

Heat capacity and entropy of fayalite (Fe_2SiO_4) between 5.1 and 383 K: comparison of calorimetric and equilibrium values for the QFM buffer reaction

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Abstract

The heat capacities of large synthetic crystals of fayalite (Fe_2SiO_4) grown by the Czochralski technique were measured between 5.1 and 381.5 K. The heat capacity exhibits an extremely sharp λ -transition at 64.88 ± 0.03 K corresponding to the paramagnetic–antiferromagnetic inversion, and a smaller hump centered near 16 K, corresponding to a spin structure change from a collinear to canted antiferromagnetic arrangement.

At 298.15 K, C_p° and S° for fayalite are respectively 131.9 ± 0.1 and 151.0 ± 0.2 J/(mol · K). From a third law analysis of six sets of high-temperature reactions involving fayalite, we obtained $\Delta H_{f,298}^\circ = -1478.17 \pm 1.30$ and $\Delta G_{f,298}^\circ = -1378.98 \pm 1.35$ kJ/mol.

Using these new data for Fe_2SiO_4 , we calculated the temperature dependence of the equilibrium constant for the reaction $2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2 = 3\text{Fe}_2\text{SiO}_4 + \text{O}_2$; *i.e.*, the quartz–fayalite–magnetite buffer reaction. Our values for $\Delta G_{f,T}^\circ$ are within 0.70 kJ of those obtained from Hewitt's equation.

Introduction

Fayalite (Fe_2SiO_4) is a common member of the olivine group minerals. Although it occurs mainly in solid solution with Mg_2SiO_4 , relatively pure Fe_2SiO_4 also occurs as a separate phase, for example, at Rockport, Mass. (Bowen *et al.*, 1933), at Pikes Peak, Colo. (Barker *et al.*, 1975), and in the Skaergaard intrusion, Greenland (Wager and Deer, 1939). It also has considerable technological importance in blast-furnace slag.

The crystal structure of Fe_2SiO_4 has been refined by Smyth (1975) and Hazen (1977) using X-ray methods. The magnetic spin structure has been determined using powder neutron diffraction at 4 and 58 K by Santoro *et al.* (1966), who have also measured the powder magnetic susceptibility between 4 and 300 K. The susceptibility has also been investigated by Kondo and Miyahara (1963).

Inasmuch as the earlier heat-capacity measurements of Kelley (1941) were made on a poorly

characterized sample, were limited to the temperature range 52.2 to 295.2 K, and involved an extrapolated contribution to S_{298}° of almost 11 percent, new measurements on well-characterized synthetic crystals of Fe_2SiO_4 are desirable in order to minimize the uncertainty in the entropy and to utilize the entropy data to obtain improved values of $\Delta H_{f,298}^\circ$ from the many high-temperature equilibrium studies involving Fe_2SiO_4 (see below).

Orr's (1953) measurements of the heat content ($H_T^\circ - H_{298}^\circ$) of Fe_2SiO_4 used in conjunction with our low-temperature C_p° data permit us to evaluate the entropy for temperatures as high as 1450 K. King (1952) has determined the enthalpy of formation of Fe_2SiO_4 at 298.15 K using HF solution calorimetry.

Materials and apparatus

The fayalite crystals used for these studies were grown from a melt between 1438 and 1473 K under an argon/hydrogen atmosphere by the Czochralski

Table 1. Experimental molar heat capacities of synthetic Fe₂SiO₄ (fayalite) crystals. Formula weight = 203.778 g/mol.

