mole per cent. calcium oxide in strontium oxide, and 1 mole per cent. strontium oxide in calcium oxide.

The pronounced effect of oxide upon the luminescent properties of phosphors[9] suggested that solid solution with the sulfide or selenide might occur. The lattice constants obtained by fluxing strontium oxide and sulfide and oxide and selenide mixtures are shown in Table IV. It can be seen that the amount of oxide which disssolves in either selenide or sulfide is quite small and lies almost within the limits of determination by X-ray diffraction.

TABLE IV

LATTICE CONSTANTS OF MIXTURES CONTAINING OXIDE

Composition by weight		Fluxing time, hours	Lattice constant Å.	
Base	Flux		SrO	Other base
SrSe 5, SrO 5	LiF 1	30	5.145	6.230
SrSe 100, SrO 0, 1, 2, 4[a]	SrF_2 7.5, $SrSO_4$ 7.5	0.75		6.232
SrS 2, SrO 1	LiF 0.3	30	5.140	6.0050
SrS 100, SrO 3	LiF 9	1.5		6.0075
SrS 100, SrO 10	LiF 9	1.5		6.0070
SrS 100, SrO 2	$SrCl_2$ 12	1.5		6.0065

[a] Phillip's Straumanis camera used.

The intersolubility of magnesium sulfide with calcium and strontium sulfides was also tested by the same procedures. The lattice constants for these mixtures are listed in Table V and should be compared with the values for the pure sulfides given in Table I. There is very little intersolubility in the MgS–SrS systems but with the CaS–MgS system about 11 weight per cent. magnesium sulfide dissolves in the calcium sulfide and about 15 weight per cent. of calcium sulfide in the magnesium sulfide lattice. This is perhaps a greater intersolubility than one would expect with a difference in cationic radii of some 50 per cent.

TABLE V

LATTICE CONSTANTS OF MIXTURES CONTAINING MAGNESIUM SULFIDE

Composition by weight		Fluxing time, hours	Lattice constant, Å.	
Base	Flux		MgS	Other base
MgS 5, SrS 10	LiF 2.2	3	5.194	6.0058
SrS 10	LiF 0.5, MgF_2 1	3		6.0062
MgS 9, SrS 1	$SrCl_2$ 1	3		6.0012
MgS 6, SrS 4	$SrCl_2$ 1	1		6.0030
MgS 3, SrS 7	$SrCl_2$ 1	1		6.0020
MgS 1, CaS 5	NaCl 1.2	1		5.614
MgS 5, CaS 1	NaCl 1.2	1	5.251	

Acknowledgments.—The authors wish to thank Professor Fankuchen for his advice and Mr. Milton Schneider for his assistance in taking some powder diagrams. We are also indebted to Miss Hilda Texin and Messrs. Richard Hall and Kenneth Stripp for some of the samples used.

Summary

Precision lattice constants were determined for magnesium, calcium and strontium sulfides, strontium selenide, calcium and magnesium oxides. The extent of solid solution among these compounds and some of the methods for forming solid solutions were studied.

Complete intersolubility exists among calcium sulfide, strontium sulfide and strontium selenide. Magnesium and calcium sulfides are intersoluble to a limited extent. Solid solution formation among the other pairs appears to be negligible.

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[9] K. Stripp and R. Ward, THIS JOURNAL, 70, 401 (1948).

[CONTRIBUTION FROM RESEARCH LABORATORY, UNITED STATES STEEL CORPORATION, KEARNY, NEW JERSEY]

Melting Points of Iron Oxides on Silica; Phase Equilibria in the System Fe–Si–O as a Function of Gas Composition and Temperature

BY L. S. DARKEN

The phase relations in the ternary system Fe–O–Si are of considerable interest to the steel industry, particularly in two respects: (1) the oxidation (scaling) of silicon steels produces in some cases a subscale and in other cases a so-called "silicon skin" (mainly metallic Fe + SiO_2). Since the primary requisite for scaling is the production of a gradient of the partial pressure of oxygen in the vicinity of the surface scaled, it is believed that a knowledge of the stability of the different oxides under various partial pressures of oxygen will aid in interpreting the observed phenomena. (2) The behavior of refractories is influenced in some cases by the form of iron oxide contained therein or deposited thereon. This is particularly so in blast furnace brick, in which metallic iron is thought to act as a catalyst for the deposition of carbon which in extreme cases disintegrates the brick. It has been observed that brick fired at high temperatures are less susceptible to this form of attack. It seems reasonable that higher temperatures effect fusion of the iron oxides forming silicates, etc., which are less easily reduced and less catalytic. The present investigation demonstrates that the temperature of fusion of iron oxides in contact with silica is a rather sensitive function of gas composition (varying from 1120 to 1447°), hence that fusion may be accomplished in some cases by control of the gas atmosphere without changing the temperature.

Experimental Procedure and Data.—A number of the univariant equilibria in the oxide region of the ternary system Fe–Si–O are identical with those of the binary system Fe–O which have been investigated previously. Others may be estimated with sufficient precision from available data, though there are but few data on the influence of gas composition on the melting temperature of the oxides. The present experimental investigation was intended partially to fill this gap by determination of the relation between gas composition and temperature for the two univariant equilibria: silica, magnetite, melt, gas; and silica, fayalite, melt, gas.

