO}_2}/p_{\text{H}_2}$ ratios are nearly parallel to the boundary curve between the fields of wüstite and metallic iron. This is in accordance with figure 3, where it was shown that this boundary curve is almost vertical (corresponding to constant $p_{\text{CO}_2}/p_{\text{CO}}$ ratio) over a large temperature interval.

This diagram shows lines representing equal $p_{\text{CO}_2}/p_{\text{H}_2}$ ratios rather than $p_{\text{CO}_2}/p_{\text{CO}}$ ratios. However, the numerical values of these ratios are almost identical because the equilibrium constant for the "water gas reaction" $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$ is not significantly different from 1 in the temperature interval considered.
Liquidus temperatures were chosen for illustration in the present case. One may of course construct $O_2$ isobars or lines representing equal $p_{H_2}/p_{H_2}$ (or $p_{O_2}/p_{O_2}$) ratios at other temperatures as well, above or below liquidus temperatures.

In order to illustrate the relationships of compositions of crystalline phases in equilibrium with liquid and gas, the above diagrams are supplemented by the fractionation curves shown in figure 8. Fractionation curves are constructed from conjugation lines in such a way that the conjugation lines are tangent to the fractionation curves. (A conjugation line joins the composition of a liquid with the composition of the crystalline phase with which it is in equilibrium). The composition of a crystalline phase in equilibrium with a liquid, therefore, may be derived from the diagram of figure 8 as the intersection with the join FeO—$Fe_2O_3$ of the tangent to the fractionation curve at the point representing liquid composition.

In the case of a quaternary system the principles are the same, but it is much more difficult to illustrate the relationships geometrically. Take as an
Fig. 7. Phase equilibrium diagram for the system FeO—Fe₂O₃—SiO₂. Heavy lines are boundary curves and dash-double dot lines are lines of equal pCO₂/pH₂ ratios of the gas phase in equilibrium with liquids at liquidus temperatures. Lines with stippling on one side indicate limit of two liquid region. (Diagram after Muan (1955)).

example the quaternary system MgO—FeO—Fe₂O₃—SiO₂ (Muan and Osborn, 1956). For our purpose it is most convenient to consider this system as formed from FeO—Fe₂O₃—SiO₂ by the addition of MgO. If, as before, we focus our attention on the liquidus temperature region, the O₂ isobars or the lines representing equal pCO₂/pH₂ ratios along the liquidus surface in the ternary system FeO—Fe₂O₃—SiO₂ are starting lines for irregularly curved surfaces ("oxygen isobaric surfaces") extending through the tetrahedron representing the MgO—FeO—Fe₂O₃—SiO₂ system. These surfaces are difficult to illustrate in perspective drawings of the tetrahedron. An indication of their location is obtained in the following way: Phase equilibria at an O₂ pressure represented by such a surface are illustrated by projecting points in the surface into a chosen plane cutting through the tetrahedron, preferably a plane located close to the surface in question. The actual location of composition points of the mixtures at liquidus temperatures, and hence the location of the

The system MgO—FeO—Fe₂O₃—SiO₂ is part of the quaternary system Mg—Fe—Si—O but is not in itself a completely quaternary system because metallic iron appears as a phase in certain composition-temperature ranges. For our purposes this may be disregarded, and the system will be considered quaternary.
Fig. 8. Diagram of the system FeO—Fe₂O₃—SiO₂ presented in order to illustrate relationship of compositions of liquid and crystalline phases in equilibrium, after Muan (1955). Heavy lines are boundary curves and medium dash lines are fractionation curves. Lines with stippling on one side indicate limit of two liquid region.

isobaric surface at liquidus temperatures, is indicated by lines in the projected diagram representing equal Fe₂O₃/FeO ratios. An example of this is given by the phase diagram MgO—FeO,Fe₂O₃—SiO₂ (fig. 9) drawn to represent phase relationships in the system MgO—iron oxide—SiO₂ in air (Muan and Osborn, 1956). Points located exactly in the plane chosen for projection have Fe₂O₃/FeO ratios of 2.22 (on a weight % basis). Mixtures located on the Fe₂O₃ side of this plane have Fe₂O₃/FeO ratios larger than 2.22, and mixtures located on the FeO side of the plane have Fe₂O₃/FeO ratios below this value.

Similarly, approximate locations of fractionation curves may be indicated by projecting them into a chosen plane. An example of this is shown in figure 10, representing phase equilibria in the system FeO—Fe₂O₃—Al₂O₃—SiO₂ in air (Muan, 1957).
Fig. 9. Diagram to illustrate phase relationships in the system MgO—FeO—Fe₂O₃—SiO₂ in air. For the sake of simplicity the relationships are pictured as a ternary system with MgO, FeO, Fe₂O₃, and SiO₂ as components. Heavy lines are boundary curves (these curves are not boundary curves in the strict meaning of the term as applied to ternary systems but rather traces of the curved boundary surfaces between two adjacent primary-phase volumes in the "plane" which the diagram represents), with arrows pointing in the directions of falling temperatures, and light solid lines are liquidus isotherms at 100°C intervals. Boundary curves and isotherms are drawn as dashed lines in regions where quenching data were not obtained. Light dash-triple dot lines are curves approximately passing through points of equal Fe₂O₃/FeO ratios at liquidus temperatures. Medium lines with stippling on one side indicate limit of two liquid region.

