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EQUILIBRIUM STUDIES IN THE SYSTEM MgO–"FeO"–TiO_2

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ABSTRACT. The main features of phase relations in the system MgO–"FeO"–TiO_2 under strongly reducing conditions have been delineated at liquidus and solidus temperatures as well as at a constant temperature of 1300°C. In addition to rutile (TiO_2) and magnesiowüstite (MgO–"FeO"), three continuous solid-solution series appear in the system in the temperature range of the present study. They are spinel between the end members Mg_2TiO_4 and Fe_2TiO_4, the rhombohedral ("α"–) phase between the end members $MgTiO_3$ and $FeTiO_3$, and magnesium–ferropseudobrookite between the end members $MgTi_2O_5$ and $FeTi_2O_5$. Considerable deviations from stoichiometry with respect to (Mg + Fe)/Ti ratios are possible in all these solid-solution series.

Liquidus and solidus temperatures decrease continuously from the MgO–TiO_2 side to the "FeO"–TiO_2 side of the diagram, with the primary phase areas of each of the solid-solution series magnesiowüstite, spinel, rhombohedral phase, and magnesium–ferropseudobrookite extending across the diagram from the MgO–TiO_2 to the "FeO"–TiO_2 side. Directions of conjugation lines between coexisting solid-solution phases were determined at 1300°C. Using known activity-composition relations in the magnesiowüstite phase as a starting point and making simplifying assumptions with regard to the non-stoichiometry of the other solid solutions, the trends in the activity-composition relations of the solid-solution series spinel, rhombohedral phase, and magnesium–ferropseudobrookite, as well as approximate stability data for end-member compounds, are derived. The spinel and rhombohedral solid solutions are found to have considerable positive deviations from ideality, whereas the data for the magnesium–ferropseudobrookite solid solution suggest close to ideal behavior ot this phase. The following approximate free energies of formation of end-member compounds from their oxide components were estimated at 1300°C: Fe_2TiO_4, −8.2 ± 1.0 kcal; $FeTiO_3$, −4.3 ± 1.0 kcal; $FeTi_2O_5$, −4.3 ± 1.0 kcal.

INTRODUCTION

In spite of the importance of titanium in geological sciences and technology, the information on the role of this element in common types of ionic structures is very limited. It is the objective of the present paper to provide equilibrium data on one of the key titanite systems, MgO–"FeO"–TiO_2, under strongly reducing conditions. Among the phases occurring in this system is magnesium–ferropseudobrookite, the solid-solution series between the end members $MgO{\cdot}2TiO_2$ and $FeO{\cdot}2TiO_2$. Special interest is attached to this phase because of its occurrence in lunar samples (Anderson and others, 1970).

The most commonly used method for studying liquid-solid phase relations in iron oxide-containing systems under strongly reducing conditions is that developed for silicate systems by Bowen and Schairer (1932), involving equilibration of oxide phases contained in iron crucibles in an inert atmosphere. In this way, essentially all iron in the oxide phases is maintained in the divalent state, and systems like "FeO"–SiO_2 (Bowen and Schairer, 1932) and MgO–"FeO"–SiO_2 (Bowen and Schairer, 1935) can be treated like binary and ternary systems, respec-

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tively, with good approximation. A practical upper temperature limit for using this method, however, is set by the melting point of iron and is less than 1500°C, and only systems in which a major part of the composition triangle has liquidus temperatures below 1500°C can be conveniently studied by this method.

Liquidus and solidus temperatures are considerably higher in titanates than in the corresponding silicate systems. Therefore, it is not possible to use the method developed by Bowen and Schairer in the study of liquid-solid equilibria in major parts of the system MgO–"FeO"–TiO_2. Indeed, at the present time, we know of no experimental method that would make it practicable to determine phase relations at liquidus temperatures in this system in equilibrium with metallic iron very accurately. Instead, a method was used that is practically feasible, that gives reliable and reasonably accurate data up to solidus temperatures, and that permit delineation of the main features of the liquidus surface. Considering the lack of data on this system, and the importance of the system, we feel it is worthwhile to present the approximate relations that can be derived by this method. The method involves equilibrations of pellets suspended with a very thin platinum wire in a quench furnace in which the oxygen pressure is kept at a constant level, in the present case 10^{-8} atm. Details of this equilibration technique are given in a succeeding section.

Whereas equilibrium data for the system MgO–"FeO"–TiO_2 have not been reported in previous literature, the three bounding binary systems[1] have been studied in considerable detail. The system MgO–"FeO" forms a continuous solid-solution series with continuously decreasing liquidus and solidus temperatures from approximately 2800°C for MgO to 1370°C for "FeO" in equilibrium with metallic iron (Bowen and Schairer, 1935; Schenck and Plaff, 1961), as illustrated in figure 1A. Phase relations in the system MgO–TiO_2 (Woermann, Brežný, and Muan, 1969) are shown in figure 1B. There are three stable compounds in the system, namely, Mg_2TiO_4, $MgTiO_3$, and $MgTi_2O_5$, of which one ($MgTi_2O_5$) melts congruently, and the other two (Mg_2TiO_4 and $MgTiO_3$) melt incongruently. Phase relations in the system "FeO"–TiO_2 under strongly reducing conditions (MacChesney and Muan, 1961) are shown in figure 1C. Again, there are three intermediate compounds appearing in equilibrium with liquids, namely, Fe_2TiO_4, $FeTiO_3$, and $FeTi_2O_5$, all congruently melting. The oxygen pressure used in the present investigation (10^{-8} atm) is only slightly higher than that for the diagram shown in figure 1C, and this diagram, therefore, adequately represents phase relations along the "FeO"–TiO_2 side of the system MgO–"FeO"–TiO_2 under the conditions of the present investigation.