In each experiment a silica rod (about 1 mm. diam., 5 cm. long) was coated with Fe_2O_3 by dipping it in an aqueous suspension of the latter. After the coated rod had dried, it was placed on a platinum suspension and hung in the gradient of a platinum-wound tubular furnace, which was controlled in the manner described previously,[1] the winding of the furnace acting as one arm of a bridge circuit which was automatically balanced. The desired atmosphere, usually delivered by a gas mixer, was introduced into the furnace (at atmospheric pressure) through the mercury seal at the bottom of the tube. The rate of flow of gas was about 50 cc. per minute, which is ample to avoid appreciable thermal separation of the gases. The time at temperature varied from fifteen minutes in some of the preliminary experiments to eighteen hours. If the temperature and gas composition were suitably chosen, the sample exhibited on removal a fairly sharp demarcation between the opaque fused region and the region in which no fusion had occurred. This transition is best seen by the naked eye using the sky as a background. In questionable cases, the demarcation was developed by immersing the rod in warm 6 *N* hydrochloric acid for a few minutes; the acid removed essentially all the iron from the unfused region, but had little effect on the fused portion. To determine the temperature, the position of the demarcation line was carefully measured and a thermocouple was inserted at the corresponding position in the furnace. If the temperature gradient in this region was too steep to yield the desired precision, the furnace temperature was readjusted so that on repetition of the experiment the transition occurred nearer the center of the furnace in a region of smaller temperature gradient.

After this temperature adjustment had been made, so that the transition in a given atmosphere occurred in a region where the gradient was about 10° per cm., the specimen was held at the determined position for different lengths of time to be sure that the observed demarcation line corresponded to equilibrium between the phases involved. Fusion of course proceeded from the hotter zone to the cooler. It was found that, within the limits of experimental measurement, motion of the boundary line between fused and unfused portions ceased after about one-half hour; however, the sharpness of the boundary line usually increased appreciably on longer treatment. For this reason, as well as to be sure of equilibration, all specimens were treated for sixteen hours. In each case a preliminary measurement was made, usually at the end of one hour, but at the lower temperatures, at a somewhat longer time. In all cases, the position of the demarcation line was the same at the end of sixteen hours as at the time of the previous preliminary measurement. The experimental data are recorded in Table I, and are presented graphically in Fig. 1 along with curves representing other equilibria subsequently discussed.

TABLE I

MELTING POINT OF IRON OXIDES IN CONTACT WITH SILICA AND VARIOUS ATMOSPHERES AT ONE ATMOSPHERE TOTAL PRESSURE

Atmosphere	Form of silica	Temperature, °C.
(the univariant equilibrium; silica, magnetite, melt, gas)		
Oxygen[a]	Vitreous	1447
Air	Vitreous	1442
$^1/_4$% O_2 in CO_2	Vitreous	1411
CO_2, CO; CO_2/CO = 308	Vitreous	1369
CO_2, CO; CO_2/CO = 79.2	Vitreous	1279
CO_2, CO; CO_2/CO = 52.8	Vitreous	1230
CO_2, CO; CO_2/CO = 26.0	Cristobalite	1159
CO_2, CO; CO_2/CO = 20.8	Vitreous	1131
(the univariant equilibrium; silica, fayalite, melt, gas)		
CO_2, CO; CO_2/CO = 14.1	Cristobalite	1120
CO_2, CO; CO_2/CO = 11.2	Cristobalite	1129
CO_2, CO; CO_2/CO = 4.02	Cristobalite	1139

[a] Actually the phases in equilibrium at this point are silica, hematite, melt and gas as may be seen from Fig. 1. It is, however, very nearly identical with quintuple point 1.

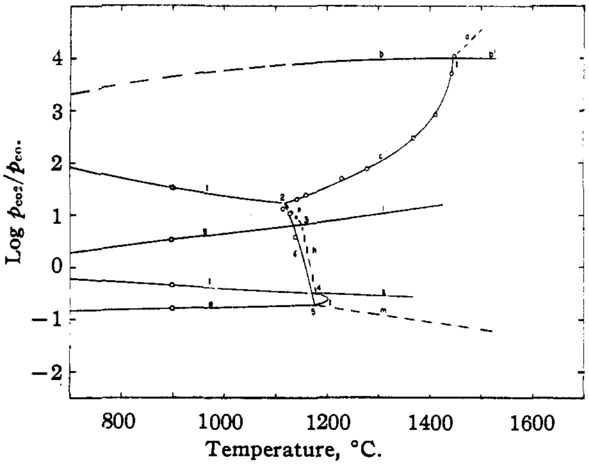

Fig. 1.—Relations between gas composition and temperature for the univariant equilibria of the system Fe–Si–O.

Since it is reasonable to expect a slight difference in equilibrium temperature depending on whether the solid silica phase is vitreous or crystalline, several determinations were made using a vitreous silica rod whose surface had been transformed to cristobalite. This conversion was accomplished by heating the rod at about 1500° for an hour; the success of this treatment was easily recognized by the shattering of the surface accompanying the high-low inversion of cristobalite (200–275°) as the specimen was cooled. From the data assembled by Mosesman and Pitzer[2] it is clear that the free energy difference between vitreous silica and any of the crystalline forms is greater, in the range covered, than the free energy difference between any two crystalline forms. Hence it is of negligible importance from the viewpoint of the present investigation that cristobalite was used, in spite of the fact that tridymite is the stable crystalline form in the temperature range investigated. Since the metastability of the vitreous form is greater at lower temperatures, it is evident that the observed temperature of the four phase equilibria would be most greatly influenced by the form of silica at the lower temperatures. For this reason, cristobalite was used in the case of all three measurements of the equilibrium between fayalite, silica, liquid and gas. Cristo-

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[1] Darken and Gurry, THIS JOURNAL, **67**, 1398 (1945).

[2] Mosesman and Pitzer, *ibid.*, **63**, 2348 (1941).

balite was also used in the case of one sample in the series determining the equilibrium between magnetite, silica, liquid, gas. Since this point falls on the same smooth curve as that for the points representing equilibrium with vitreous silica it is concluded that the influence of the form of silica is smaller than the experimental error, which is estimated to be about 5°.

