Composition of Fayalite and Its Standard Free Energy of Formation

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Data on fayalite (Fe_2SiO_4) stability have previously been studied by Schenck, Franz, and Laymann¹⁾ at 900°C, and by Cirilli²⁾ at 900, 1000, and 1100°C, both controlled by the CO_2/CO equilibria in a gas phase co-existing with fayalite, silica, and metallic iron. These data have summarized by Richardson, Jeffes, and Withers,³⁾ and they proposed a linear free energy equation on the basis of the data obtained by Schenck *et al.* Pitzer and Brewer⁴⁾ also calculated the free energy function of fayalite based on H°_{298}. Recently Taylor and Schmalzried⁵⁾ determined the free energy of formation of fayalite by electromotive-force measurements between 900 and 1100°C, and they recalled a complication met with the formation of solid solutions at high temperatures.

Schwerdtfeger and Muan⁶⁾ determined the equilibrium ratio of CO/CO_2 of a gas phase co-existing with fayalite, silica and metallic iron, and calculated the standard free energy of formation of fayalite at temperatures of 1000, 1100, and 1150°C. Berliner and Shapovalova⁷⁾ determined the equation, $\Delta G^\circ = -135{,}320 + 33.20\,T$, for the reaction (3) which will be seen in later, on the basis of the reduction of fayalite by H_2 gas.

The present objectives are first to ascertain whether or not there exists an appreciable composition range in fayalite within the ternary system FeO-Fe_2O_3-SiO_2, and then to determine the standard free energy of formation of fayalite at temperatures slightly below the solidus after finding an equilibrium oxygen partial pressure obtained by a CO_2/H_2 gas mixture.

Experimental

Reagent grade chemicals are served as starting materials. Ferric oxide is heated at 900°C and silicic acid is heated at 1300°C for several hours in a global furnace. The desired amounts of the dry oxides are mixed and ground for several hours. Approximately a 20 g of each mixture is then heated in a platinum crucible in the globar furnace at 1300°C for 10—24 hr. The sintered mass is re-ground and re-heated at the same temperature for several hours. From the new sintered mass cut a disc weighing approximately 2 g and with a central bore for suspending the disc by

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1) Von R. Schenck, H. Franz and A. Laymann, *Z. anorg. u. allgem. Chem.*, **206**, 129 (1932).

2) V. Cirilli, *Gazz. Chim. Ital.*, **76**, 331 (1946).

3) F. D. Richardson, J. H. E. Jeffes and G. Withers, *J. Iron Steel Inst.*, **166**, 213 (1950).

4) K. S. Pitzer and L. Brewer, "Thermodynamics," 2nd Ed., McGraw-Hill, New York (1961).

5) R. W. Taylor and H. Schmalzried, *J. Phys. Chem.*, **68**, 2444 (1964).

6) K. Schwerdtfeger and A. Muan, *Trans. AIME*, **236**, 201 (1966).

7) L. D. Berliner and R. D. Shapovalova, *Zh. Fiz. Khim.*, **40**, 2905 (1966).

means of a thin platinum wire from one beam of an analytical balance.

Pellets consisting of fayalite-silica mixtures are kept at chosen constant temperature and chosen levels of oxygen partial pressure until equilibrium is attained.

Composition changes of the sample in response to changes in oxygen partial pressure are determined by both thermogravimetric and wet chemical analyses of quenched samples. Phases present are determined by microscopic and X-ray examination of quenched samples. The apparatus used in this study are the same as those used in a previous work.8)

For determining the free energy of formation of fayalite, reagent grade chemicals are used without purification as starting materials. Ferric oxide is reduced to ferrous at 1200°C in an atmosphere consisting of CO_2/H_2 mixed gas ($CO_2/H_2=1$). The ferrous oxide is stoichiometrically mixed with silica to prepare fayalite. The mixtures are melted in the same atmosphere at 1300°C in a 80% platinum - 20% rhodium container which is previously saturated with iron. The melts are quenched and pulverized in an agate mortar. The powder (fayalite) is mixed with silica to avoid excess free iron oxide. The mixture is again melted, quenched and pulverized. The fayalite-silica powder is caked at 1154°C in the CO_2-H_2 atmosphere in the same container.