PATHS OF EQUILIBRIUM CRYSTALLIZATION

Phase equilibrium relationships can best be described by derivation of paths of equilibrium crystallization. This term has been used primarily by petrologists concerned with the differentiation of a magma into various minerals and rocks, but because of its general usefulness in phase equilibrium considerations it deserves much wider attention. As originally defined the path of equilibrium crystallization means the course along which the liquid composition changes as heat is withdrawn from the system under equilibrium conditions. It also, however, implies the changes taking place in the composition of the gas and crystalline phases during crystallization. In a wider meaning, therefore, the path of equilibrium crystallization is a continuous description of the changes in phase assemblage taking place as the tempera-
Fig. 10. Diagram of the system iron oxide Al₂O₃—SiO₂ in air presented in order to illustrate relationship of composition of liquid and crystalline phases in equilibrium. Heavy lines are boundary curves and medium dashed lines are fractionation curves. Lines with stippling on one side indicate limit of two liquid region. (Diagram after Muan (1957)).

ture is lowered from liquidus temperature, and equilibrium maintained among the phases. The same sequence of phase changes of course occurs upon heating under equilibrium conditions, only in the opposite direction, and one could equally well talk about a "path of melting". Thus a knowledge of the path of equilibrium crystallization in a system enables one to determine the composition of all phases present and their relative amounts at any temperature within the interval in which the system has been investigated.

In most dry oxide systems, where the gas phase can be neglected, the path of equilibrium crystallization can be derived on the assumption that the total composition of condensed phases remains constant. In systems where changes in oxidation states take place, this relationship usually does not hold. In reacting with the atmosphere, as temperature is changed, oxygen is added to or subtracted from the condensed phases concomitant to a proportional change in the MeOₓ/MeOᵧ ratio. The total composition of the condensed phases thus changes continuously during crystallization of the liquid, but only with respect to the relative proportions of the two components MeOₓ and MeOᵧ. This change can be described by straight lines passing through the O corner of the system in question. By combining these lines with liquidus isotherms, fractionation curves, O₂ isobars or lines of equal p⁺CO₂/p⁺H₂ ratios,
one is able to derive paths of equilibrium crystallization for various idealized conditions, which conditions in practice approach more or less closely. In the following, methods for derivation of paths of equilibrium crystallization in binary, ternary and quaternary systems involving changes in oxidation states will be reviewed briefly, using the systems Fe—O, FeO—Fe₂O₃—SiO₂ and MgO—FeO—Fe₂O₃—SiO₂ as examples. Four different idealized conditions will be considered:

1. Constant total composition of condensed phases
2. Constant O₂ pressure
3. Constant mixing ratio \( p_{\text{CO}_2} / p_{\text{N}_2} \) of the gas phase
4. Crystallization in contact with metallic iron

The first of these conditions is closely approximated in a closed system when the volume of the gas phase is small. Conditions under (2) and (3) are easily realized experimentally and have been used extensively in recent phase equilibrium studies (Muan, 1955; Muan and Osborn, 1956; Muan and Gee, 1956; Muan, 1957a, b). Finally, the fourth condition obtains under the experimental conditions first used by Bowen and Schairer for studying iron silicate systems (Bowen and Schairer, 1932). Throughout the following discussion it is assumed that perfect equilibrium exists among the phases. Also, it is assumed that no reaction takes place between the sample and the material of the crucible in which the sample is contained, except where iron crucibles are used (case 4 above).

The System Fe—O.—In a binary system the situation is usually so simple that the term path of equilibrium crystallization is rarely used at all. However, for the sake of completeness and because the present system is more complicated than ordinary dry binary systems, the relationships will be discussed briefly. Under conditions of constant total composition of condensed phases (case 1) the path of equilibrium crystallization can be read from the diagram in figure 4 by following a vertical (constant composition) line from high to low temperatures. For instance, a mixture of composition 24 weight \% oxygen will go through the following sequence of phase changes as heat is withdrawn from the closed system under equilibrium conditions. Above 1395°C the mixture is all liquid. At 1395°C the first traces of wüstite appear, and wüstite and liquid coexist in equilibrium over the temperature range 1395 to 1388°C. At the latter temperature the last trace of liquid disappears, and wüstite is the only condensed phase present in the interval 1388-740°C. Magnetite starts forming at 740°C, and this phase coexists in equilibrium with wüstite down to 560°C. At this temperature, corresponding to an invariant situation, the four phases wüstite, magnetite, metallic iron, gas are present together in equilibrium. Finally, below 560°C metallic iron and magnetite are the stable condensed phases. During the crystallization process the O₂ pressure changes continuously in a manner which may be read directly off the diagram in figure 4. The intersection of the vertical (constant composition) line and the O₂ isobar at any temperature gives the equilibrium O₂ pressure of the gas phase.

At constant O₂ pressure (case 2) the path of equilibrium crystallization
coincides with the O$_2$ isobar corresponding to the chosen O$_2$ pressure. As an example, consider crystallization at a constant O$_2$ pressure of 10$^{-8}$ atm. Above 1626°C a metallic liquid is the only condensed phases present. At 1626°C a metallic liquid and an oxide liquid coexist in equilibrium with the gas phase. Between 1626 and 1397°C liquid oxide is the only condensed phase existing under equilibrium conditions. At 1397°C liquid and crystals of wüstite and gas are present together in equilibrium. In the temperature interval 1397-1280°C wüstite is in equilibrium with the gas, and at 1280°C wüstite and magnetite coexist with the gas. From 1280 to 840°C magnetite is the stable phase in an atmosphere of this O$_2$ pressure. At 840°C, magnetite and hematite coexist, and below 840°C hematite is in stable equilibrium with the gas. One important difference between this case and the case discussed under (1) should be emphasized: In the present case two condensed phases (such as for instance liquid and wüstite) can coexist in equilibrium only at one temperature. This is because we have “used up” one degree of freedom by choosing the O$_2$ pressure. Under the conditions stipulated under (1), however, no restrictions in the sense of the phase rule are imposed on the system, and two condensed phases can coexist over a temperature interval.