Temp. kelvin	Heat Capacity J/(mol·K)	Temp. kelvin	Heat Capacity J/(mol·K)	Temp. kelvin	Heat Capacity J/(mol·K)	Temp. kelvin	Heat Capacity J/(mol·K)
Series 1		Series 7		Series 11		Series 14	
300.04	132.3	136.19	74.16	63.92	69.11	270.66	124.8
305.35	133.7	141.90	77.02	64.10	71.25	276.55	126.4
		147.84	79.91	64.26	73.70	282.41	128.0
Series 2		154.02	82.81	64.42	76.43	288.16	129.5
311.65	135.1	160.17	85.66	64.58	79.37	293.85	130.9
316.91	136.3			64.74	82.27		
322.20	137.1	Series 8		64.89	81.58	Series 15	
327.59	138.5	166.30	88.42	65.06	53.44	64.628	79.40
333.36	139.9	172.35	91.07	65.26	46.87	64.679	81.14
339.56	141.1	178.21	93.57	65.47	44.41	64.728	82.15
345.70	142.4	184.15	95.98	65.76	42.77	64.778	83.76
351.80	143.5	190.16	98.43	66.11	41.48	64.827	84.51
		196.07	100.7	66.53	40.64	64.875	86.05
Series 3		202.06	103.0	67.04	40.01	64.924	78.17
356.14	144.2			67.54	39.70	64.979	61.83
362.20	145.4	Series 9					
368.31	146.6	208.01	105.1	Series 12		Series 16	
		213.96	107.2	5.11	.2586	112.55	61.32
Series 4		219.77	109.2	5.25	.3790	113.55	61.98
375.27	147.7	225.50	111.2	6.15	.6386	114.54	62.54
381.47	148.8	231.16	113.0	7.08	1.120	115.53	63.12
		236.92	114.9	8.08	1.726	116.53	63.66
Series 5		242.94	116.8	8.95	2.286		
53.67	37.89	249.05	118.7	9.98	2.992		
57.42	44.98	255.09	120.4	11.38	3.911		
60.64	53.11	261.06	122.2	12.91	4.813		
63.42	66.12*	266.97	123.8	14.32	5.565		
66.21	45.66			15.84	6.269		
69.26	39.34	Series 10		17.59	6.968		
72.28	39.82	59.71	38.58	19.41	7.669		
76.09	41.30	60.41	52.35	21.46	8.429		
81.19	43.83	61.08	54.45	23.78	9.346		
86.53	46.74	61.57	56.10	26.28	10.48		
91.80	49.68	61.88	57.23	28.65	11.73		
97.16	52.76	62.19	58.42	31.10	113.24		
		62.49	59.65				
Series 6		62.79	60.97	Series 13			
94.34	51.13	63.08	62.51	25.52	10.12		
100.17	54.48	63.33	64.02	28.34	11.56		
106.02	57.80	63.54	65.49	31.32	13.39		
111.76	61.02	63.74	67.23	34.46	15.66		
117.41	64.16			37.90	18.54		
123.29	67.36			41.70	22.18		
129.42	70.66			45.59	26.45		
135.32	73.65			49.72	31.75		
				54.08	38.58		

*Mean heat capacity between 62.14 and 64.71 K

technique. The starting materials were >99.999 percent pure Fe₂O₃ and SiO₂ powders. Finch *et al.* (1980) give a complete description of the growth method, as well as a chemical and X-ray characterization of these crystals.

The heat capacity measurements were made by the intermittent heating method under quasi-adiabatic conditions using the cryostat described by Robie and Hemingway (1972), together with the

calorimeter and semi-automatic data-acquisition system described by Robie *et al.* (1976). Temperatures were determined with a Minco model S 1059-1¹ platinum resistance thermometer (R₀ = 100.02 ohms) which had been calibrated by the Temperature Measurements Section of the U.S. National

¹ Use of trade names in this report is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

Bureau of Standards on the International Practical Temperature Scale of 1968 (IPTS-68) between 13.8 and 505 K, and on a provisional temperature scale used in this laboratory between 4.2 and 13.8 (discussed by Robie *et al.*, 1978). The samples were sealed in the calorimeter under purified helium gas at a pressure of 5 kPa (approximately 4×10^{-5} mol of He).

The formula weight used is based on the 1975 values for the atomic weights and was 203.778 g mol⁻¹ for Fe₂SiO₄. The sample weight, corrected for buoyancy, was 40.282 g.