The standard quenching technique is adopted for the present study under controlled atmospheric conditions. The cakes are kept at chosen temperature and chosen levels of oxygen partial pressure. After 24 hr, these samples are quenched and metallic iron separated is ascertained by microscopic and dilute hydrochloric acid method. After repeating the procedure, a CO_2/H_2 ratio just appearing the metal iron is determined at four temperatures. The oxygen partial pressures corresponding to the CO_2/H_2 ratio are measured directly by a solid electrolyte. Details of the measurement have been reported by Katsura and Hasegawa.9)

Results and Discussion

Composition of Fayalite. The FeO content of fayalite present in sample A through D after equilibration at various oxygen partial pressures at 1125, 1156, and 1170°C are listed in Table 1. Within the limit of experimental error (±0.4 mol%), the composition of fayalite is constant and corresponds to the formula $2FeO \cdot SiO_2$ around 1150°C

Free Energy of Formation of Fayalite. Phase equilibrium studies previously reported for the system Fe–Si–O (Bowen and Schairer10): Darken11): Muan12)) are useful for defining the

TABLE 1. COMPOSITION OF FAYALITE AS A FUNCTION OF OXYGEN PRESSURE AT VARIOUS TEMPERATURES

Temp. °C	Mixture	Starting composition (mol%)		Time hr	$\log P_{O_2}$ atm	Mole% FeO in Mixture	Calculated Mole% FeO in Fayalite phase
		Fe_2O_3	SiO_2				
1125	A	44.4	55.6	41	−10.62	61.1	66.3
				18	−11.56	61.3	66.4
				15	−12.32	61.3	66.4
				12	−12.73	61.3	66.4
	C	36.1	63.9	12	−12.75	53.0	66.6
				12	−12.80	53.0	66.6
1156	A	44.4	55.6	41	−11.57	61.2	66.3
				29	−12.43	61.4	66.6
	C	36.1	63.9	18	−11.28	53.0	66.6
				10	−11.52	53.0	66.6
				11	−11.67	53.0	66.6
				12	−12.16	53.0	66.6
1170	A	44.4	55.6	38	−10.11	61.1	66.3
	B	41.1	58.9	25	−12.08	58.2	66.4
				14	−12.33	58.3	66.5
	D	27.3	72.7	28	−11.39	42.8	66.4
				17	−12.34	42.9	66.7
				9	−12.40	42.9	66.7

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8) T. Katsura and S. Kimura, This Bulletin, **38**, 1664 (1965).

9) T. Katsura and M. Hasegawa, *ibid.*, **40**, 561 (1967).

10) N. L. Bowen and J. F. Schairer, *Am. J. Sci.*, **24**, 177 (1932).

11) L. S. Darken, *J. Am. Chem. Soc.*, **70**, 2046 (1948).

12) A. Muan, *Trans. AIME*, **7**, 965 (1955).

Table. 2. Oxygen partial pressure $P_{O_2}(1)$ and $\Delta G°(1)$ together with previous data at various temperatures

Temperature °C	$\log P_{O_2}(1)$ atm present study	$\Delta G°(1)$ kcal			
		present study	Schenck	Taylor	Schwerdtfeger
1129	-13.40 ± 0.05	-86.0 ± 0.3	-87.1	-86.2	-86.6
1144	-13.14	-85.2	-86.6	-85.7	-86.1
1160	-12.87 ± 0.01	-84.4 ± 0.1	-86.0	-85.2	-85.5
1174	-12.77 ± 0.02	-84.6 ± 0.1	-85.5	-84.7	-85.0

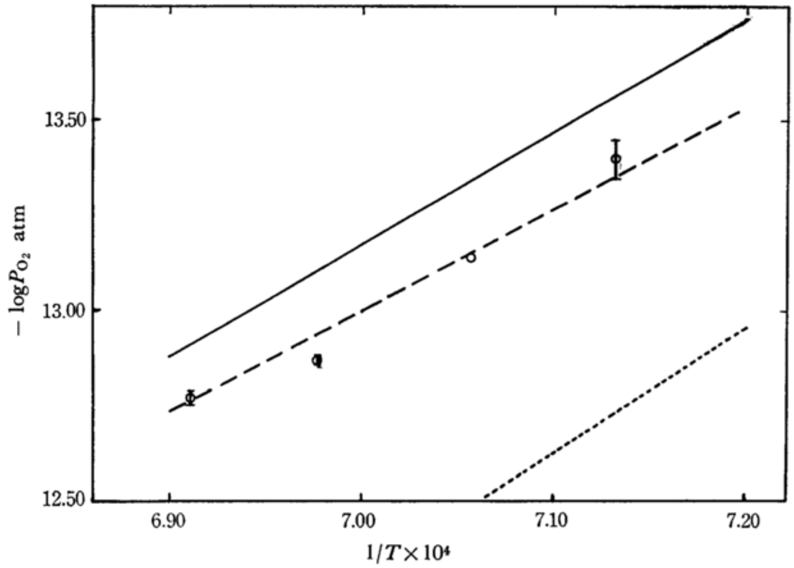

Fig. 1. Relation between oxygen partial pressures and reciprocal absolute temperatures in the present study. Schenck's data and Darken and Gurry's data for Eq. (2) are also represented for comparison.
—— from Schenck *et al.*, …… from Darken and Gurry, ---- present study