The third case, crystallization under conditions of constant p$_{O_2}$/p$_{H_2}$ ratios of the gas phase, is very similar to the case just discussed and needs no special description. Lines of equal p$_{O_2}$/p$_{H_2}$ ratios are paths of equilibrium crystallization under these conditions.

If the crystallization takes place in contact with metallic iron (case 4), the changes in phase assemblage can be read from the diagram (fig. 4) by following the boundary curve between metallic iron and the lowest stable oxide, from high to low temperatures. Between 1535 and 1524°C solid iron is in equilibrium with a metallic liquid and gas. At 1524°C solid iron, a metallic liquid and an oxidic liquid coexist in equilibrium with gas. Between 1524 and 1371°C liquid oxide is in equilibrium with iron and gas. In the temperature interval from 1371 to 560°C wüstite is the equilibrium condensed phase in contact with iron, and below 560°C magnetite coexists in equilibrium with iron. Again, the variation in O$_2$ pressure during crystallization is determined as the intersections between the O$_2$ isobars and the boundary curve along which iron is one of the equilibrium phases.

*The System FeO—Fe$_2$O$_3$—SiO$_2$.*—Paths of equilibrium crystallization under conditions of constant total composition of condensed phases (case 1) can be derived by methods analogous to those used for ordinary dry silicate systems. Such methods have been described in detail in many papers emanating from the Geophysical Laboratory of the Carnegie Institution of Washington. The application of these principles to the system FeO—Fe$_2$O$_3$—SiO$_2$ has been described in detail elsewhere (Muan, 1955). Only one example will be given here for the purpose of illustrating the general relationships. The crystallization paths can be derived from diagrams showing liquidus isotherms (fig. 5). O$_2$ isobars along liquidus surface (fig. 6) and fractionation curves.

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(fig. 8) on the basis of the assumption that the total composition of condensed phases remains constant.

![Diagram of oxide system](image)

Fig. 11. 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. Heavy lines are boundary curves, medium solid line equilibrium crystallization curve and medium dash lines fractionation curves. Light solid lines are liquidus isotherms, light dash-dot lines O$_2$ isobars for points on liquidus surface, and light dash lines conjugation lines. (Diagram after Muan (1955)).

On the basis of these diagrams, paths of equilibrium crystallization for a part of the system FeO—Fe$_2$O$_3$—SiO$_2$ are shown in figure 11. Heavy lines are boundary curves. Medium dash lines are fractionation curves, medium solid lines are equilibrium crystallization curves and light dash lines are conjugation lines. Light solid lines are liquidus isotherms and light dash-dot lines are O$_2$ isobars.

Mixture D is chosen to illustrate paths of crystallization in the field of wüstite. At approximately 1370°C wüstite starts separating out and the liquid composition moves along the equilibrium crystallization curve D-d (medium solid line). The composition of the wüstite in equilibrium with liquid, determined by the tangent to the fractionation curve through the points representing liquid composition, changes continuously from d'" (31 weight % Fe$_2$O$_3$) to d'"" (28 weight % Fe$_2$O$_3$). Fayalite starts separating out together with
wüstite from the liquid at point \( d \), and the liquid composition moves along the boundary curve wüstite-fayalite towards \( d' \). From the point \( d \) where the boundary curve is reached, a reversal occurs in the direction of change in composition of wüstite. The \( \text{Fe}_2\text{O}_3 \) content increasing as the liquid composition moves along the boundary curve. The liquid disappears at point \( d' \), the end product being a mixture of fayalite and wüstite. The composition \( d'''' \) of wüstite at this point, determined by the conjugation line \( d''-d'''' \), falls on the extension of the straight line from \( 2\text{FeO} \cdot \text{SiO}_2 \) through point \( D \). During the crystallization process, the \( \text{O}_2 \) pressure changes continuously. It first decreases along the curved path \( D-d \) from approximately \( 10^{-8} \) atm. at \( D \) to \( 10^{-10.5} \) atm. at \( d \). From here on, with fayalite and wüstite coprecipitating, the change in \( \text{O}_2 \) pressure reverses itself, increasing to approximately \( 10^{-10.4} \) atm. at point \( d' \).

In contrast to this behavior, consider the path of crystallization at constant \( \text{O}_2 \) pressure. This case, likewise, has been discussed in detail in a previous publication (Muan, 1955). Under these conditions of crystallization, the composition of the condensed phases does not in general remain constant during the process. By reacting with the gas phase, oxygen is continuously added to or subtracted from the condensed phases as temperature varies, concomitant to a proportional change in \( \text{Fe}_2\text{O}_3/\text{FeO} \) ratio of condensed phases, while the amount of the other constituent (\( \text{SiO}_2 \)) remains unchanged. These compositional changes are described by straight lines pointing to the \( \text{O} \) corner of the triangle representing the system \( \text{Fe}--\text{Si}--\text{O} \), of which \( \text{FeO}--\text{Fe}_2\text{O}_3--\text{SiO}_2 \) is a part. In the previous discussion of this system (Muan, 1955) these lines were referred to as iso-silica lines to designate the constant amount of \( \text{SiO}_2 \) present in the condensed phases during the reaction between condensed phases and gas. These lines have the same meaning as the curves referred to as dissociation paths by Richards and White (1954). Because oxygen can either be added to or subtracted from the condensed phases, the term oxygen reaction lines seems more appropriate and will be used as a general term to designate these lines in this and in future papers from this laboratory. An example of path of crystallization at constant \( \text{O}_2 \) pressure is illustrated in figure 12. Here the same line symbols have been used as before and in addition dash-cross lines are used to indicate changes in total composition of condensed phases.