[1] The bounding systems with iron oxide as a component, namely MgO–"FeO" and "FeO"–TiO_2, are not truly binary, because iron is present in different oxidation states (Fe^{2+} and Fe^{3+}) in varying proportions. However, the compositions of the phases are close to the MgO–FeO and FeO–TiO_2 joins, respectively, and as a first approximation the two systems may be referred to as binary.

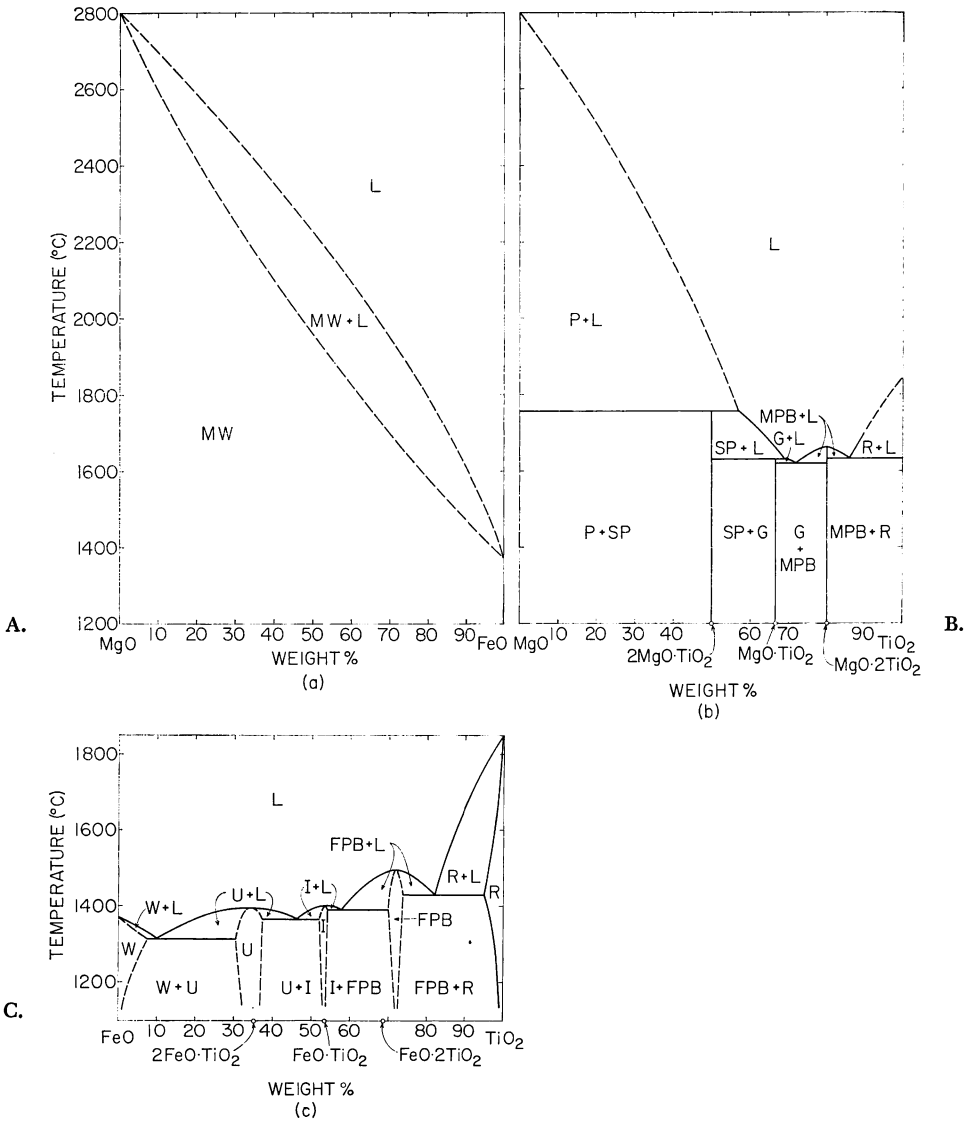

Fig. 1. Phase relations in (A) the system MgO–"FeO", mainly after Bowen and Schairer (1935), (B) the system MgO–TiO_2, mainly after Woermann, Brezny, and Muan (1969), and (C) the system "FeO"–TiO_2 under strongly reducing conditions, after MacChesney and Muan (1961). Abbreviations used have the following meanings: MW = magnesiowüstite; P = periclase; SP = spinel; L = liquid; G = geikielite; MPB = magnesium–pseudobrookite; FPB = ferro–pseudobrookite; R = rutile; I = ilmenite.

EXPERIMENTAL METHODS

Phase relations in the liquidus and solidus regions of the system were determined by the well-known quenching technique. Suitably pre-reacted samples were held at desired temperatures in desired atmospheres for a sufficient length of time for equilibrium to be attained. The samples were then quenched rapidly to room temperature, and the phases present were determined, usually by microscopic and X-ray examination.