upper temperature limit for the present investigation. An application of the phase rule to the various phase assemblages show that in composition area, where three crystalline phases coexist in equilibrium with, the oxygen pressure of the gas phase must be fixed. For instance, in the two areas where silica (tridymite) + fayalite + iron and fayalite + wüstite + iron coexist in equilibrium, diferent oxygen partial pressures, $P_{O_2}(1)$ and $P_{O_2}(2)$ respectively, prevail at equilibrium. The standard free energy changes, $\Delta G°(1)$ and $\Delta G°(2)$, are determined from the oxygen partial pressures in the isothermal invariant equilibrium as follow:

$$2Fe + SiO_2 + O_2 = Fe_2SiO_4 \qquad (1)$$

$$K = a_{Fe_2SiO_4}/a^2_{Fe_2}\cdot a_{SiO_2}\cdot P_{O_2}(1)$$

$$\Delta G°(1) = 2.303\boldsymbol{R}T\log P_{O_2}(1)$$

and

$$1.90Fe + O_2 = 2Fe_{0.95}O \qquad (2)$$

$$\Delta G°(2) = 2.303\boldsymbol{R}T\log P_{O_2}(2)$$

By substracting of Eq. (2) from Eq. (1) the standard free energy of formation of fayalite according to the equation

$$0.1Fe + 2Fe_{0.95}O + SiO_2 = Fe_2SiO_4 \qquad (3)$$

is calculated as:

$$\Delta G°(3) = 2.303\boldsymbol{R}T\log P_{O_2}(1)/P_{O_2}(2)$$

The experimental results obtained are summarized in Table 2 together with Schenck's, Taylor's and Schwerdtfeger's data for comparison, while they are illustrated graphically in Fig. 1 with the width of experimental errors.

The standard free energy changes of reaction (1) are −86.0, −85.2, −84.4 and −84.6 kcal at temperatures 1129, 1144, 1160 and 1174°C, respectively. The values at each temperature in Table 2 and Fig. 1 are a mean for three experimental results except for the value at 1144°C, and we get an equation as a function of temperature:

$$\Delta G°(3) = -122{,}000+26.0\,T\ \text{(cal)}$$

by means of the method of least squares.

The oxygen partial pressures for Eq. (2) obtained from Darken and Gurry's data[13] is shown in the second column of Table 3. Using these values for Eq. (2) and the present results for Eq. (1), $\Delta G°(3)$, that is the standard free energy of formation of fayalite relative to the oxide components SiO_2 and wüstite, is easily calculated. In the Table 3, $\Delta G°(3)$ is indicated at various temperatures together with other two experimental results. $\Delta G°(3)$ varies between -2.8 and -3.4 kcal in the present temperature range. Except for the value at 1160°C, the change in free energy of formation of fayalite relative to oxides is nearly constant (about -3.3 kcal) regardless of the temperature in this experiment. According to recent tabulations by Kelley,[14] $\Delta G°(3)$ varies approximately linearly between -2.3 and -1.7 kcal in the temperature range 1000 to 1150°C. His values are very larger than those in Table 3. The present value, -3.3 kcal, is in fairly good agreement with Taylor's.

TABLE 3. OXYGEN PARTIAL PRESSURES FOR EQ. (2) AND $\Delta G°(3)$ TOGETHER WITH PREVIOUS DATA AT VARIOUS TEMPERATURES

Temp. °C	$\log P_{O_2}(2)$ atm*	$\Delta G°(3)$, kcal		
		Present study	Taylor	Schwerdtfeger
1129	-12.87	-3.4	-3.6	-4.0
1144	-12.66	-3.1	-3.6	-4.0
1160	-12.45	-2.8	-3.6	-3.9
1174	-12.26	-3.4	-3.5	-3.8

* from Darken and Gurry

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[13] L. S. Darken and R. W. Gurry, *J. Am. Chem. Soc.*, **67**, 1398 (1945).

[14] K. K. Kelley, *U. S. Bur. Mines, Rept. Invest.* No. 5901 (1962).