In mixture \( C \) wüstite starts separating out at about \( 1350^\circ\text{C} \), and as heat is withdrawn, the liquid composition moves along the wüstite liquidus surface following the \( 10^{-8} \) atm. isobar. The wüstite composition changes continuously in a way which can be derived from the fractionation curves. These curves are not drawn in figure 12, in order to avoid the confusion caused by too many lines. When the liquid composition reaches point \( c \), wüstite disappears and magnetite starts separating out with temperature remaining constant. When the last trace of wüstite disappears, the liquid composition starts moving along the magnetite liquidus surface following the \( 10^{-8} \) atm. isobar, with magnetite continuously separating out. When the boundary curve magnetite-tridymite is reached, at point \( c' \), the liquid disappears, leaving as end product a mixture of magnetite and tridymite. The total composition during this
Fig. 12. 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. 11 light dash-cross lines are used to represent changes in total composition of condensed phases during crystallization, and lines with stippling on one side indicate limit of two liquid region. (Diagram after Muan (1955)).

Process changes along the straight line from C to C'. The sudden discontinuous change in total composition of condensed phases as a boundary curve is reached (points c and c' in fig. 12) is analogous to the change along a horizontal line in a two phase (two condensed phases) region in the system Fe—O (fig. 4). This situation is caused by the requirement of disappearance of one phase before the temperature can change due to the restrictions imposed on the system resulting from our choosing the O₂ pressure.

An O₂ isobaric section through the ternary system FeO—Fe₂O₃—SiO₂ is not a true binary system, because the compositions of all phases cannot be represented in terms of two chosen components. However, aside from this limitation, the system can be treated like a binary system as far as the crystallization process is concerned. The liquid compositions will always be represented by points along the O₂ isobar in question, regardless of the nature of the crystalline phases separating out, whether they be pure phases or solid solution crystals. The O₂ of the atmosphere acts as a regulator to bring the
liquid composition back to its equilibrium value in spite of the crystallizing solids trying to bring the liquid compositions off the isobar. The lowest temperature at which a liquid can exist in equilibrium under these conditions, therefore, is the lowest liquidus temperature along the O₂ isobar corresponding to the chosen atmosphere.

Crystallization under conditions of constant $p^{\text{O}_2}/p^{\text{H}_2}$ ratio (case 3) is so similar to the case considered above that no special discussion of this case is necessary. The relationships are analogous to the above, with lines of equal $p^{\text{O}_2}/p^{\text{H}_2}$ ratios replacing O₂ isobars (fig. 7).

Crystallization in contact with metallic iron is a situation corresponding to the experimental conditions used by Bowen and Schairer (1932). The path of equilibrium crystallization in the FeO—Fe₂O₃—SiO₂ system under these conditions are the boundary curves between the field of metallic iron and, with increasing SiO₂ content, wüstite, fayalite, tridymite, cristobalite, in that order (figs. 5-7). A mixture whose composition is located at the boundary curve metallic iron—wüstite behaves as follows: Above liquidus temperatures¹³ a liquid oxide phase is in equilibrium with iron. As temperature is lowered below the liquidus, wüstite crystallizes out, with liquid composition changing along the boundary curve. At 1177°C the liquid is also saturated with fayalite, and this phase starts separating out, with temperature remaining constant as heat is withdrawn from the system. As the last trace of liquid disappears, temperature decreases, with wüstite and fayalite coexisting with metallic iron below 1177°C (but above 560°C). In a mixture of composition located at the boundary curve between the fayalite composition¹⁴ and the 1177°C peritectic, fayalite crystallizes out, with liquid composition changing along the fayalite-iron boundary curve until the temperature of 1177°C is reached. At this temperature the liquid disappears, leaving as end product a mixture of fayalite and wüstite in equilibrium with metallic iron. A mixture with a composition corresponding to fayalite¹⁴ is all liquid above 1205°C (Bowen and Schairer, 1932). At this temperature the mixture crystallizes completely to fayalite in equilibrium with metallic iron. Similarly, any mixture of composition on the SiO₂ side of the fayalite composition crystallizes to a mixture of fayalite and tridymite at the peritectic temperature of 1178°C. Fayalite is the primary crystalline phase in mixtures located between 2FeO;SiO₂ and this peritectic, while tridymite or cristobalite is the primary phase in mixtures located between SiO₂ and the peritectic composition. The system iron oxide—SiO₂ in contact with metallic iron is not truly binary, because compositions of condensed phases can not be represented in terms of two chosen components. Aside from this limitation, however, the path of crystallization can be treated in a manner analogous to that for a binary system. The usual representation of the system in terms of a projection into the join FeO—SiO₂ as illustrated in figure 13, after Bowen and Schairer (1932), is therefore very instructive and quite sufficient for most purposes. It should be pointed out

¹³ Liquidus temperature is used here to indicate highest temperature of stable existence of a crystalline oxide phase.

¹⁴ The exact location of this composition is determined as the point of intersection between the boundary curve and the oxygen reaction line passing through the 2FeO;SiO₂ composition point.
specifically, however, that the apparent eutectics in the join FeO—SiO₂ are in reality peritectics in the ternary system FeO—Fe₂O₃—SiO₂.