Although the system investigated comprises four elements (iron, oxygen, silica, carbon) the solubility of carbon (or carbon monoxide or carbon dioxide) in the condensed phases is negligibly small in the region investigated; hence, the system may be regarded as a three component one. It is convenient, however, to give the pressure in terms of the ratio of carbon dioxide to carbon monoxide in the gas phase rather than in terms of the partial pressure of oxygen; it is clear that these are interconvertible by means of the equilibrium constant for the homogeneous gaseous reaction $CO + {}^1/_2O_2 = CO_2$. Values of this constant, calculated from the tabulated values of $(F^0 - E_0^0)/T$ for CO,[3] O_2,[4] and CO_2,[5] using the value of ΔE_0^0 given by Rossini,[6] were given by Darken and Gurry.[2] The uncertainty of this equilibrium constant is negligibly small compared to other errors involved in construction of the diagram.

Construction of the Remainder of the Diagram.—In order to construct the diagram (Fig. 1) showing the equilibrium ratio of carbon dioxide to carbon monoxide in the presence of various stable phases and at various temperatures the general procedure was as follows. The known invariant points (five phase equilibria) and the known univariant curves (four phase equilibria) or points thereon were plotted. A number of these are identical with the invariant curves of the binary system iron–oxygen. In general for a ternary system five univariant curves intersect at an invariant point; however, one of these univariant curves represents the small effect of pressure on the completely condensed system (no gas phase present), and does not appear in the representation chosen since the total pressure is essentially one atmosphere. Hence the construction consisted mainly of interconnecting the univariant curves to accord with this condition, using directly determined data together with indirect data related thermodynamically to the diagram.

There are five invariant points occurring in the region considered; at these points the following phases are in equilibrium (the numbers correspond to those in Fig. 1).

(1) hematite, magnetite, silica, melt, gas
(2) magnetite, fayalite, silica, melt, gas
(3) magnetite, wüstite, fayalite, melt, gas
(4) wüstite, fayalite, metal, melt, gas
(5) fayalite, metal, silica, melt, gas

Of the various stable phases listed, hematite (Fe_2O_3), fayalite ($2FeO{\cdot}SiO_2$), silica (SiO_2), and metal (Fe) are essentially of fixed composition; magnetite (Fe_3O_4) and wüstite ("FeO") are binary compounds containing no appreciable amount of silica, although the ratio of iron to oxygen is variable; the melt contains all three components in variable amounts.

There are fifteen univariant curves derived from these five invariant points. In addition to the gas phase the following phases are present along the univariant curves shown in Fig. 1.

(a) hematite, silica, melt
(b) hematite, magnetite, silica
(b′) hematite, magnetite, melt
(c) magnetite, silica, melt
(d) fayalite, silica, melt
(e) magnetite, fayalite, melt
(f) magnetite, fayalite, silica
(g) magnetite, wüstite, fayalite
(h) wüstite, fayalite, melt
(i) magnetite, wüstite, melt
(j) metal, fayalite, melt
(k) wüstite, metal, melt
(l) wüstite, fayalite, metal
(m) metal, silica, melt
(n) metal, fayalite, silica

Of these fifteen equilibria b, b′, g, i, k, and l are essentially identical with those of the binary system iron–oxygen determined in part by Darken and Gurry.[1,7] Equilibrium c and part of d was determined by the present investigation. Invariant points 1 and 2 are thus established by the intersection of b and c and of c and d, respectively. The temperature of invariant point 4 was determined by Bowen and Schairer[8] as 1175°; its position is thus fixed by this temperature and the fact that it lies on the curves *l* and *k*.

The equilibria of this system at 900° have been investigated by Schenck, Franz and Laymann,[9] whose data on the various univariant equilibria are thermodynamically consistent and in good agreement with the data of Darken and Gurry on the binary system iron–oxygen. At this temperature the ratio p_{CO_2}/p_{CO} is 0.163 for equilibrium n, and is 34.5 for equilibrium f.[10] Curve f is thus reasonably well established by this point at 900° and quintuple point 2 at 1118°. It was constructed under the assumption that $\log p_{CO_2}/p_{CO}$ is linear with $1/T$. Curve n is determined by the point at 900° and a calculated point[11]

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(3) Clayton and Giauque, THIS JOURNAL, **55**, 5071 (1933).

(4) Johnston and Walker, *ibid.*, **57**, 682 (1935).

(5) J. S. Kassel, *ibid.*, **56**, 1838 (1934).

(6) F. D. Rossini, *J. Research Nat. Bur. Standards*, **22**, 407 (1939).

(7) Darken and Gurry, THIS JOURNAL, **68**, 798 (1946).

(8) Bowen and Schairer, *Am. J. Sci.*, **24**, 177 (1932).

(9) Schenck, Franz and Laymann, *Z. anorg. allgem. chem.*, **206**, 126 (1932).

(10) The thermodynamic consistency of these values may be demonstrated in the following manner. The chemical reaction corresponding to equilibria f, g, l and n may be written

(f) $3(2FeO{\cdot}SiO_2) + 2CO_2 = 2Fe_3O_4 + 3SiO_2 + 2CO$
(g) $3FeO$ (in wüstite) $+ CO_2 = Fe_3O_4 + CO$
(l) $Fe + CO_2 = FeO$ (in wüstite) $+ CO$
(n) $2Fe + SiO_2 + 2CO_2 = 2FeO{\cdot}SiO_2 + 2CO$

It will be noticed that these four equations are not independent but that any one may be expressed in terms of the others—for example (f) = 6(l) + 2(g) − 3(n). The following relation must then hold between the thermodynamic equilibrium constants: $K_f = K_l^6K_g^2/K_n^3$. The values of K_l and K_g (including the activity of (FeO) were taken from Darken and Gurry[1] and that for K_n from Schenck, *et al.*[9] The calculated value for the ratio p_{CO_2}/p_{CO} corresponding to (f) is 34.7 in agreement with the observed value[9] 34.5.