In the present study, equilibria in the liquidus and solidus regions were determined at a constant oxygen pressure of 10^{-8} atm. This is somewhat higher than the oxygen pressures corresponding to equilibrium of the oxide phases with metallic iron, but sufficiently low to keep essentially all iron in the divalent state. Small samples of finely powdered, pre-reacted mixtures were pressed into pellets and suspended with a very fine (0.004 in. diam) platinum wire in a vertical quench furnace. The area of contact between the oxide samples and the Pt wire was very small, thus minimizing the loss of iron from the sample by alloying with platinum. Equilibration runs with this technique were successfully carried out in the presence of moderate amounts of a liquid phase, but it was not practicable with this technique to determine liquidus temperatures accurately. Therefore, the data on the solidus surface are considered more reliable than those on the liquidus surface.

The quench runs were made in a vertical tube furnace with 80 percent Pt 20 percent Rh winding. The oxygen pressure of 10^{-8} atm in the furnace was attained by mixing CO_2 and H_2 in controlled proportions by a method described by Darken and Gurry (1945). Temperature constancy was maintained with commercial electronic controllers, and actual temperatures within the furnace were measured with Pt versus 90 percent Pt 10 percent Rh thermocouples up to 1550°C and with 95 percent Pt 5 percent Rh versus 80 percent Pt 20 percent Rh thermocouples at temperatures above 1550°C. The thermocouples were calibrated against the melting points of synthetic diopside (1391.5°C), synthetic pseudowollastonite (1546°C), and the liquidus temperatures of a 90 wt percent SiO_2 10 wt percent CaO mixture (1707°C).

Subsolidus data were obtained for oxide mixtures in contact with metallic iron at 1300°C. Directions of conjugation lines were derived from a determination of CO_2/H_2 ratios of a gas phase coexisting with metallic iron and pairs of coexisting solid-solution phases in accordance with methods described previously for iron silicates (see for instance Schwerdtfeger and Muan, 1966; Johnson and Muan, 1967). The most crucial part of the experimental procedure in these subsolidus equilibrations is that of attaining homogeneity of each of the solid solutions of the starting sample prior to the metal-precipitation runs. Toward this end, each mixture was pre-reacted for several days at 1300°C in CO_2–H_2 atmospheres slightly more oxidizing than those that cause precipitation of metallic iron. Attainment of homogeneity was first judged by the

sharpness of the X-ray reflections of the solid solutions thus obtained and then checked by the pattern of distribution of the metallic iron in the subsequent equilibration runs. If the metallic iron was evenly distributed as tiny specks throughout the sample, this was taken as a sign that satisfactory homogeneity had been attained. If, however, the iron precipitated unevenly and locally in larger particles, this was taken as a sign of heterogeneity of the solid solutions, or unreacted iron oxide, in the starting materials. These runs were rejected, and the mixtures involved were returned for further pre-reaction until satifactory homogeneity was attained.

RESULTS

Results of quenching experiments for determination of liquidus and solidus relations are listed in table 1 and illustrated graphically in figures 2 to 4. The diagram in figure 2 is a sketch of the liquidus surface, inferred on the basis of data listed in table 1 and previously available data for the bounding "binary" systems (see Introduction), and reasonable assumptions regarding composition- and temperature profiles along univariant boundary curves.

The diagram in figure 3 is a sketch of the solidus surface of the system MgO–iron oxide–TiO_2 at an oxygen pressure of 10^{-8} atm, based on data listed in table 1 and previously available data for the bounding "binary" systems. Shown in figure 4 are conjugation lines between pairs of coexisting solid-solution phases and metallic iron at 1300°C. This diagram was drawn on the basis of data contained in table 2.

The directions of conjugation lines between coexisting solid solutions in ternary systems can be used to derive activity-composition relations in the solid solutions involved and the stabilities of their end-member compounds (see for instance Schwerdtfeger and Muan, 1966; Muan, 1967). In the present case, complications arise from the considerable deviations from stoichiometry of the solid solutions present in the system (note the width of the magnesiowüstite, spinel, α, and magnesium–ferropseudobrookite fields in figures 3 and 4). A detailed thermodynamic treatment of the thermodynamics of these solid solutions would require data on the FeO-activities as a function of composition within each of these ternary solid solutions. Such data are not available at the present time. However, inasmuch as the permutation of Fe^{2+} for Mg^{2+} is the main reaction involved in each of the coexisting solid-solution phases in going from the MgO–TiO_2 to the "FeO"–TiO_2 side of the diagram, the directions of the conjugation lines can be used to derive the general trends of activity-composition relations in the solid solutions and relative stabilities of end-member compounds. As a first approximation, therefore, the Mg/Fe ratios of the coexisting non-stoichiometric solid solutions may be used in the equations describing the directions of the conjugation lines, as derived previously (see for instance Muan, 1967). Using the magnesiowüstite–spinel equilibrium as an example and intro-

TABLE 1

Results of quench runs for determination of liquidus and solidus relations in the system MgO–iron oxide–TiO_2 at an oxygen pressure of 10^{-8} atm