![Diagram illustrating phase equilibrium relationships at liquidus temperatures in the system iron oxide—SiO₂ in contact with metallic iron. The diagram has been plotted with the appearance of a binary system with FeO and SiO₂ as components. (After Bowen and Schairer (1932)).](image)

The System MgO—FeO—Fe₂O₃—SiO₂.—Crystallization under conditions of constant total composition of condensed phases is analogous to the situation in ordinary dry oxide systems. Methods for describing path of crystallization in dry quaternary silicate systems have been discussed in the literature. Applications of such methods to the system MgO—FeO—Fe₂O₃—SiO₂ were discussed in detail in a previous paper from this laboratory (Muan and Osborn, 1956). Suffice it here to summarize the relationships briefly: In figure 14 the system MgO—FeO—Fe₂O₃—SiO₂ is illustrated as a regular tetrahedron. Quaternary univariant lines along which three crystalline phases, one liquid and a gas phase coexist in equilibrium, extend through the tetrahedron from the left hand face to the right hand face. As an example of crystallization at constant total composition consider a mixture of composi-

*Compare footnote 12.*
Fig. 14. Diagram illustrating phase relationships in the system MgO–FeO–Fe₂O₃–SiO₂, after Muan and Osborn (1956). The system is pictured as a regular tetrahedron with one component at each apex. Compounds, with compositions given in terms of the components, are plotted in weight per cent. The plane MgO–FeO–Fe₂O₃–SiO₂ is indicated with light solid lines. Boundary curves are drawn as medium solid lines in the base (the system MgO–FeO–SiO₂) and in the right-hand face (the system FeO–Fe₂O₃–SiO₂) and as light lines in the plane MgO–FeO–Fe₂O₃–SiO₂ (corresponding approximately to the system MgO–FeO–Fe₂O₃–SiO₂ in air). Quaternary univariant lines, extending into the tetrahedron from the bounding ternary systems, are also drawn as medium solid lines. Medium dashed lines represent inferred boundary curves in the bounding ternary systems MgO–FeO–Fe₂O₃ and MgO–FeO–Fe₂O₃. Medium lines with stippling or one side indicate limit of region of coexistence of two silicate liquids.

...gion c as illustrated in figure 15. This point is located on the univariant line along which magnesioferrite, pyroxene, olivine, liquid and gas exist together in equilibrium. Immediately above liquidus temperature a liquid of composition c is in equilibrium with gas. At liquidus temperature, magnesioferrite (composition c'), pyroxene (composition c''), and olivine (composition c'''), start separating out, and as heat is continuously withdrawn from the system, the liquid composition changes to the right along the boundary curve from c.
toward $m$. As crystallization proceeds, the three crystalline phases change compositions along the joins MgO.\textsubscript{2}Fe\textsubscript{2}O\textsubscript{3}—FeO.\textsubscript{2}Fe\textsubscript{2}O\textsubscript{3}, MgO.\textsubscript{Si}O\textsubscript{2}—FeO.\textsubscript{Si}O\textsubscript{2}, and 2MgO.\textsubscript{Si}O\textsubscript{2}—2FeO.\textsubscript{Si}O\textsubscript{2} respectively, and the $O_2$ pressure decreases continuously. When the liquid composition reaches point $m$, the crystalline phases in equilibrium have the compositions $m'$, $m''$, and $m'''$ respectively. These points are located so that point c, representing the constant total composition, falls in the plane $m'-m''-m'''$. Complete crystallization therefore takes place when the liquid reaches point $m$. The final product is a mixture of magnesioferrite of composition $m'$, pyroxene of composition $m''$, and olivine of composition $m'''$.

![Diagram](image)

**Fig. 15. Diagram to illustrate paths of equilibrium crystallization for mixtures in the system MgO—FeO—Fe\textsubscript{2}O\textsubscript{3}—SiO\textsubscript{2} under conditions of constant total composition of condensed phases.** Open circles and solid dots represent compositions of liquid and crystalline phases, respectively, for mixtures whose paths of crystallization are discussed in the text. Light solid lines indicate the joins MgO.\textsubscript{2}Fe\textsubscript{2}O\textsubscript{3}—FeO.\textsubscript{2}Fe\textsubscript{2}O\textsubscript{3}, MgO.\textsubscript{Si}O\textsubscript{2}—FeO.\textsubscript{Si}O\textsubscript{2}, and 2MgO.\textsubscript{Si}O\textsubscript{2}—2FeO.\textsubscript{Si}O\textsubscript{2}. The two shaded triangular planes are formed by lines connecting points representing compositions of crystalline phases in equilibrium with liquid at the quaternary univariant situation. (Diagram after Muan and Osborn (1956)).

A mixture located in the plane $g'-g''-g'''$ will crystallize completely only after the liquid composition has reached point $g$. Here $g'$, $g''$ and $g'''$ represent compositions of magnesioferrite, pyroxene and olivine, respectively, that together with tridymite are in equilibrium with melt of composition $g$ at the
quaternary liquidus invariant point. Thus, under conditions of constant total composition of condensed phases, the lowest temperature of liquid existence in a quaternary system is the temperature of a liquidus invariant point (eutectic or peritectic) or the temperature of that point on a quaternary univariant line representing composition of the liquid phase in equilibrium with crystalline phases whose composition points form a plane in which the composition of the original starting mixture is located.