(11) At 1100° the logs of the ratio p_{CO_2}/p_{CO} are 1.28, 0.785 and −0.450, for the equilibria f, g and l, respectively. The log of the ratio of the activity of FeO in wüstite equilibrated with iron to the activity of FeO in wüstite equilibrated with magnetite is 0.124. Hence for equilibrium n at 1100°:

$$\log \frac{CO_2}{CO} = \frac{-1.28}{3} - 0.450 + \frac{0.785}{3} - 0.124 = -0.74$$

at 1100° where p_{CO_2}/p_{CO} is found to be 0.182.

Quintuple point 5 is established as the point on curve n at 1180°, the temperature determined by Bowen and Schairer.[8]

Curve j is constructed connecting quintuple points 4 and 5; it passes through a maximum at 1208°, the melting point of pure fayalite as determined by Bowen and Schairer.

Curve m, radiating from quintuple point 5, is estimated roughly in the following manner: Iron melts in contact with its molten oxide at about 1525°, at which temperature $\log p_{CO_2}/p_{CO} = -0.68$; it is estimated that the activity of ferrous oxide in the oxide phase in equilibrium with iron is depressed by saturation with silica to about one-third,[12] thus at 1525° on curve m the value of $\log p_{CO_2}/p_{CO}$ is $-0.68 - \log 3 = -1.16$. The remainder of the curve is determined approximately by these two points.

Estimation of Position of Quintuple Point 3.—Of the five quintuple points occurring in the region covered by Fig. 1 four have already been considered and their positions established; the position of quintuple point 3 remains to be determined. Of the fifteen univariant equilibrium curves only three remain to be considered. Curve a is of little interest since the corresponding equilibrium can exist only at pressures above one atmosphere; its general direction is indicated by a dotted line in the diagram. The positions of curves e and h, which connect quintuple point 3 to quintuple points 2 and 4, respectively, are undetermined since there are no available experimental data on either of these curves; also the position of quintuple point 3 is undetermined except that it must be on the curves g, i. Thus from the direct data available, the only facts known concerning curves e and h are that they start from quintuple points 2 and 4, respectively, and terminate at a common point on the curves g, i which is quintuple point 3.

Some insight into possible constructions of these curves is gained by consideration of a theorem relating the order of curves about a quintuple point to the isothermal (triangular) composition diagram. This theorem is due in part to Roozeboom, Schreinemakers and Smits. An original derivation for the general case was given by Morey and Williamson.[13] Since a quintuple point represents the equilibrium of five phases each of a definite composition, the representation of this point on a composition diagram consists of five points, each of which represents the composition of one of the five phases present. The five univariant equilibria derived from the quintuple point correspond to the five possible combinations of four of the five phases. Thus at quintuple point 3, the five phases are magnetite, wüstite, fayalite, melt and gas. It will be noted that the five univariant equilibria correspond to the absence from the five phases present at the quintuple point of wüstite, melt, magnetite, fayalite and gas, respectively. The theorem states that if the points representing the composition of any three phases are colinear on the composition diagram, the two pressure–temperature curves representing the two univariant equilibrium involving these three phases are identical, that is, one is the extension of the other. At quintuple point 3 it is obvious that the compositions of magnetite, wüstite and gas (oxygen) are colinear on the triangular composition diagram; (they all lie on the Fe-O edge of the triangle) hence the curves g and i in Fig. 1 are extensions one of the other, as already anticipated from the consideration that the equilibrium of wüstite, magnetite and gas is not influenced by a third substance which is not appreciably soluble in any of these three phases.

The theorem gives further information as to the more general case in which three points are not colinear. This extended part of the theorem may best be visualized by imagining that five pins are stuck in the composition diagram at the five points corresponding to the compositions of the five phases present at the quintuple point. These pins are then each connected to each of the other four by elastic strings as in Fig. 2a. This particular set of compositions A, B, C, D, E, may be regarded as derived from any one of a variety of sets of compositions (imaginary quintuple points) in which colinearity of three points does occur—for example, the set A, B′, C, D, E. The theorem states in effect that if the pin at B with its attached elastic strings may be moved to B′ without any of the interconnecting lines (elastic strings) crossing any of the points (or *vice versa*) then the two univariant curves corresponding to the equilibria ABCD and ABCE are adjacent at the quintuple point on the pressure–temperature diagram, *i.* no other univariant curve lies between them at their intersection. In the present example B may be so moved to B′ colinear with A and C but may not be so moved as to be colinear with any other two of the five points. The same type of operation may be performed with each of the other points (A, C, D and E). Thus the order of all the univariant curves around a quintuple point may be established provided that the composition of the five phases is known. It is also necessary to establish the stable direction of each univariant curve since each curve is continuous through the quintuple point but represents a stable equilibrium in one direction and a metastable equilibrium in the other. Returning to the illustration, this matter is determined as follows: if the two points E and D lie on the same side of the line AB′C then the two univariant curves for equilibria ABCD

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(12) This is based on the data of Körber and Oelson [*Mitt. Kaiser-Wilhelm Inst. Eisenforsch Dusseldorf*, **15**, 271 (1933)] that at steel making temperatures the equilibrium oxygen content of iron under an iron-oxide slag saturated with silica is about $^1/_3$ the oxygen content of iron under an iron oxide slag.

(13) Morey and Williamson, THIS JOURNAL, **40**, 59 (1918). Further discussion and applications are given by G. W. Morey in "Commentary on the Scientific Writings of J. Willard Gibbs." Yale University Press, New Haven, Conn., 1936.

