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Activity Measurements in Orthosilicate and Metasilicate Solid Solutions. II. $MgSiO_3$-$FeSiO_3$ at 1154, 1204, and 1250°C

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The activity-composition relation in the pyroxene solid solution, $MgSiO_3$–$FeSiO_3$, is determined by the quenching method in the atmosphere of a gas mixture of CO_2 and H_2 at 1154, 1204, and 1250°C. A non-ideality is found in the solution at these temperatures, and it increases with a decrease in the temperature. The standard free energy values of the formation of ferrosilite, $FeSiO_3$, from metallic iron, silica, and oxygen are -42.5 ± 0.3, -41.7 ± 0.2, and -41.3 ± 0.2 kcal per mole of $FeSiO_3$ at 1154, 1204, and 1250°C respectively. Using the data by Darken and Gurry, the standard free energies of the formation of ferrosilite from wüstite and silica are obtained as -1.8 ± 0.3, -1.5 ± 0.2, and -1.8 ± 0.2 kcal per mole of $FeSiO_3$ at 1154, 1204, 1250°C respectively.

In the previous paper[1] it was concluded that both olivine, Mg_2SiO_4–Fe_2SiO_4, and pyroxene, $MgSiO_3$–$FeSiO_3$, solid solutions showed significant deviations from ideality at 1204°C. The non-ideality in the olivine solid solution was also recognized by Nafziger and Muan,[2] but their results on the pyroxene solid solution are very different from ours; they found the pyroxene solid solution to be practically ideal in its activity-composition relation, though their data were from an experiment at 1250°C and the difference in temperature may have caused the difference in the deviations from ideality. The objectives of the present paper are to find the activity-composition relation in the pyroxene solid solution, to determine the standard free energy change in the formation of ferrosilite, and to confirm whether or not the deviations from ideality in the activity of $FeSiO_3$ in the pyroxene solid solution depend on the temperature. As has been described above, we have already reported data at 1204°C but the samples used in the present experiment are newly prepared by adding some silicon oxide to the previous samples in order to position, in the two-phase region, the silica+pyroxene solid solution. Therefore, the same experiment was repeated in order to check the first results.

Method of the Calculation of the Activity. The method of the calculation of the activity of the pyroxene solid solution has been described in the previous paper.[1] The activity of the $FeSiO_3$ in the pyroxene solid solution is represented by Eq. (1):

$$a_{(FeSiO_3)ss} = (P_{O_2}/P_{O_2}^*)^{1/2} \tag{1}$$

The subscript ss means a solid solution. The P_{O_2} in Eq. (1) represents the oxygen partial pressures of the decomposition of pyroxene solid-solution samples with various compositions, and the equation:

$$(FeSiO_3)_{ss} = Fe + SiO_2 + \tfrac{1}{2}O_2 \tag{2}$$

indicates the corresponding chemical reaction. The $P_{O_2}{}^*$, which is used as the standard oxygen partial pressure, is the oxygen partial pressure corresponding to the reaction (2) of a pure ferrosilite that does not exist at ordinary temperatures and pressures but which is obtained at each temperature by extrapolating, by means of the α-function method, to $(1-N_{FeSiO_3})^2=0$ (Fig. 1).

Experimental

Preparation of Samples. The pyroxene solid solutions were prepared by the method of the previous paper.[1] It is very difficult to prepare one-phase samples with the desined composition. If the samples prepared had a lower silica content than that of the expected one-phase composition, the total composition of the samples would lie in the two-phase area of pyroxene and olivine solid solutions. Therefore, such samples must give a large oxygen partial pressure corresponding to the olivine solid solution. To avoid problems like this, the samples which contained excess silica were prepared.[3] The samples thus prepared were confirmed to be in the two-phase area, to be, that is, silica and pyroxene solid solution, by a chemical analysis of the iron and magnesium contents and by the use of an X-ray diffractometer. Excess silica does not participate the reaction (2), as can be seen from the phase diagram in the previous paper.[1] Table 1 shows the analytical values of the samples used in the present experiment in

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[1] K. Kitayama and T. Katsura, This Bulletin, **41**, 1146 (1968).

[2] R. H. Nafziger and A. Muan, *Amer. Mineral.*, **52**, 1364 (1968).