Fig. 16. Diagram to illustrate paths of equilibrium crystallization for mixtures in the system MgO—FeO—Fe₂O₃—SiO₂ in air. Open circles and solid dots represent compositions of liquid and crystalline phases, respectively. Light solid lines indicate the joins MgO,Fe₂O₃—FeO,Fe₂O₃, MgO,SiO₂—FeO,SiO₂, and 2MgO,SiO₂—2FeO,SiO₂ and outlines of the plane MgO—FeO,Fe₂O₃—SiO₂. Medium solid lines are boundary curves. The shaded planes are formed by lines connecting points representing compositions of crystalline phases. (Diagram after Muan and Osborn (1956)).

In contrast to this behavior, consider crystallization at constant O₂ pressure, as demonstrated by a specific case illustrated in figure 16. Crystallization in air is chosen as an example, i.e. at a constant O₂ pressure of 0.21 atm. Compositions of mixtures at liquidus temperatures in air are located in an irregularly curved surface, the 0.21 atm. O₂ isobaric surface, which extends into the tetrahedron from the corresponding isobaric line in the system FeO—Fe₂O₃—SiO₂ (fig. 6). For the sake of simplicity this O₂ isobaric surface has been pictured as a plane MgO—FeO,Fe₂O₃—SiO₂ in figure 16. Consider a mixture of composition represented by point N on the boundary curve between tridymite and magnesioferrite in this plane. At the liquidus temperature for
this mixture, liquid of composition \( N \) is in equilibrium with infinitesimal amounts of tridymite (\( \text{SiO}_2 \)) and magnesioferrite of composition \( n' \). With magnesioferrite of changing composition and tridymite crystallizing out together, the liquid composition moves along the boundary curve in the surface \( \text{MgO} - \text{FeO.Fe}_2\text{O}_3 - \text{SiO}_2 \). The total composition during this process changes along the oxygen reaction line through the point of original composition from \( N \) in the direction toward \( N' \). Complete crystallization takes place when the liquid composition reaches point \( p \), at which point the magnesioferrite has a composition \( p' \). This latter point is located so that a line from the silica corner to \( p' \) goes through \( N' \), the point of intersection of the oxygen reaction line with the plane \( \text{MgO.Fe}_2\text{O}_3 - \text{FeO.Fe}_2\text{O}_3 - \text{SiO}_2 \). The final product is thus a mixture of tridymite and magnesioferrite of composition \( p' \), the relative amounts being determined by the ratio \( N'p'/\text{SiO}_2N' \).

Similarly it can be shown that all mixtures in the plane \( \text{MgO} - \text{FeO.Fe}_2\text{O}_3 - \text{SiO}_2 \) located on the \( \text{SiO}_2 - \text{FeO.Fe}_2\text{O}_3 \) side of the dashed curve from \( \text{SiO}_2 \) to \( q \) will crystallize completely to a mixture of magnesioferrite and tridymite. The significance of the dashed line \( \text{SiO}_2 - q \) is the following: As the liquid composition changes along the tridymite-magnesioferrite boundary curve from \( r \) to \( d \), the magnesioferrite composition changes continuously from \( \text{FeO.Fe}_2\text{O}_3 \) to \( d' \) (\( d' \) is the composition of magnesioferrite in equilibrium with liquid \( d \)). For mixtures in the \( \text{MgO} - \text{FeO.Fe}_2\text{O}_3 - \text{SiO}_2 \) plane to crystallize completely to magnesioferrite and tridymite, the oxygen reaction line through the point of starting composition must intersect the plane \( \text{SiO}_2 - \text{FeO.Fe}_2\text{O}_3 - d' \). In other words, the oxygen reaction lines through the \( \text{SiO}_2 \) and \( d' \) edge of this plane, when cutting through the plane \( \text{MgO} - \text{FeO.Fe}_2\text{O}_3 - \text{SiO}_2 \) along the line \( \text{SiO}_2 - q \), separate the mixtures into two groups with respect to crystallization paths. Mixtures located on the \( \text{SiO}_2 - \text{FeO.Fe}_2\text{O}_3 \) side of the line \( \text{SiO}_2 - q \) crystallize completely to a mixture of magnesioferrite and tridymite at a temperature corresponding to the liquidus for a mixture of composition located on the boundary curve \( r - d \). Mixtures located on the other side of the line \( \text{SiO}_2 - q \) have oxygen reaction lines that intersect the plane \( \text{SiO}_2 - d'' = d''' \), \( d''' \) being the composition of the pyroxene in equilibrium with liquid of composition \( d \). The final product for these mixtures, therefore, is magnesioferrite, tridymite and pyroxene, and the last trace of liquid disappears at the liquidus temperature for a mixture of composition \( d \).

Noteworthy among the relationships explained above is the fact that the liquid composition during crystallization remains in the 0.21 atm. \( O_2 \) surface (here pictured as the plane \( \text{MgO} - \text{FeO.Fe}_2\text{O}_3 - \text{SiO}_2 \)). The reason for this is the same as explained for \( \text{FeO} - \text{Fe}_2\text{O}_3 - \text{SiO}_2 \). The \( O_2 \) of the atmosphere compensates for the tendency of the crystallizing solid phases to push the liquid composition out of the isobaric surface. Hence, at constant \( O_2 \) pressure, a liquid phase can never exist in equilibrium at a temperature lower than the lowest liquidus temperature in the \( O_2 \) isobaric surface corresponding to the chosen atmospheric conditions. This temperature is usually that correspond-

\[ \text{The oxygen reaction lines have a direction pointing towards the O apex of the ternary tetrahedron representing the system Mg} - \text{Fe} - \text{Si} - \text{O}, \text{and have the same significance as the corresponding lines for the system FeO} - \text{Fe}_2\text{O}_3 - \text{SiO}_2 \] (compare page 194).
ing to the intersection between the $O_2$ isobaric surface and a quaternary univariant line. Only on the $O_2$ isobaric surface which passes through the point representing composition of the liquid at a quaternary liquidus invariant situation will a liquid phase exist in equilibrium with four crystalline phases at the temperature of this situation. The isobaric surfaces are not true ternary systems, because the compositions of the phases can not be represented by three components. However, in spite of this limitation, in the derivation of paths of equilibrium crystallization at constant $O_2$ pressure, they can be treated like ternary systems.