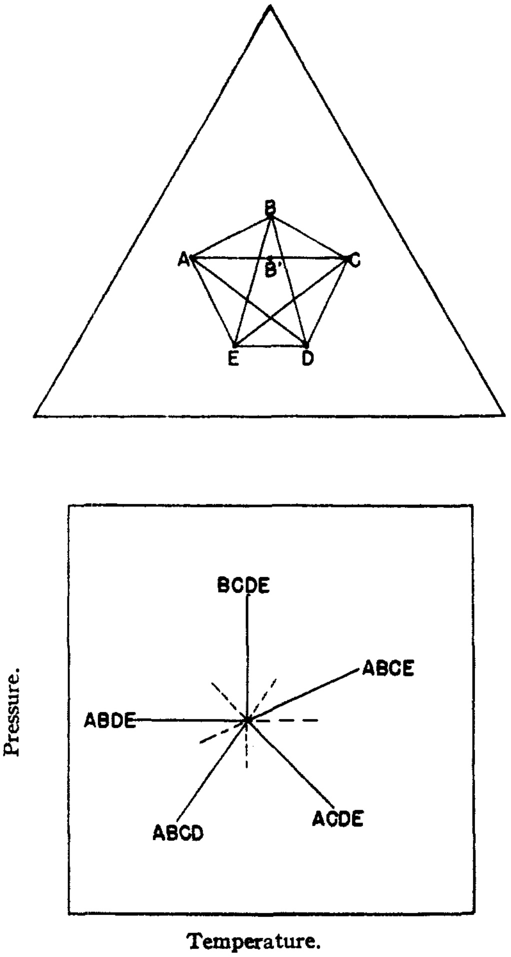

Fig. 2.—Schematic representation of the relation between *a* the composition of the five phases in equilibrium at the quintuple point and *b* the order of the univariant equilibrium curves about the quintuple point.

and ABCE are adjacent stable to metastable (*i. e.*, the stable portion of each, designated by a full line, is adjacent to the metastable portion of the other, designated by a dashed line). If E and D happened to lie on opposite sides of AB′C then these two univariant curves would be adjacent stable to stable. Application of this theorem to the postulated compositions shown in Fig. 2a leads to the order of univariant curves in the pressure temperature diagram as shown in Fig. 2b. Obviously the theorem is equally valid if the logarithm of the pressure is used as ordinate instead of the pressure itself.

Application of this theorem to quintuple point 4 in Fig. 1, using the composition data of Bowen and Schairer, leads to the conclusion that curve h radiates upward from this point and slightly to the left; this follows from the fact that the composition of the melt is very nearly colinear with that of wüstite and fayalite but is slightly higher in oxygen. It is assumed that the curvature of h is small. Quintuple point 3 is thus very roughly estimated as the point at 1150° lying on the curve g,i. The diagram is completed by constructing the short curve e connecting quintuple points 2 and 3.

Temperature Maxima and Minima of the Univariant Curves.—In the case of a univariant equilibrium in a ternary system involving three condensed (solid or liquid) phases and a gaseous phase it is rather unusual to find that all the condensed phases have fixed compositions independent of temperature. It is this variation of composition of the phases with temperature which introduces the most serious complexities into the treatment of such systems. Of the various equilibria here considered only two (f and n) of the truly ternary equilibria, *i. e.*, equilibria in which all components participate, as distinguished from equilibria which may be represented as binary since the third component is inert, consist exclusively of phases of reasonably fixed composition. Thus, equilibrium f may be represented by the chemical equation

$$3(2FeO{\cdot}SiO_2) + O_2 = 2Fe_3O_4 + 3SiO_2$$

The equilibrium constant may be written

$$K_f = \frac{a^2_{Fe_3O_4}a^3_{SiO_2}}{a_{2FeO\cdot SiO_2}a_{O_2}}$$

Since the solid phases involved are all of fixed composition, or very nearly so, the activities may be set equal to unity. The activity of oxygen is equal to its partial pressure in the gas phase and hence $K_f = 1/p_{O_2}$. The change of K_f and hence of $1/p_{O_2}$ is given by the simple equation: $d \ln K_f/d(1/T) = -\Delta H_f/R$. The treatment of this is relatively simple and leads to the well known linear relation between log K and $1/T$ if the heat of reaction (ΔH) is essentially independent of temperature. The use of carbon dioxide–carbon monoxide mixtures as the gas phase introduces no further complexities since the ratio CO_2/CO may be regarded as simply a measure of $p_{O_2}^{1/2}$ through the homogeneous gas equilibrium involving carbon monoxide, carbon dioxide, and oxygen. Hence for this equilibrium the plot of log p_{CO_2}/p_{CO} *versus* $1/T$ exhibits only the slight curvature occasioned by the difference in heat capacities. The use of temperature instead of $1/T$ as ordinate in Fig. 1 does not lead to any serious distortion of the relationship but simply produces a mild curvature.

A very different situation prevails, however, in the equilibria involving the molten oxide phase (curves a, c, d, e, h and j). In each of these cases it is impossible to write a chemical equation with integral or even constant coefficients to represent the reaction. The relation between log $p_{O_2}^{1/2}$ (or log p_{CO_2}/p_{CO}) and temperature is a function not only of the heats of reaction but also of the variable composition of the liquid phase. In general, these curves cannot be estimated even approximately by assuming log $p_{O_2}^{1/2}$ to be linear with $1/T$; for example, curve j passes through a maximum temperature. The occurrence of such a temperature maximum (or minimum) may be predicted, if the compositions are known, by aid of the theorem that at such a maximum (or minimum or stationary value) the composition of the three condensed phases is represented by three colinear points on the composition diagram[14]: The converse of this theorem is also true. Thus, at the maximum temperature of curve j the compositions of metal, fayalite and melt are colinear; the melt may be considered as molten fayalite from which some iron has been removed. It will be observed that the experimentally determined curve c is obviously approaching a maximum at its high temperature end. It does not actually pass through a maximum since it ends at quintuple point 1 first. It may, however, be inferred from the steep vertical rise of curve *c* near quintuple point 1 that the composition of the liquid oxide at this quintuple point is nearly colinear with the compositions of magnetite and silica; *i. e.*, this melt may be regarded approximately as composed of Fe_3O_4 and SiO_2.