[3] K. Kitayama and T. Katsura, This Bulletin, **41**, 525 (1968).

TABLE 1. ANALYTICAL DATA OF SAMPLES (mol%)

Sample No.	$N^*_{FeSiO_3}$	FeO	MgO	SiO_2
1	0.100	4.7	41.1	54.2
2	0.206	9.4	35.6	55.0
3	0.301	13.4	31.0	55.6
4	0.401	18.0	26.7	55.3
5	0.497	22.0	22.4	55.6
6	0.599	26.9	18.0	55.1

* The compositions of pyroxene solid solution are determined by the same method as in the case of Table 2.

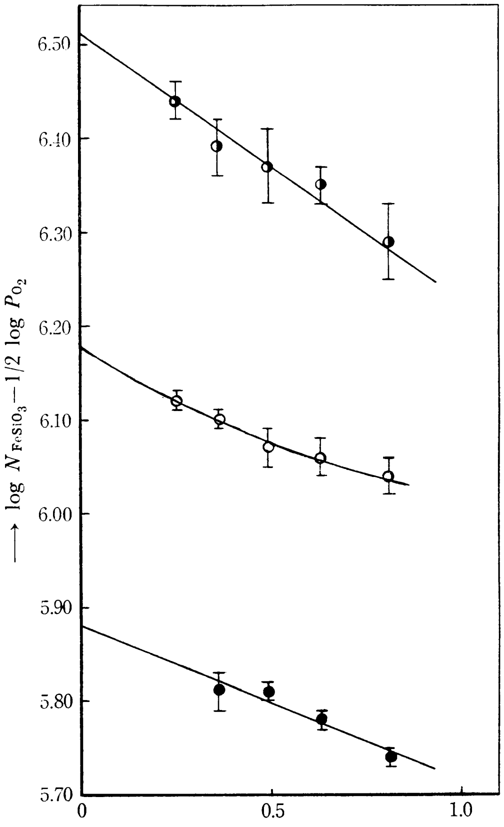

Fig. 1. Relationship between (log N_{FeSiO_3} − 1/2 log P_{O_2}) and $(1-N_{FeSiO_3})^2$ at 1154, 1204, and 1250°C.

◑ 1154°C ○ 1204°C ● 1250°C

TABLE 2. RESULTS OF EQUILIBRIUM EXPERIMENTS AT 1154, 1204, AND 1250°C

	N_{FeSiO_3}	$-\log P_{O_2}$	a_{FeSiO_3}	$\log N_{FeSiO_3} - 1/2 \log P_{O_2}$
1154°C	0.100Fs	14.57±0.07	0.17±0.03	6.29±0.04
	0.206	14.07±0.03	0.30±0.05	6.35±0.02
	0.301	13.78±0.08	0.42±0.07	6.37±0.04
	0.401	13.58±0.06	0.53±0.09	6.39±0.03
	0.497*	13.48±0.04	0.60±0.11	6.44±0.02
	0.599*	13.48±0.04		
1204°C	0.100	14.08±0.04	0.13±0.02	6.04±0.02
	0.206	13.49±0.03	0.27±0.02	6.06±0.02
	0.301	13.18±0.03	0.38±0.04	6.07±0.02
	0.401	12.97±0.02	0.49±0.03	6.10±0.01
	0.497	12.83±0.02	0.58±0.04	6.12±0.01
	0.599*	12.70±0.02		
1250°C	0.100	13.49±0.01	0.13±0.01	5.74±0.01
	0.206	12.94±0.02	0.26±0.01	5.78±0.01
	0.301	12.66±0.02	0.35±0.02	5.81±0.01
	0.401	12.42±0.03	0.47±0.03	5.81±0.02

* These values are determined assuming total composition were in the two-phases area as in the case of other samples.

mole percentages. The iron(II) was volumetrically determined with potassium permanganate, while the total iron was determined colorimetrically with α,α′-dipyridyl. The magnesium contents were gravimetrically determined by precipitating it as magnesium ammonium phosphate.

Apparatus. The vertical-type furnace, gas mixer, and other pieces of equipment were the same as those used in a previous paper.[4] Mixed gases of CO_2 and H_2 were used to obtain low oxygen partial pressures in the present experiment.