Composition (wt %)			Temp, °C	Phases present*
MgO	TiO_2	FeO		
14.4	67.2	18.4	1482	MFPB + α
12.4	62.9	24.7	1480	α + MFPB + L
27.4	54.2	18.4	1480	α + SP
24.2	48.0	27.8	1474	α + SP + tr. L
21.0	41.5	37.5	1475	SP + L
17.7	35.0	47.3	1472	SP
7.3	14.4	78.3	1471	L
			1385	MW + SP + L
4.1	77.5	18.4	1476	MFPB + R
6.1	75.5	18.4	1469	MFPB + R
12.2	69.4	18.4	1480	MFPB + L
17.3	64.3	18.4	1473	α + MFPB
21.4	60.2	18.4	1480	
23.5	58.2	18.3	1469	α + SP
14.6	47.9	37.5	1455	α + SP + L
			1447	α + SP + L
20.0	32.6	47.4	1471	SP + MW
			1445	SP + MW
16.0	26.6	57.4	1473	SP + MW + tr. L
21.5	10.8	67.7	1476	MW
			1475	MW
15.2	6.5	78.3	1475	MW + tr. L
			1423	MW
18.0	58.0	24.0	1475	MFPB + α + s.a. L
26.0	41.0	33.0	1478	SP
27.0	38.0	34.0	1475	SP + tr. MW
8.3	63.9	27.8	1453	MFPB + L
20.6	51.6	27.8	1473	α + SP
14.4	57.8	27.8	1472	α + MFPB + L
12.4	59.8	27.8	1469	α + L
8.6	23.7	67.7	1467	SP + MW + L
			1463	SP + MW + L
			1443	SP + MW + L
6.5	25.8	67.7	1394	SP
32.9	9.6	57.5	1549	MW
9.4	53.1	37.5	1437	α + MFPB + L
			1417	α + MFPB + tr. L
6.3	46.4	47.3	1466	L
			1437	tr. SP + L
			1401	SP + α + s.a. L
12.0	9.8	78.2	1436	MW + L
			1430	MW
3.1	74.7	22.2	1479	MFPB + R + tr. L
			1465	MFPB + R
8.1	77.4	14.5	1548	MFPB + L
			1530	MFPB + tr. L
16.8	75.7	7.5	1553	MFPB + L
			1539	MFPB + s.a. L
			1527	MFPB + tr. α
5.1	59.0	35.9	1413	MFPB + s.a. α + L
			1409	MFPB + α
			1389	MFPB + α
13.5	62.5	24.0	1488	α + MFPB + s.a. L
			1471	α + MFPB + s.a. L
			1452	α + MFPB

TABLE 1 (continued)

Composition (wt %)			Temp, °C	Phases present*
MgO	TiO_2	FeO		
23.2	66.5	10.3	1551	L
			1539	α + MFPB
5.8	53.0	41.2	1391	α + s.a. L
			1368	α + s.a. SP
15.5	57.0	27.5	1470	α + tr. L
			1458	α + SP + tr. L
			1453	α + SP + tr. L
			1448	α + SP
			1437	α + SP
26.6	61.6	11.8	1547	α + SP + L
			1539	α + SP
7.0	43.5	49.5	1395	SP + α + s.a. L
			1393	SP + α + tr. L
			1386	SP + α
			1380	SP + α
19.1	46.9	34.0	1488	SP + α + s.a. L
			1468	SP + α + tr. L
			1457	SP + α
33.9	51.0	15.1	1553	SP + α + L
			1535	SP + α
8.0	35.2	56.8	1394	SP
21.9	39.2	38.9	1550	SP + L
			1526	SP
38.8	43.9	17.3	1604	SP + MW
3.4	73.0	23.6	1487	MFPB + s.a. L
			1475	MFPB + s.a. L
			1467	MFPB + tr. R + tr. L
3.8	69.5	26.7	1446	MFPB + L
			1423	MFPB + s.a. L
4.1	67.0	28.9	1396	MFPB + L
5.4	47.0	37.6	1380	α + MFPB
5.8	54.0	40.2	1426	α + tr. L
			1381	α
6.2	51.0	42.8	1393	α + SP + s.a. L
			1382	α + SP + tr. L
			1376	α + SP
8.4	33.0	58.6	1387	SP
			1374	SP
22.8	37.0	40.2	1470	SP
12.0	5.0	83.0	1465	MW + L
			1445	MW
			1400	MW
34.8	4.0	61.2	1488	MW
			1462	MW
67.0	3.0	30.0	1604	MW + SP
7.4	41.0	51.6	1391	α + SP + tr. L
			1377	α + SP
18.3	78.0	3.7	1565	MFPB + α + s.a. L
			1535	MFPB + α
28.3	66.0	5.7	1593	α + L
			1565	α + MFPB + s.a. L
30.1	64.2	5.7	1624	L
			1593	α + SP + L
			1588	α + SP + s.a. L
			1565	α + SP
42.4	49.0	8.6	1624	L
			1568	SP
			1552	SP

TABLE 1 (continued)

Composition (wt %)			Temp, °C	Phases present*
MgO	TiO_2	FeO		
44.2	47.0	8.8	1604	SP + MW
			1592	SP + s.a. MW
			1588	SP + s.a. MW
			1552	SP + s.a. MW
82.6	1.0	16.4	1604	MW + SP

* Abbreviations used have the following meanings: R = rutile; MFPB = magnesium–ferropseudobrookite ($MgTi_2O_5$–$FeTi_2O_5$ solid solution); α = rhombohedral phase ($MgTiO_3$–$FeTiO_3$ solid solution); SP = spinel (Mg_2TiO_4–Fe_2TiO_4 solid solution); MW = magnesiowüstite (MgO–"FeO" solid solution); L = liquid; s.a. = small amount; tr. = trace.