Equilibria in Special Cases.—Although Fig. 1 shows the various possible univariant equilibria curves in the region under consideration, it is not possible to decide from this diagram alone what equilibria are pertinent for a given composition. In other words, the regions between the curves in this figure do not correspond to a unique set of phases. In general, the diagram may be applied to a specific case only if some composition data are available. In case a large amount of silica is present, the pertinent equilibria (taken from Fig. 1) are shown in Fig. 3. The stable phases, in addition to the gas, in the various fields are designated in this diagram. This diagram may be taken as a guide to the various iron oxide phases that may be present in contact with silica brick under different conditions of temperature and gas composition.

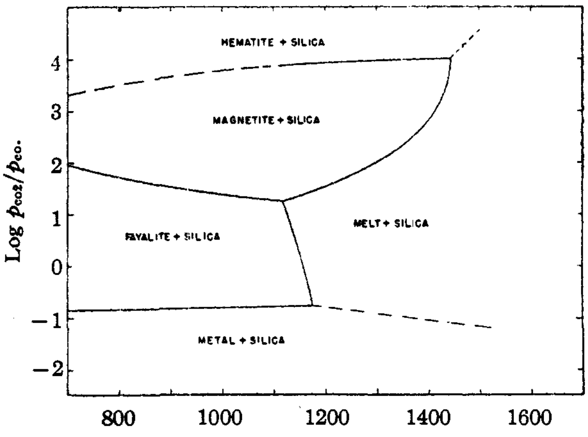

Fig. 3.—Stable phases of the system Fe–Si–O in the presence of solid silica.

If the ratio of total silicon to total iron is low, as in the case of a silicon steel and the oxides formed therefrom, the stable phases under various conditions of temperature and gas composition are as shown in Fig. 4. The temperature of complete melting is not shown in either Fig. 3 or Fig. 4, since this temperature is a continuous function of composition and may not be readily expressed on this type of diagram. In the region on the right of the diagrams, designated as corresponding to melt plus a solid phase, the relative proportions of the two phases depend on the composition as does the temperature of complete melting corresponding to the complete disappearance of the solid phase.

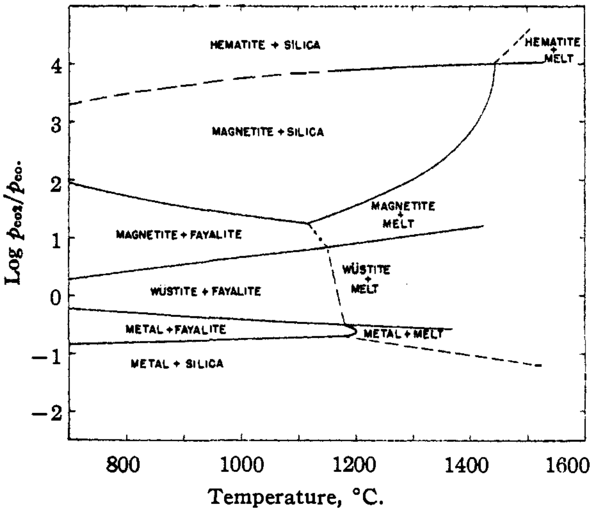

Fig. 4.—Stable phases of the system Fe–Si–O at low amounts of silicon.

The Migration of Silica During the Scaling of Steel.—It has been observed that the presence of a relatively small amount of silica or siliceous material on an iron or steel surface which is heated in an oxidizing atmosphere causes the scale to be more adherent to the metal than is the case in the absence of silica. The siliceous scale forms a very irregular boundary with the metal and is thus anchored so that it does not separate cleanly from the metal when bent, quenched or subjected to impact. The most peculiar part of the behavior is that the silica does not grow out appreciably with the scale, but remains principally near the scale–metal interface and spreads laterally so that the adherent zone increases with time of scaling. Clearly this phenomenon is very undesirable at any stage in the heat treatment of steel since it may occasion surface defects in the finished product.

In an elementary sense some insight is given by the consideration that silica forms a compound with ferrous though not with ferric oxide. It would be expected to migrate toward the region where it can form the most stable compound, which in this case is the scale–metal interface

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[14] This theorem is similar to that of Morey and Williamson, used previously; a proof is given in the appendix. A less explicit derivation was given by Gibbs.

where the composition of the iron oxide is nearest that corresponding to the formula FeO. This same line of reasoning may be developed in a quantitative manner by consideration of the activity of silica in the metal and various scale layers. At constant temperature silica will tend to move in such manner as to lower its free energy and hence its activity. The activity of silica differs appreciably from unity only when the silica is present in compound form, *i. e.*, combined as fayalite. From the equilibria (f) and (n)[9] it is found that at 900° in the presence of metallic iron and fayalite the activity of silica is given by the expression

$$a_{SiO_2} = 0.0268(p_{CO}/p_{CO_2})^2$$

and in the presence of magnetite and fayalite

$$a_{SiO_2} = 0.094(p_{CO_2}/p_{CO})^{2/3}$$

In the presence of wüstite and fayalite the activity of silica is inversely proportional to the square of that of ferrous oxide; a_{FeO} was taken from Darken and Gurry.[1] The variation of the activity of silica thus calculated with the degree of oxidation is shown in Fig. 5. The lowest activity is seen to be at the scale–metal interface, thus accounting for the observation that silica tends to move to and remain at this interface.