Experimental results

Our experimental heat capacity data are listed in Table 1 in chronological order of measurement. The heat capacity of fayalite exhibits a sharp maximum (λ -point) at 64.88 ± 0.03 K. This transition corresponds to the ordering of the magnetic moments (spins) of the Fe²⁺ ions into a collinear antiferromagnetic arrangement at temperatures below 64.88 K (Santoro *et al.*, 1966). In the neighborhood of 16 K there is also a rounded maximum or "shoulder" which we suspect arises from the canting of the spins away from exact antiparallelism as deduced from neutron diffraction studies at 4 K by Santoro *et al.* (1966). In order to characterize the exact shape of the C_p° curve in the immediate vicinity of the λ -transition, shown in Figure 1, we made three series of measurements (Table 1, series 10, 11, and 15) using very small temperature increments. Measurements in series 10 and 11 were taken at increments of 0.7 to 0.16 K while those in series 15 were made with temperature increments of approximately 0.05 K. Our raw heat capacities (sample plus calorimeter) were smoothed by a computer program²

² The computer program first sorts the data into an ascending array in the independent variable and then generates the smoothest curve that satisfies the condition

$$\sum_{i=1}^n \left[\frac{f(x) - y_i}{dy_i} \right]^2 \leq S$$

where the y_i are the ordinates of the observed data points and S is a parameter that determines the degree of smoothing. From this smoothed curve, values of the first and second derivatives of $f(x)$ are then calculated at the experimental temperatures and are used to calculate the curvature correction (*i.e.*, to convert the $\Delta H/\Delta T$ values to dH/dT 's, *e.g.*, see Robie and Hemingway (1972)). Next, values for the empty calorimeter are calculated from stored coefficients of an orthogonal polynomial and are subtracted from the curvature-corrected gross heat capacity-measurements. Finally, the heat capacity (C_v) of the helium gas, used to promote rapid heat exchange between the sample and the

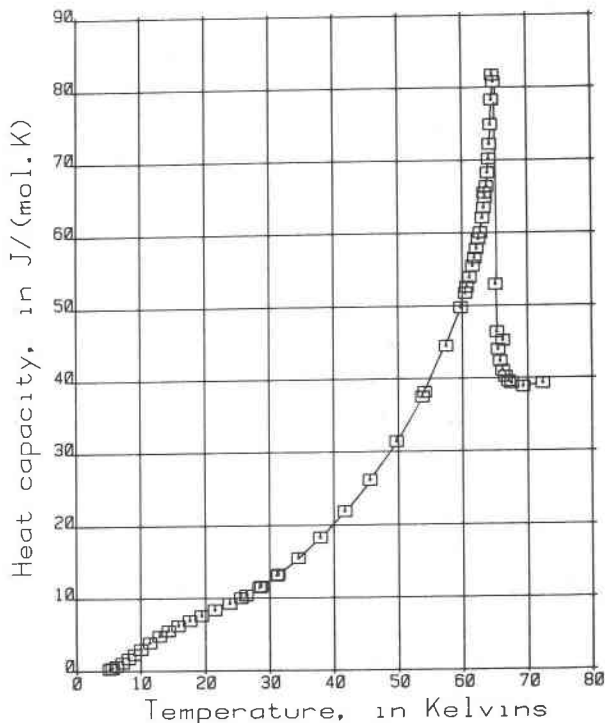


Fig. 1. Heat capacity of Fe₂SiO₄ between 5 and 70 K.

based on the *smoothing spline* approach of Reinsch (1967) (see also de Boor, 1979).

We did not correct our data for possible deviation of the sample composition from the formula Fe₂SiO₄. Finch *et al.* (1980) indicated a possible maximum value for Fe³⁺ of 0.86 wt.%. This Fe³⁺ content corresponds to the presence of a possible 1.7 wt.% magnetite in the sample. However, above 130 K the specific heats (J/g) of magnetite and fayalite are the same to 1 percent or better.

Inasmuch as Fe₃O₄ itself has a sharp λ transition in C_p° between 110 and 120 K, and a maximum heat capacity which exceeds that at 110 and 120 K by a factor of 3, the presence of 1.7 percent magnetite in our sample should lead to a measurable bump in our C_p° data between 110 and 120 K. The measurements of series 16 (Table 1) were made at temperature increments of approximately 1 K in order to see if we could detect the presence of magnetite. No bump was found in the 110–120 K range, and we conclude that the amount of magnetite in our sample is more in keeping with the lowest amounts of

calorimeter, is subtracted to yield C_p° for the sample. The computer program uses the International Mathematics and Statistics Library (IMSL) subroutines.