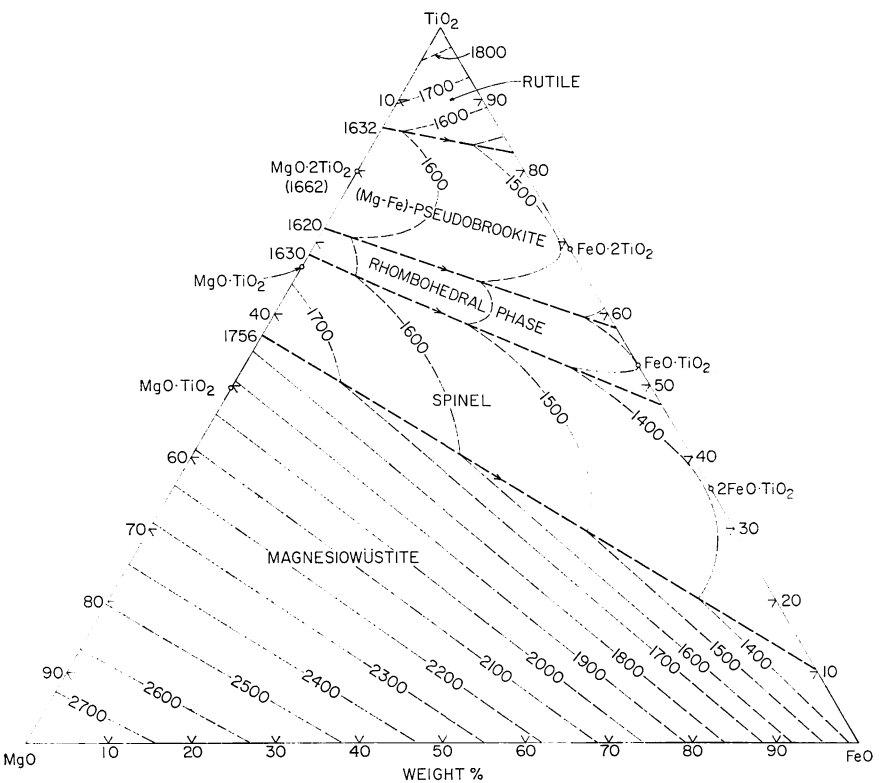

Fig. 2. Sketch showing main features of the liquidus surface of the system MgO–iron oxide–TiO_2 at an oxygen pressure of 10^{-8} atm. Heavy lines are boundary curves, and light lines are liquidus isotherms.

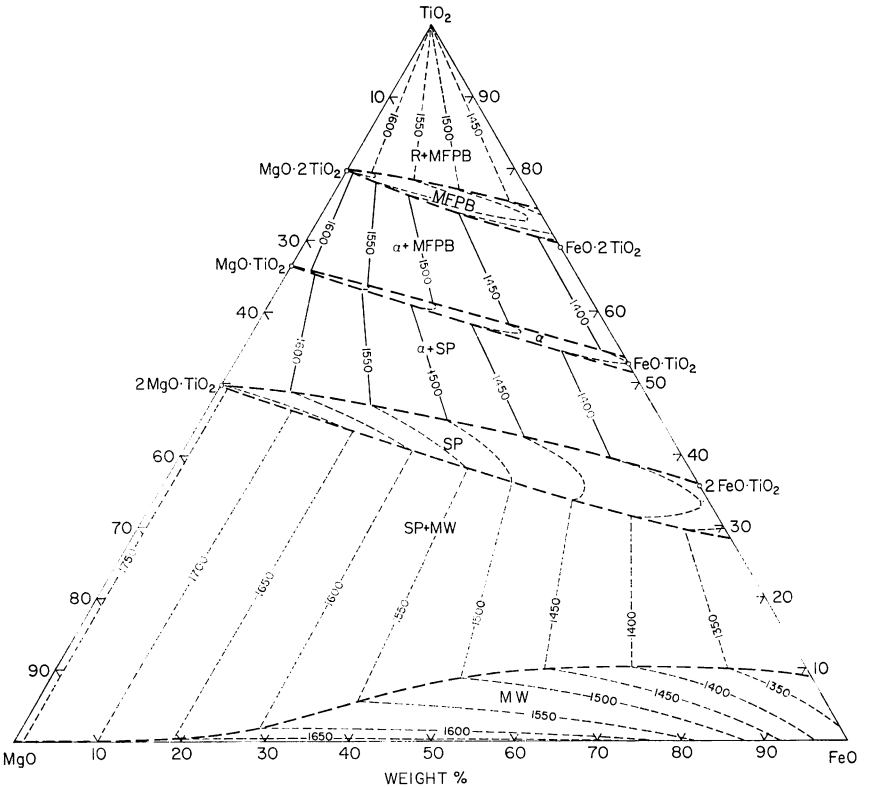

Fig. 3. Approximate solidus surface for the system MgO–iron oxide–TiO_2 at an oxygen pressure of 10^{-8} atm. Heavy lines are boundary curves between various phase areas, and light lines are solidus isotherms. Abbreviations used have the following meanings: MW = magnesiowüstite; SP = spinel; α = rhombohedral phase; MFPB = magnesium–ferropseudobrookite, R = rutile.