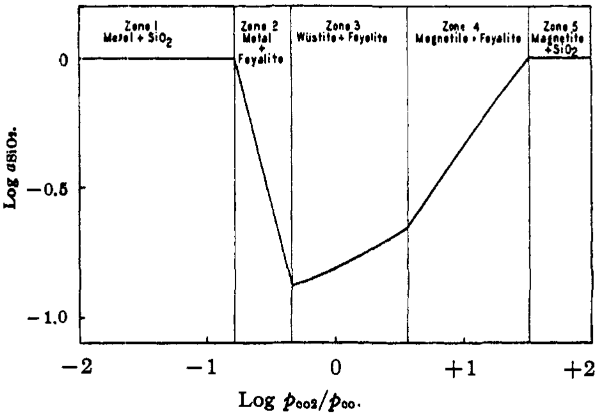

Fig. 5.—Activity of silica in iron and iron oxide systems at 900°.

Appendix

Proof of Theorem.—If a univariant equilibrium in a ternary system has a maximum (or minimum) temperature on a pressure temperature plot, then at this temperature the compositions of the three condensed phases, one of variable and two of fixed composition, are colinear. By the fundamental theorem of partial differentiation the total derivatives of the activities (at constant total pressure), of each of the three components may be written as follows

$$(1)\quad \frac{d \ln a_1}{d(1/T)} = \left(\frac{\partial \ln a_1}{\partial(1/T)}\right)_{N_2,N_3} + \left(\frac{\partial \ln a_1}{\partial N_2}\right)_{N_3,T} \frac{dN_2}{d(1/T)} + \left(\frac{\partial \ln a_1}{\partial N_3}\right)_{N_2,T} \frac{dN_3}{d(1/T)}$$

$$(2)\quad \frac{d \ln a_2}{d(1/T)} = \left(\frac{\partial \ln a_2}{\partial(1/T)}\right)_{N_2,N_3} + \left(\frac{\partial \ln a_2}{\partial N_2}\right)_{N_3,T} \frac{dN_2}{d(1/T)} + \left(\frac{\partial \ln a_2}{\partial N_3}\right)_{N_2,T} \frac{dN_3}{d(1/T)}$$

$$(3)\quad \frac{d \ln a_3}{d(1/T)} = \left(\frac{\partial \ln a_3}{\partial(1/T)}\right)_{N_2,N_3} + \left(\frac{\partial \ln a_3}{\partial N_2}\right)_{N_3,T} \frac{dN_2}{d(1/T)} + \left(\frac{\partial \ln a_3}{\partial N_3}\right)_{N_2,T} \frac{dN_3}{d(1/T)}$$

The *a*'s refer to activities and the *N*'s to mole fractions. If these three equations are multiplied by N_1, N_2 and N_3, respectively, and added, then all terms on the right-hand side except the first of each equation disappear by virtue of the Gibbs–Duhem relationship.

$$(4)\quad \frac{N_1\, d \ln a_1 + N_2\, d \ln a_2 + N_3\, d \ln a_3}{d(1/T)} = N_1\left(\frac{\partial \ln a_1}{\partial(1/T)}\right)_{N_2,N_3} + N_2\left(\frac{\partial \ln a_2}{\partial(1/T)}\right)_{N_2,N_3} + N_3\left(\frac{\partial \ln a_3}{\partial(1/T)}\right)_{N_2,N_3}$$

If the liquid phase is in equilibrium with two solid phases of fixed composition and a gaseous phase, then the two solid phases may arbitrarily be selected as components (designated components 1 and 2). The standard state for these components is selected as the solid and hence the activity of each is unity and its total derivative is zero. Then

$$(5)\quad N_3 \frac{d \ln a_3}{d(1/T)} = N_1\left(\frac{\partial \ln a_1}{\partial(1/T)}\right)_{N_2,N_3} + N_2\left(\frac{\partial \ln a_2}{\partial(1/T)}\right)_{N_2,N_3} + N_3\left(\frac{\partial \ln a_3}{\partial(1/T)}\right)_{N_2,N_3}$$

If component 3 be selected as a gaseous component (oxygen in the present case) then $p_{O_2}{}^{1/2}$ may be written for a_3; further the partial derivatives on the right multiplied by R are equal to the partial molal heats of solution $\overline{H}_1$, $\overline{H}_2$, $\overline{H}_3$, ($\overline{H}_1$ and $\overline{H}_2$ being heats of melting).

$$(6)\quad R\frac{d \ln p_{O_2}{}^{1/2}}{d(1/T)} = \frac{N_1}{N_3}\overline{H}_1 + \frac{N_2}{N_3}\overline{H}_2 + \overline{H}_3$$

In terms of the ratio p_{CO_2}/p_{CO}

$$(7)\quad R\frac{d \ln (p_{CO_2}/p_{CO})}{d(1/T)} = \frac{N_1}{N_3}\overline{H}_1 + \frac{N_2}{N_3}\overline{H}_2 + \overline{H}_3'$$

where $\overline{H}_3'$ is equal to the change of the heat content of oxygen on transfer from the gas phase to the liquid. Since N_3 occurs in the denominator it follows that whenever $N_3 = 0$ the expression becomes infinitely great. But by the choice of components, the equality of N_3 to zero is synonymous with the colinearity (on the composition triangle) of melt, component 1, and component 2. Hence whenever the composition of the melt is colinear with the composition of the two solid phases in equilibrium with it, it follows that the plot of log p_{CO_2}/p_{CO} (or log p_{O_2}) *vs.* $1/T$ (or *vs.* temperature) is vertical. Conversely, since the heats of solution are never infinite, any vertical portion of the plot corresponds to colinearity of the three phases on the composition diagram. A general proof of this theorem was given by Gibbs.[15]

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[15] J. W. Gibbs, "Collected Works," Vol. I, Longmans Green & Co., New York, N. Y., 1928, pp. 99–100.