Procedure. Mixed gases with various ratios of CO_2 and H_2 are introduced from the bottom to the top of the furnace tube. Then the samples are suspended by thin platinum wires at a definite position in the furnace controlled at the expected temperature. After 24 hr the suspended sample is quenched and a formation of iron metal corresponding to the reaction (2) is confirmed by dipping the sample into dilute hydrochloric acid. The details of the procedure are the same as those of the previous paper.[1] After determining the hydrogen-to-carbon dioxide ratio corresponding to that of the (2) reaction, the oxygen partial pressure is immediately measured by means of a solid electrolyte cell.[5]

Results and Discussion

The experimental results are listed in Table 2. In the second column, the compositions of the pyroxene solid solution are shown. It is found that the chemical compositions (Table 1) of the samples are in the two-phase area (SiO_2+pyroxene solid solution) of the phase diagram of the previous paper (Fig. 1).[1] Tie lines can then be drawn so as to pass through points of the sample composition in the two-phase area to the SiO_2 apex. The intersections of the tie lines and the pyroxene solid-solution line show the composition of the pyroxene solid solution. In the third column, the oxygen partial pressures corresponding to that of the reaction (2) are listed. The activities calculated with Eq. (1) are shown in the fourth column. The

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[4] T. Katsura and S. Kimura, *ibid.*, **38**, 1664 (1965).

[5] T. Katsura and M. Hasegawa, *ibid.*, **40**, 561 (1967).

oxygen partial pressures of 0.599 Fs and 0.497 Fs samples at 1154°C have the same value. This fact suggests that the total compositions of both the samples may be situated within the three-phase area (SiO_2+pyroxene solid solution+olivine solid solution) at 1154°C. The data at 1204 and 1250°C are also shown in Table 2. At 1204°C the oxygen partial pressure of 0.599 Fs is different from that of 0.497 Fs. Therefore, the 0.497 Fs sample seems to be positioned in the two-phase area, while the 0.599 Fs sample in the three-phase area. Judging from the experimental results, the composition of 0.497 Fs seems to be near the boundary between the two- and three-phase areas. Moreover, the results presented above show that the boundary line between two- and three-phase areas must move toward the iron-rich side in the present subsolidus condition with an increase in the temperature. This result is in great contrast to those of Nafziger and Muan[2] and of Bowen and Schairer.[6]

In Fig. 1 the relationship between ($\log N_{FeSiO_3} - 1/2 \log P_{O_2}$) and $(1-N_{FeSiO_3})^2$ is shown at 1154, 1204, and 1250°C. Errors are given as the deviations of the results of three experiments. It may be concluded from Fig. 1 that α[1] is not zero, but 0.28, at 1154°C, that is, the pyroxene solid solution deviatives slightly from ideality. Extrapolating graphically to $(1-N_{FeSiO_3})^2=0$, $\log P_{O_2}=-13.03\pm0.08$ atm is obtained as the value of the oxygen partial pressure of pure ferrosilite, corresponding to Eq. (2) at 1154°C. By substituting this value into the equation:

$$\Delta G^0 = 1/2RT \ln P_{O_2} \tag{3}$$

-42.5 ± 0.3 kcal per mole is obtained as the standard free energy change of the formation of ferrosilite at 1154°C. The same relationships are shown at both 1204 and 1250°C. The values of 0.22 at 1204°C and 0.17 at 1250°C are obtained as the α values. They are smaller than that at 1154°C. That is, the higher the temperature becomes, the more ideal is the activity-composition relation. Nafziger and Muan's data show that α is nearly parallel to the abscissa at 1250°C. The present results show non-ideality even at 1250°C. The extrapolated values of $\log P_{O_2}$ for pure ferrosilite are determined to be -12.35 ± 0.04 and -11.76 ± 0.02 atm at 1204 and 1250°C respectively.