ducing the above approximations, the types of equations applicable to the present system are as follows:

The change in free energy, $\Delta(\Delta G°)$, for the reaction

$$(FeO) + (MgTi_{0.5}O_2) = (MgO) + (FeTi_{0.5}O_2) \qquad (1)$$

is calculated from the equation

$$-\frac{\Delta(\Delta G°)}{2.303RT} = \log C + \log\gamma_{FeTi_{0.5}O_2} - \log\gamma_{MgTi_{0.5}O_2} \qquad (2)$$

Here $\Delta(\Delta G°) = \frac{1}{2}\,\Delta G°_{Fe_2TiO_4} - \frac{1}{2}\,\Delta G°_{Mg_2TiO_4}$ and $\Delta G°_{Fe_2TiO_4}$ and $\Delta G°_{Mg_2TiO_4}$ are the free energies of formation of the two end members Fe_2TiO_4 and Mg_2TiO_4, respectively, from their oxide components (2FeO + TiO_2 and 2MgO + TiO_2, respectively). The activity coefficients of the spinel solid solution are calculated from the expressions

$$\log\gamma_{FeTi_{0.5}O_2} = -N_{MgTi_{0.5}O_2}\log C + \int_0^{N_{MgTi_{0.5}O_2}} \log C\, d\, N_{MgTi_{0.5}O_2} \qquad (3)$$

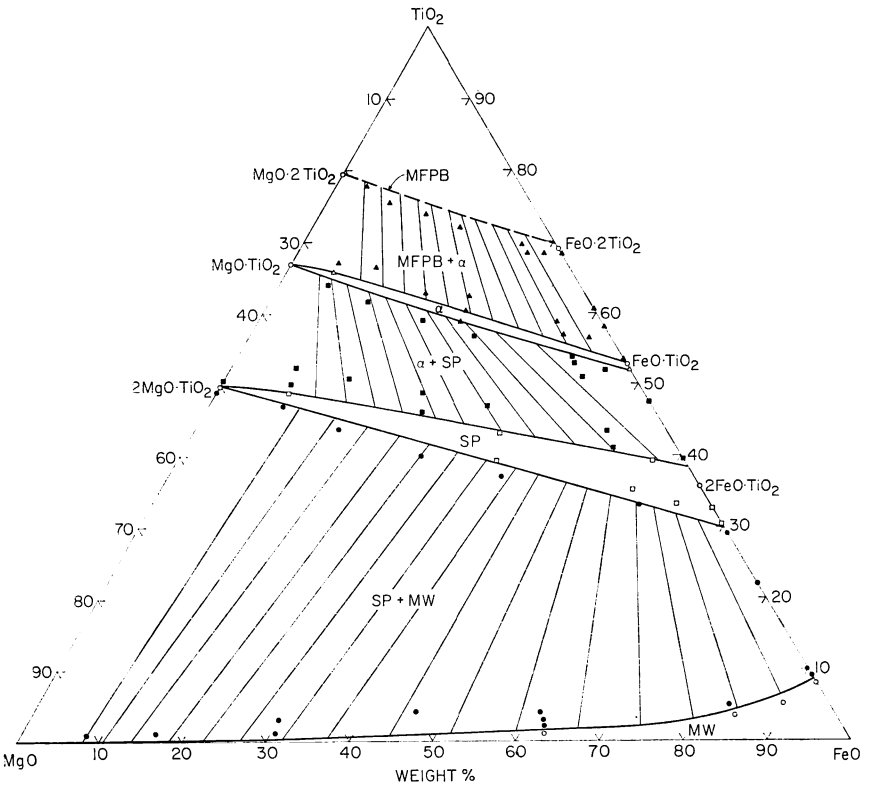

Fig. 4. The 1300°C isothermal section of the system MgO–iron oxide–TiO_2 in contact with metallic iron, showing boundaries of the various phase areas as heavy curves and conjugation lines as light lines. Abbreviations used have the same meanings as in figure 3.

and

$$\log \gamma_{MgTi_{0.5}O_2} = (1-N_{MgTi_{0.5}O_2}) \log C + \int_{O}^{N_{MgTi_{0.5}O_2}} \log C \, d \, N_{MgTi_{0.5}O_2} \qquad (4)$$

Similar equations apply to the other pairs of coexisting solid solutions.

Results of such calculations are shown in the form of approximate activity-composition curves along the spinel and rhombohedral solid solutions at 1300°C in figure 5. A moderate positive deviation from ideality is suggested for both solid solutions. The data for the pseudobrookite phase suggest that this solid solution is close to ideal.