Summary

The melting point of iron oxides in contact with silica has been determined as a function of the partial pressure of oxygen or the ratio of carbon dioxide to carbon monoxide in the gas phase. With the aid of these and other available data, a large part of the diagram .showing the stable phases under various conditions of temperature and gas composition has been constructed for the ternary system iron–silicon–oxygen. The data have been used to interpret the migration of silica through iron oxide to the scale–metal interface during the scaling of steel.

KEARNY, NEW JERSEY RECEIVED JANUARY 28, 1948

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Reactions of Diborane with Hydrocarbons[1]

BY DALLAS T. HURD

A number of experiments have been conducted to delineate the character of the complex reactions that occur between hydrocarbons and diborane at elevated temperatures. In these experiments the effect of the highly reactive diborane on the reaction products has been minimized by using only small amounts of diborane with relatively large amounts of hydrocarbon. Under these conditions several different reactions have been observed:

1. The addition of diborane to olefins occurs with saturation of the double bonds and the formation of trialkyls of boron.
2. Substitution on the benzene ring occurs with the formation of phenyl boron compounds.
3. Diborane reacts with paraffins to form polymeric reaction products containing boron, carbon, and hydrogen. Breakdown and synthesis of hydrocarbon chains effected by the diborane obscures the nature of the reaction.

Experimental

The general technique employed in studying the addition and substitution reactions was to seal mixtures of diborane with various hydrocarbons in heavy-walled Pyrex tubes. The tubes were frozen in liquid nitrogen and evacuated before sealing. The tubes then were encased in protecting tubes of steel pipe and either heated in an oven or allowed to stand at room temperature. After the time allotted for the reaction had elapsed the tubes were immersed in liquid nitrogen to freeze their contents, their tops were cracked off under a blanket of dry nitrogen, and the reaction products together with any unchanged materials were removed from the tubes, generally by distillation on a vacuum chain.

A. Reactions with Olefins. 1. Isobutylene.—The reaction of isobutylene with diborane was studied with mixtures containing from two to ten per cent. by weight of diborane. Within this range of composition no significant differences in the results were observed. Most of the reactions were conducted by heating the tubes at 100° for twenty-four hours but it also was noticed that the addition reaction took place at room temperature although somewhat more slowly. Since no pressure of noncondensable gas developed in the tubes during these reactions it was presumed that the addition of diborane to the olefin was rapid and almost quantitative. Otherwise the pyrolysis of unreacted diborane at the elevated temperature would develop a pressure of hydrogen that would become apparent when the tubes were opened.

Distillation of excess isobutylene from a reaction mixture left a clear colorless oil of low volatility. Upon exposure of this oil to the air it quickly became warm from spontaneous oxidation. Inflammation was observed if a few drops were placed on a filter paper or in a watch glass.

Fractionation of a fresh sample of the oil under a nitrogen atmosphere in a distillation column of approximately twenty plates separated the sample into two fractions of almost equal volume, one boiling at 181.5° and the other at 188.5°. The boiling point calculated from reduced pressure data for tri-*t*-butylboron is 182°[2] and the reported boiling point of tri-isobutylboron is 188°.[3] Each fraction was shaken individually in a separatory funnel with aqueous sodium hydroxide and air until the oil had been oxidized completely and had been dissolved as the sodium salt of the corresponding butylboric acid. The solutions were concentrated by boiling and, after cooling, were neutralized by the addition of hydrochloric acid. This caused the precipitation of the white crystalline butylboric acids. A determination was made of the melting points of the isomeric acids thus isolated and the values obtained checked very closely with those reported in the literature (*t*-butylboric acid, m. p. 113-114°; reported m. p. 113°[2]; isobutylboric acid, m. p. 112-113°; reported m. p. 112°[3]). Although these two butylboric acid isomers have melting points lying within one degree of each other it was clear that the original reaction product comprised a mixture of isomeric tributylboron compounds since oxidation of an unfractionated sample of the oil and isolation of the mixed butylboric acids by the technique described above yielded a crystalline white solid with no sharply defined melting point melting over the range from 80–90°.

2. **Ethylene.**—Ethylene containing two per cent. by weight of diborane was heated at 100° for four days. The tube then was opened and the unreacted ethylene was removed by distillation on the vacuum chain. A small amount of clear liquid remained in the tube. This liquid inflamed immediately upon exposure to air. Since the liquid had an appreciable volatility it could be analyzed most conveniently on the mass spectrometer. Strong maxima in the pattern indicated large amounts of triethylboron. Examination of a vapor sample taken during the last stages of the removal of ethylene from the sample revealed no volatile ethyldiborane compounds.[4]

B. Reaction with Benzene.—Pure benzene was heated with five per cent. by weight of diborane in sealed tubes or in a stainless steel bomb for twelve hours at 100°. During the course of the reaction it was observed that the benzene gradually developed a dark yellow color. Upon opening the tubes after freezing the contents in liquid nitrogen it

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[1] Presented before the Physical and Inorganic Division. American Chemical Society, New York, September, 1947.

[2] E. Krause and P. Nobbe, *Ber.*, **64B**, 2112 (1931).

[3] E. Krause and R. Nitsche, *ibid.*, **54**, 2784 (1921).

[4] These analyses were performed by Dr. Francis J. Norton.