The crystallization process at constant $CO_2/H_2$ ratios requires no detailed discussion. The relationships are analogous to above, with lines of equal $CO_2/H_2$ ratios replacing the $O_2$ isobars.

The paths of equilibrium crystallization of mixtures in the system $MgO—FeO—Fe_2O_3—SiO_2$ in contact with metallic iron can be derived by methods analogous to those described for the systems $FeO—O$ and $FeO—Fe_2O_3—SiO_2$. The small primary field of metallic iron in the $FeO—Fe_2O_3—SiO_2$ system (figs. 5-7) extends as a thin phase volume into the tetrahedron $MgO—FeO—Fe_2O_3—SiO_2$, adjacent to the basal plane $MgO—FeO—SiO_2$. This phase volume was left out of figures 14-16 in order to simplify the drawings. A pure iron oxide liquid in contact with metallic iron contains approximately 10 weight % $Fe_2O_3$ at liquidus temperature. As $SiO_2$ is added, the $Fe_2O_3/FeO$ ratio of the liquid in equilibrium with iron (see boundary curve between metallic iron and oxide phases in figs. 5-7) decreases. The decrease is caused by the increase in acidity of the liquid as $SiO_2$ content increases. This effect more than balances the opposite effect on $Fe_2O_3/FeO$ ratio of the decrease in liquidus temperatures caused by the first $SiO_2$ additions. As more $SiO_2$ is added, liquidus temperatures vary relatively little with $SiO_2$ content in the region where fayalite ($2FeO.SiO_2$) is the primary crystalline phase. When the liquid becomes saturated with $SiO_2$, liquidus temperatures rise sharply as $SiO_2$ content increases. This increase in liquidus temperatures magnifies the acidity effect of $SiO_2$ on $Fe_2O_3/FeO$ ratios, and hence the boundary curve between metallic iron and cristobalite approaches the join $FeO—SiO_2$ as the temperature of melting of iron is reached. As $MgO$ is added to silica-iron oxide mixtures, the basic character of $MgO$ may be expected to increase the $Fe_2O_3/FeO$ ratio of the liquid phase. However, the $MgO$ addition at the same time raises liquidus temperatures very markedly. The $Fe_2O_3$ content of liquids in equilibrium with metallic iron is therefore very low for all compositions in the system $MgO—iron oxide—SiO_2$ except those close to the iron oxide apex of the tetrahedron representing the system. The relationships can be seen quantitatively from the analytical data of Bowen and Schairer (1935). The $Fe_2O_3$ content is less than 2 weight % for most compositions, and hence

17 According to Darken and Gurry (1946) the $Fe_2O_3$ content is 8.22 weight %, while Bowen and Schairer (1932) give a value of 11.56 weight %.

18 A quantitative acid-base scale is not available for melts like we have for aqueous solutions. The term acid is used here to describe the behavior of an ion of high field strength ($Si^+$), in accordance with modern concepts of acid-base relationships in oxide systems (Weyl, 1956).
the iron phase volume extends only as a very thin slice into the tetrahedron of figures 14-16, adjacent to the basal plane.

It will be recalled that in the system FeO—Fe₂O₃—SiO₂ the path of crystallization for mixtures in contact with metallic iron was the boundary curve between metallic iron and the adjacent phase areas. In the present case, similarly, liquid compositions during crystallization must remain in the boundary surface between the primary phase volume of metallic iron and the adjacent phase volumes in the quaternary system, magnesio-wüstite, olivine, pyroxene, tridymite, cristobalite, depending on composition of the mixture. Projections of these phase volumes are indicated in figure 17, which is a reproduction of the system MgO—“FeO”—SiO₂ after Bowen and Schairer (1935). Their diagram is obtained by projecting actual compositions of mixtures located along the boundary surface limiting the iron phase volume, into the base (MgO—FeO—SiO₂) of the tetrahedron representing the MgO—
FeO—Fe₂O₃—SiO₂ system. Analogous to the situation in an O₂ isobaric section through the quaternary system, liquid compositions in the present case remain in a fixed surface, namely the surface bounding the phase volume of metallic iron. While in the former case reaction with oxygen of the gas phase was the mechanism for keeping the liquid composition in the appropriate surface, the same is accomplished in the present case by reaction of the oxide melt with the iron of the crucible in which the mixture is contained. Regardless of the nature of the crystalline phases separating out, the liquid composition remains in the surface bounding the phase volume of metallic iron. The system is not truly ternary under these conditions, because liquid compositions in the irregularly curved surface can not be represented in terms of three chosen components. However, aside from this limitation it can be treated like a ternary system. Because of the closeness of the iron boundary surface to the basal plane, MgO—FeO—SiO₂, the paths of crystallization can be discussed very satisfactorily in terms of a projection into this plane. The diagram obtained in this way has the appearance of a ternary system, and was treated as such by Bowen and Schairer. The reader is referred to their paper for a detailed discussion of paths of equilibrium crystallization. It should be kept clearly in mind, however, that the condensed phases contain some Fe³⁺, and that metallic iron is present as a phase in addition to the oxide phases, Hence apparent ternary invariant situations in the projected diagram are actually quaternary liquidus invariant situations with metallic iron as one of the crystalline phases present.