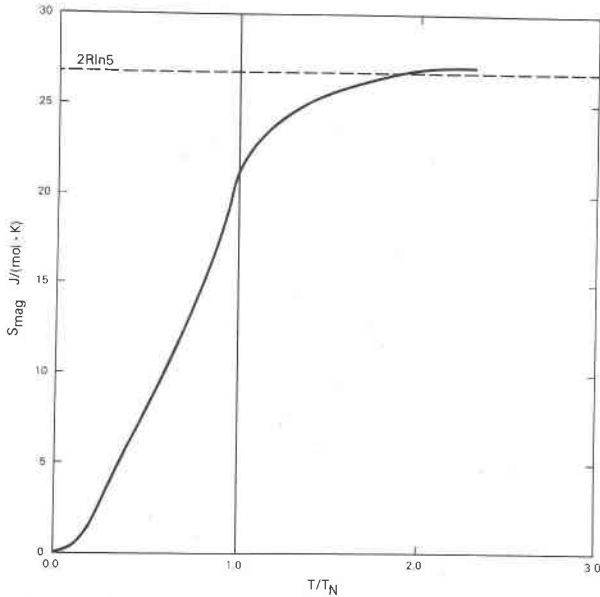


Fig. 2. Magnetic entropy of Fe_2SiO_4 .

Fe^{3+} found by Finch *et al.* (1980), *i.e.*, 0.27 wt.% Fe^{3+} , or possibly less than this amount.

Magnetic entropy of Fe_2SiO_4

In going from 0 K to a temperature considerably above the Néel temperature (T_N), Fe_2SiO_4 gains an entropy of $2R\ln 5 = 26.76 \text{ J}/(\text{mol}\cdot\text{K})$, arising from the disordering of the magnetic spins of the Fe^{2+} ions. This magnetic entropy is in addition to the entropy due to lattice vibrations.

In order to separate the magnetic part of the entropy from the total (observed) entropy, we followed the procedure used by Robie *et al.* (1982), *i.e.*, we used $\gamma\text{-Ca}_2\text{SiO}_4$ estimate the lattice contribution to the entropy. Subtraction of this lattice entropy from the measured total entropy yields the magnetic entropy shown in Figure 2. At the Néel temperature, 64.88 K, the magnetic entropy is only 21.6 $\text{J}/(\text{mol}\cdot\text{K})$ —about 81 percent of the theoretical entropy. Because the magnetic entropy is less than predicted, we conclude that an appreciable short-range ordering of the spins is retained above T_N , and is not removed until temperatures of about 130 K are exceeded.

Thermodynamic properties of Fe_2SiO_4

Our experimental heat capacity data (corrected for curvature) were extrapolated to 0 K by use of a plot of C_p°/T versus T^2 . The extrapolated values were combined with our experimental data and

smoothed in two segments (0–64.88 K and 64.88 to 380 K) to give the values for the thermodynamic functions C_p° , $S_T^\circ - S_0^\circ$, $H_T^\circ - H_0^\circ/T$, and $-(G_T^\circ - H_0^\circ)/T$ listed in Table 2 for temperatures between 5 and 380 K.

Our value for the entropy at 298.15 K is $151.0 \pm 0.2 \text{ J}/(\text{mol}\cdot\text{K})$ and is 2.9 $\text{J}/(\text{mol}\cdot\text{K})$ greater than that obtained by Kelley (1941), $148.1 \pm 5.9 \text{ J}/(\text{mol}\cdot\text{K})$, on the basis of measurements between 52.2 and 295.2 K. The major part of this difference arises from Kelley's extrapolation of his data from 52.2 to 0 K.

King (1952) determined the enthalpy of formation of Fe_2SiO_4 by HF solution calorimetry. The reac-

Table 2. Molar thermodynamic properties of Fe_2SiO_4 (fayalite). Formula weight = 203.778 g/mol.