The $\log P_{O_2}$ value at 1204°C is in good agreement with the our previous result, -12.35 ± 0.03.[1]

It gives the standard free energy changes of the formation as -41.7 ± 0.2 and -41.3 ± 0.2 kcal/mol respectively. Those values are shown in Table 3 together with a previously determined value. At 1250°C Nafziger and Muan[2] reported -40.6 kcal/mol as the standard free energy change of the formation of ferrosilite. By combining the standard free energy change of the formation of ferrosilite corresponding to Eq. (2) with the value of that of wüstite obtained by Darken and Gurry,[7] the free energy changes of the formation of ferrosilite from wüstite and silica, followed by the reaction:

TABLE 3. RESULTS FOR THE STANDARD FREE ENERGY CHANGE OF FORMATION OF FERROSILITE FROM IRON, SILICA, AND OXYGEN TOGETHER WITH PREVIOUS VALUE

Temperature (°C)	ΔG° (kcal/mol)	
	Present values	Previous value
1154	-42.5 ± 0.3	
1204	-41.7 ± 0.2	
1250	-41.3 ± 0.2	-40.6[2]

TABLE 4. PRESENT VALUES FOR THE STANDARD FREE ENERGY GHANGE OF FORMATION OF FERROSILITE FROM Wüstite AND SILICA TOGETHER WITH PREVIOUS VALUES

Temperature (°C)	ΔG° (kcal/mol)	
	Present values	Previous values
1080		-1.1[12]
1150		-1.3 ± 0.3[-14]
1154	-1.8 ± 0.3	-1.5[9]
1204	-1.5 ± 0.2	-1.4[9]
1250	-1.8 ± 0.2	-0.9 ± 0.5[2], -1.6[9]
1300		-1[a]

[a] A. Muan, R. H. Nafziger and P. L. Roeder, *Nature*, **202**, 688 (1964).

$$\text{"FeO"} + SiO_2 = FeSiO_3 \tag{4}$$

are determined to be -1.8 ± 0.3, -1.5 ± 0.2, and -1.8 ± 0.2 kcal per mole at 1154, 1204, and 1250°C respectively. In the calculation of P_{CO_2}/P_{CO} ratios in Darken and Gurry's data to the oxygen partial pressure, the thermochemical data of Elliot and Gleiser[8] are used. The previous values relating to Eq. (4) are summarized in Table 4, together with the above present values. As may be seen from Table 4, the present values agree very well with the values of Akimoto *et al.*,[9] but they are smaller than those of the others. The relationship between the activity and the mole fraction of $FeSiO_3$ are represented in Fig. 2. As is shown in Fig. 2, and as can be expected from Fig. 1, the non-ideality is the largest at 1154°C, but the differences in the other values are small. It is also shown in Fig. 2 that nonideality increases with

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6) N. L. Bowen and J. F. Schairer, *Amer. J. Sci.*, **29**, 151 (1935).

7) L. S. Darken and R. W. Gurry, *J. Amer. Chem. Soc.*, **67**, 1398 (1945).

8) J. E. Elliot and M. Gleiser, "Thermochemistry for Steelmaking," Addison-Wesley Pub. Co., Mass., U.S.A. (1960).

9) S. Akimoto, T. Katsura, Y. Syono, H. Fujisawa and E. Komada, *J. Geophy. Res.*, **70**, 5269 (1965).

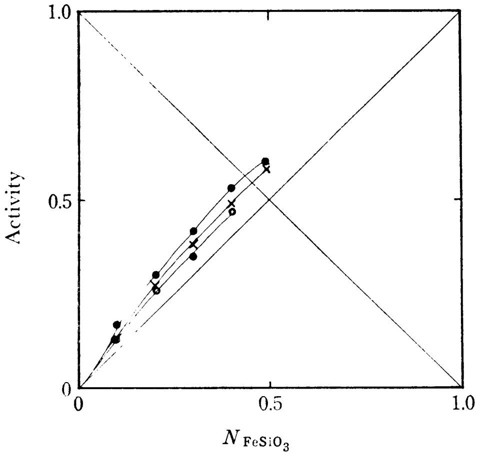

Fig. 2. Activity-composition relations in pyroxene solid solution at 1154, 1204, and 1250°C.
○ 1250°C × 1204°C ● 1154°C

a decrease in the temperature.

The variations in the activity with the temperature in other system have been reported by many investigator. In the MgO - FeO system[10] no apparent difference in activity between at 1100 and 1300°C is found. Aukrust and Muan[11] studied the activity-composition relations in the Co_3O_4-Mn_3O_4 system and did not find any differences in the activity in the 1100—1400°C temperature range.