**SUMMARY**

Phase equilibrium studies of oxide systems at high temperatures have been restricted in the past largely to systems containing only oxides of noble gas type ions such as for instance CaO, MgO, Al₂O₃, SiO₂. Data are essentially lacking on oxide systems involving elements where changes in oxidation states occur. The study of the latter systems is complicated because the composition of the gas phase must be controlled carefully and varied between wide limits. At reasonably high levels of O₂ pressures (1 atm.—10⁻³ atm.) such equilibria may be studied experimentally in O₂ atmospheres where the desired pressure is adjusted by vacuum techniques or by mixing O₂ with an inert gas. When the partial pressure of O₂ becomes low (<10⁻³ atm.) the gas phase is so dilute in O₂ that a very substantial volume of gas would be necessary to change the composition of the condensed phases to the equilibrium value. With a moderate rate of flow of gas through the furnace in which the equilibrium study is made, it is therefore not possible to reach equilibrium within a reasonable period of time. In such cases indirect methods of obtaining the desired O₂ pressure must be used. The most convenient method is to use a mixed gas system containing an O₂ bearing species which upon heating dissociates under liberation of O₂. Convenient gases for this purpose are CO₂ or H₂O. The degree of dissociation and hence the O₂ pressure may be controlled by mixing CO or H₂ with the gas in controlled proportions.

Most of the few available phase diagrams for oxide systems involving changes in oxidation states are very incomplete. In addition to the usual
representation of composition of condensed phases such diagrams should contain information regarding the equilibrium composition of the gas phase as well. It is suggested that binary systems be represented in an usual composition-temperature diagram with O₂ isobars or lines of equal CO₂/H₂ equilib-rium ratios superimposed to indicate gas composition. In ternary systems showing phase relationships at liquidus temperatures the ordinary projection of liquidus surface with liquidus isotherms should be supplemented by di-agrams showing O₂ isobars (or lines of equal pCO₂/pH₂ ratios) along the liquidus surface and fractionation curves. Quaternary systems are difficult to represent graphically. Phase relationships at liquidus temperatures are best illustrated by projecting compositions from their actual locations in irregularly curved O₂ isobaric surfaces into chosen planes. In the resulting diagrams, which have the appearance of ternary systems, the actual compositions of mixtures are indicated by lines of equal ratios (MeOₓ/MeOᵧ) of the oxides of the element with changing oxidation state (such as for instance Fe₂O₃/FeO).

Path of equilibrium crystallization is a term used for the continuous description of changes in phase assemblage taking place as heat is withdrawn from a system and equilibrium is maintained among the phases during the process. Iron oxides and iron oxide containing silicates are chosen as examples of paths of equilibrium crystallization in systems where changes in oxidation states occur. Four idealized conditions of crystallization are considered, each one corresponding to a situation which can be closely approximated experimentally. The first condition is that of crystallization at constant total composition of condensed phases. This situation is approximated in a closed system when the volume of the gas phase is small. The path of crystallization can be derived by well known methods by the use of diagrams showing liquidus isotherms, fractionation curves and O₂ isobars. The second condition is crystallization at constant O₂ pressure. In this case the criteria used for derivation of crystallization path in ordinary dry silicate systems are not appli-cable, because total composition of condensed phases does not in general remain constant. By reaction with the gas phase oxygen is added to or subtracted from the condensed phases concomitant to a proportional change in the oxide ratio MeOₓ/MeOᵧ. This composition change is described by oxygen reaction lines, which are straight lines pointing towards the O apex of the model representing the system in question. By choosing the O₂ pressure, we have “used up” one degree of freedom, and the system possesses one degree of freedom less than in the first case considered, for the same number of phases present. In a binary system, therefore, two condensed phases, such as for instance one crystalline and one liquid phase, can coexist only at one temperature at a chosen O₂ pressure. In a ternary system the O₂ isobars along the liquidus surface are the paths along which the liquid composition changes during crystallization. The lowest temperature of stable existence of a liquid phase is usually the intersection between a boundary curve and the O₂ isobar in question. In a quaternary system, similarly, the liquid composition remains in the particular O₂ isobaric liquidus surface corresponding to the chosen O₂ pressure. The lowest temperature of liquid formation under equilibrium con-
ditions is usually the intersection between a quaternary liquidus univariant line and the O₂ isobaric surface in question.

Crystallization under conditions of constant \( \frac{p_{CO_2}}{p_{N_2}} \) ratio is analogous to the case above, with \( \frac{p_{CO_2}}{p_{N_2}} \) ratios replacing the O₂ pressures in the discussion.

When crystallization takes place in contact with metallic iron, the liquid composition is forced to move along the boundary surface (or boundary curve) between the phase volume (area) of metallic iron and the adjacent oxide phase volumes (areas). In a binary system liquid oxide and a crystal-line oxide phase can coexist in equilibrium with iron at one temperature only. In a ternary system the lowest temperature of stable existence of an oxide liquid is usually the temperature of a liquidus invariant situation where metallic iron is one of the phases present. In a quaternary system the lowest temperature of liquid formation, likewise, is usually the temperature of one of the quaternary liquidus invariant situations where metallic iron is one of the phases present.

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