From the magnesiowüstite–spinel equilibrium, the calculated value of $\Delta(\Delta G^\circ)$ ($= \frac{1}{2} \Delta G^\circ_{Fe_2TiO_4} - \frac{1}{2} \Delta G^\circ_{Mg_2TiO_4}$, see equation (4)) is −1.6 kcal. Using the value of $\Delta G^\circ_{Mg_2TiO_4}$ at 1300°C as determined by Brežný and Muan (1971) (−5.1 kcal), the value of $\Delta G^\circ_{Fe_2TiO_4}$ at 1300°C, as cal-

TABLE 2

Results of equilibration runs at 1300°C in the system MgO–"FeO"–TiO_2 in contact with metallic iron

Mixture (Wt %) MgO	Composition (Wt %) TiO_2	Composition (Wt %) FeO	Phases Present*	CO_2/H_2	Log P_{O_2}
36.0	1.0	63.0	MW		
12.0	3.5	84.5	"		
5.6	5.0	89.4	"		
0.0	8.0	92.0	"		
91.0	1.0	8.0	MW + SP	0.125	−12.38
82.6	1.0	16.4	" "		
68.5	1.0	30.5	" "		
67.0	3.0	30.0	" "	0.321	−11.45
49.0	4.0	47.0	" "	0.370	−11.30
35.5	2.0	62.5	" "		
35.0	3.0	62.0	" "		
34.8	4.0	61.2	" "	0.406	−11.20
12.0	5.0	83.0	" "	0.506	−10.96
0.0	9.0	91.0	" "		
0.0	10.0	90.0	" "		
51.0	49.0	0.0	SP + MW		
44.2	47.0	8.8	" "	0.116	−12.45
38.8	43.9	17.3	" "	0.169	−12.09
30.6	40.0	29.4	" "	0.272	−11.62
22.8	37.0	40.2	" "	0.340	−11.39
8.0	33.0	59.0	" "	0.469	−11.04
0.0	29.0	71.0	" "		
0.0	22.0	78.0	" "	0.588	−10.79
42.4	49.0	8.6	SP		
21.9	39.2	38.9	"		
20.0	43.0	37.0	"		
3.9	33.0	63.1	"		
3.6	39.5	56.9	"		
0.0	32.5	67.5	"		
49.5	50.5	0.0	SP + α		
42.0	49.5	8.5	" "		
39.5	52.5	8.0	" "	0.089	−12.70
33.9	51.0	15.1	" "	0.109	−12.51
27.6	46.0	26.4	" "		
26.5	49.0	24.5	" "	0.167	−12.10
19.1	46.9	34.0	" "	0.217	−11.85
7.4	41.0	51.6	" "	0.357	−11.34
7.0	43.5	49.5	" "		
0.0	39.5	60.5	" "		
30.0	64.0	6.0	α + SP	0.117	−12.44
26.6	61.6	11.8	" "	0.145	−12.24
20.9	59.0	20.1	" "	0.194	−11.96
15.4	57.1	27.5	" "	0.280	−11.59
5.8	54.0	40.2	" "		
5.8	53.0	41.2	" "	0.380	−11.28
6.2	51.0	42.8	" "		
2.8	52.0	45.2	" "		
0.0	47.5	52.5	" "	0.388	−11.25
28.3	66.0	5.7	α		
16.5	59.0	24.5	"		
0.0	52.0	48.0	"		
27.5	67.0	5.5	α + MFPB	0.082	−12.77
23.2	66.5	10.3	" "	0.109	−12.51
18.3	63.6	18.1	" "	0.139	−12.28
15.5	60.0	24.5	" "		

TABLE 2 (continued)

Mixture	Composition (Wt %)		Phases Present*	CO_2/H_2	Log P_{O_2}
MgO	TiO_2	FeO			
13.5	62.5	24.0	" "	0.185	−12.00
5.4	57.0	37.6	" "		
5.1	59.0	35.9	" "	0.324	−11.44
2.6	56.5	40.9	" "		
0.0	53.5	46.5	" "		
0.0	58.0	42.0	" "	0.406	−11.20
0.0	60.5	39.5	" "		
18.3	78.0	3.7	MFPB + α	0.101	−12.58
16.8	75.7	7.5	" "	0.122	−12.40
13.3	74.0	12.7	" "	0.148	−12.22
10.0	72.1	17.9	" "	0.216	−11.85
3.8	69.5	26.7	" "		
3.9	68.7	27.4	" "	0.346	−11.32
1.9	68.5	29.6	" "		
0.0	68.5	31.5	" "		

* Abbreviations used have the same meanings as in table 1.

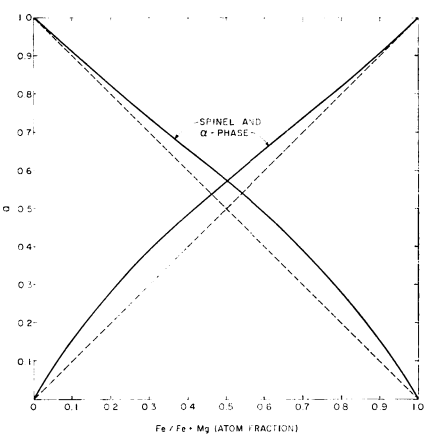

Fig. 5. Sketch of approximate activity-composition relations in spinel (Mg_2TiO_4–Fe_2TiO_4) and α ($MgTiO_3$–$FeTiO_3$) solid solutions in the system MgO–"FeO"–TiO_2 at 1300°C, as estimated from directions of conjugation lines between pairs of coexisting solid-solution phases in contact with metallic iron.

culated from the experimental data of the present investigation, is −8.3 ± 1 kcal. This is considerably more negative than the value (−5.0 kcal) estimated for this reaction by extrapolation from 1100 to 1300°C of the data of Taylor and Schmalzried (1964) based on EMF measurement. Part of this discrepancy may be due to differences in stoichiometry of the phases used in the two investigations.