Three metasilicate solid solutions, the Ca - Fe system[12] at 1080°C, the Mn - Co system[13] at from 1200 to 1250°C, and the Fe - Mn system[14] at 1154°C, are all ideal in their activity-composition relation, differing from the results obtained in the present experiment. In Fig. 3 the relation between the oxygen partial pressures of the formation of ferrosilite and the temperatures are shown. The abscissa represents a reciprocal of the absolute temperature. The log P_{O_2} is related to the standard free-energy change in the formation by the equation:

$$\Delta G^0 = 1/2\boldsymbol{R}T\ln P_{O_2} = \Delta H^0 - T\Delta S^0 \quad (5)$$

Therefore, the gradient of the line in Fig. 3 indicates the 2 $\Delta H^0/\boldsymbol{R}$ of the ferrosilite formation in the present experimental temperature ranges. The data for the fayalite formation:

$$2Fe + SiO_2 + O_2 = Fe_2SiO_4 \quad (6)$$

have already been reported.[3] The values are plotted in Fig. 3, as open circles, together with the present ferrosilite results. The data for fayalite are plotted on just the present temperature-oxygen partial pressure line. That is, oxygen partial pressures of Eq. (2) for pure ferrosilite and Eq. (6) for fayalite are nearly equal. Strictly speaking, the oxygen partial pressure of the ferrosilite decomposition, shown in Eq. (2), should be lower than that of fayalite. The correspondence of the oxygen partial pressures in the two reaction may be due to the experimental technique. The difference is, however, so small that it can not be detected, and it may be due to the extrapolation done with the present, insufficient data. As has been described above, the difference in the changes in the free energy of formation is merely that of the factors of oxygen in the two equations. Therefore, the standard free-energy change in the formation of the ferrosilite must be one-half of that of fayalite.

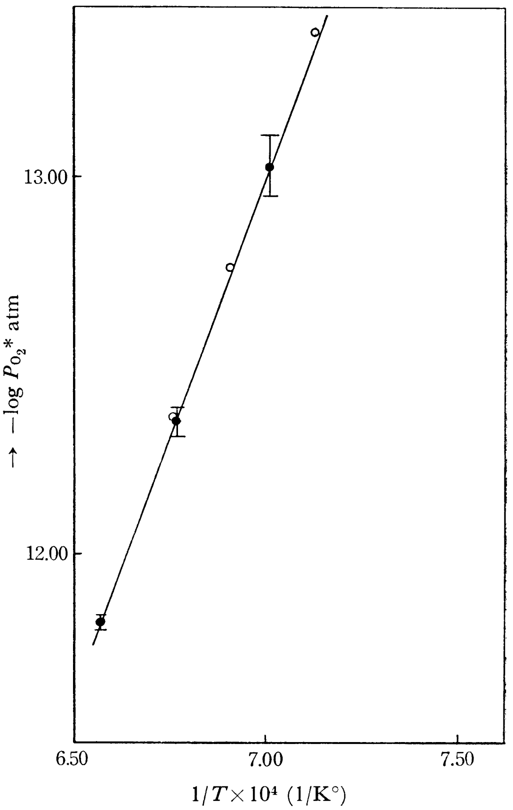

Fig. 3. Relationship between log P_{O_2}* and $1/T$ (K°)
○ $2Fe+SiO_2+O_2=Fe_2SiO_4$
$\frac{I}{\bullet}$ $Fe+SiO_2+1/2O_2=FeSiO_3$

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10) W.C. Hahn, Jr., and A. Muan, *Trans. Met. Soc. AIME* (*Amer. Inst. Minig., Met., Eng.*), **224**, 416 (1962).

11) E. Aukrust and A. Muan, *ibid.*, **230**, 378 (1964).

12) R. E. Johnson and A. Muan, *ibid.*, **239**, 1931 (1967).

13) J. V. Biggers and A. Muan, *J. Amer. Chem. Soc.*, **50**, 230 (1967).

14) K. Schwerdtfeger and A. Muan, *Trans. Met. Soc. AIME* (*Amer. Inst. Mining, Met., Eng.*), **236**, 201 (1966).