The free energy of formation of Fe_2TiO_4 at 1300°C from its oxide components cannot be determined conveniently by direct equilibrations between metallic iron and pairs of oxide phases by the same method as was used for cobalt titanates (Brežný and Muan, 1969). Equilibration runs involving metallic iron and iron oxide–titanium oxide mixtures

of TiO_2 contents higher than that of the $FeO{\cdot}2TiO_2$ composition produced phases in which titanium is probably present in appreciable amounts in oxidation states below 4+, for example, in the form of Ti_3O_5. Instead, as a supplement to the present calculations based on the oxide-spinel equilibrium in the system MgO–FeO–TiO_2, the free energy of formation of Fe_2TiO_4 from its oxide components was estimated also from directions of conjugation lines between coexisting oxide and spinel solid solutions in the central part of the system CoO–"FeO"–TiO_2 in contact with metallic iron at 1300°C. In this system, the stability of Co_2TiO_4 ($\Delta G^\circ_{Co_2TiO_4}$) is known from previous work (Brežný and Muan, 1969) as is the activity-composition curve for the oxide solid solution CoO–"FeO" (Aukrust and Muan, 1963). A plot of log $a_{FeO}{\cdot}N_{CoTi_{0.5}O_2}/a_{CoO}{\cdot}N_{FeTi_{0.5}O_2}$ versus $(N_{FeTi_{0.5}O_2} - N_{CoTi_{0.5}O_2})$ (see Muan, 1967) gives a straight line, and the value of log C at $(N_{FeTi_{0.5}O_2} - {}_{CoTi_{0.5}O_2}) = 0$ is a good approximation for the value of $-\Delta(\Delta G^\circ)/2.303RT$ for the reaction

$$CoO + FeTi_{0.5}O_2 = FeO + CoTi_{0.5}O_2 \qquad (5)$$

where

$$(\Delta G^\circ) = \tfrac{1}{2}\,\Delta G^\circ_{Co_2TiO_4} - \tfrac{1}{2}\,\Delta G^\circ_{Fe_2TiO_4} \qquad (6)$$

The value of $\Delta G^\circ_{Fe_2TiO_4}$ thus obtained is -8.0 ± 1.0 kcal, which is in good agreement with the value (−8.3 kcal) obtained from the system MgO–FeO–TiO_2. The average value of $\Delta G^\circ_{Fe_2TiO_4} = -8.2$ kcal will be used in subsequent calculations of this paper.

From the spinel–rhombohedral phase equilibrium, the value of $\Delta(\Delta G^\circ)$ for the reaction

$$FeTi_{0.5}O_2 + MgTiO_3 = MgTi_{0.5}O_2 + FeTiO_3 \qquad (7)$$

is calculated to be 2.3 kcal. Based on the previously determined ΔG°-values for $MgTiO_3$ (−4.8 kcal, Brežný and Muan, 1969), Fe_2TiO_4 (−8.2 kcal, this investigation), and $MgTi_2O_5$ (−6.8 kcal, Brežný and Muan, 1969), the calculated value of $\Delta G^\circ_{FeTiO_3}$ at 1300°C is -4.3 ± 1.0 kcal. This is somewhat more negative than the value of $\Delta G^\circ_{FeTiO_3} = -3.7$ kcal as listed by Elliott, Gleiser, and Ramakrishna (1963).

From the rhombohedral phase-pseudobrookite equilibrium, the $\Delta(\Delta G^\circ)$-value for the reaction

$$FeTiO_3 + MgTi_2O_5 = MgTiO_3 + FeTi_2O_5 \qquad (8)$$

at 1300°C is calculated to be 2.0 kcal. Combination of this value with the ΔG°-values of $MgTiO_3$ (−4.8 kcal) and $FeTiO_3$ (−4.3 kcal) as discussed in the preceding section and with the free energy of formation of $MgTi_2O_5$ (−6.8 kcal) as determined from equilibria in the system MgO–CoO–TiO_2 (Brežný and Muan, 1971), the free energy of formation of $FeTi_2O_5$ at 1300°C is calculated to be -4.3 ± 1.0 kcal. To our knowledge, no free-energy data for this compound have been reported previously.

The free-energy data obtained for the various iron titanates in the present investigation are in qualitative agreement with the observed stability relations among the crystalline phases in the system FeO–TiO_2.

It is seen that $FeTiO_3$ is stable relative to the phase assemblage Fe_2TiO_4 + TiO_2, and that the phase $FeTi_2O_5$ has practically the same free energy as that of the phase assemblage $FeTiO_3$ + TiO_2. The latter observation is in accord with the finding of Haggerty and Lindsley (1969) that $FeTi_2O_5$ decomposes to $FeTiO_3$ and TiO_2 at a temperature (1140°C) only slightly lower than that of the present investigation (1300°C).

The data obtained in the present investigation show that the mineral armalcolite, which has been identified in lunar samples (Anderson and others, 1970), represents a range of compositions along a solid-solution series which is continuous at 1300°C between the end-member compounds $FeTi_2O_5$ and $MgTi_2O_5$. Furthermore, the present work establishes the distribution of iron and magnesium between coexisting titanate solid-solutions (spinel, α-phase, and pseudobrookite) in a simplified system under equilibrium conditions at 1300°C. As a first approximation, these distributions may be used as a guide in evaluating natural phase assemblages, although in natural occurrences additional composition variables, and temperature and pressure variations will modify the relations observed in the idealized, simplified system studied in the present investigation.

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