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_p°	$(S_T^\circ - S_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	$-(G_T^\circ - H_0^\circ)/T$
KELVIN		$\text{J}/(\text{mol}\cdot\text{K})$		
5	0.232	0.062	0.047	0.015
10	3.012	0.950	0.744	0.206
15	5.984	2.752	2.010	0.742
20	7.892	4.731	3.239	1.492
25	9.895	6.780	4.363	2.337
30	12.56	8.727	5.495	3.232
35	16.14	10.92	6.75	4.170
40	20.53	13.35	8.19	5.160
45	25.79	16.07	9.84	6.230
50	32.17	19.10	11.75	7.350
55	40.30	22.53	13.96	8.570
60	51.25	26.47	16.57	9.900
65	63.65	31.42	20.07	11.350
70	39.40	34.45	21.55	12.900
80	43.16	39.91	23.98	15.93
90	48.68	45.30	26.41	18.89
100	54.39	50.73	28.92	21.80
110	60.03	56.18	31.50	24.68
120	65.57	61.64	34.11	27.53
130	70.93	67.10	36.73	30.37
140	76.06	72.55	39.36	33.19
150	80.95	77.96	41.97	35.99
160	85.60	83.34	44.55	38.78
170	90.04	88.66	47.10	41.56
180	94.28	93.93	49.60	44.32
190	98.34	99.13	52.06	47.07
200	102.2	104.3	54.47	49.80
210	105.8	109.4	56.83	52.52
220	109.3	114.4	59.14	55.22
230	112.7	119.3	61.40	57.89
240	115.8	124.2	63.60	60.55
250	118.9	128.9	65.75	63.19
260	121.9	133.7	67.85	65.81
270	124.7	138.3	69.91	68.41
280	127.4	142.9	71.91	70.99
290	129.9	147.4	73.87	73.55
300	132.3	151.9	75.78	76.09
310	134.7	156.2	77.64	78.60
320	136.9	160.6	79.46	81.10
330	139.1	164.8	81.23	83.57
340	141.1	169.0	82.96	86.02
350	143.1	173.1	84.65	88.45
360	145.0	177.2	86.30	90.86
370	146.8	181.2	87.91	93.24
380	148.6	185.1	89.49	95.61
273.15	125.5	139.8	70.54	69.23
298.15	131.9	151.0	75.43	75.62

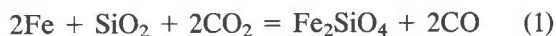
tion scheme used by King involved ten separate reactions, four of which were taken from other workers. Hemingway and Robie (1977) corrected King's result to modern values for several of the steps used in his reaction scheme. However, before we adopt a value for the enthalpy or Gibbs free energy of formation for Fe_2SiO_4 , we shall first consider the several high-temperature equilibrium studies involving Fe_2SiO_4 that have been made between 1932 and 1978. In order to evaluate these equilibrium data, we combined our heat-capacity and entropy values with the heat-content ($H_T^\circ - H_{298}^\circ$) measurements of Orr (1953) to obtain the heat capacity of Fe_2SiO_4 for temperatures as high as 1450 K. A least-squares fit to Orr's heat-content data, combined with our measured heat capacities between 300 and 380 K, gives the following equation for Fe_2SiO_4 :

$$C_p^\circ = 176.02 - 8.808 \times 10^{-3} T + 2.471 \times 10^{-5} T^2 - 3.889 \times 10^6 T^{-2} \quad (298-1450 \text{ K})$$

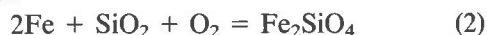
where T is in K and C_p° is in J/(mol·K).

Our new entropy data and the C_p° equation were used to obtain more accurate values of the enthalpy and Gibbs free energy of formation of Fe_2SiO_4 . We used equilibrium data presented by Schwerdtfeger

and Muan (1966), Cirilli (1946), Schenck *et al.* (1932), and Lebedev and Levitskii (1962) for the reaction



and equilibrium data presented by Taylor and Schmalzried (1964), Kitayama and Katsura (1968), Nafziger and Muan (1967), and Williams (1971) for the reaction



(For the temperature range of the equilibrium measurements, tridymite is the stable form of SiO_2 .) The internal consistency of the data was tested by using the relation

$$-\Delta H_{r,298}^\circ = RT \ln K + T \Delta[(G_T^\circ - H_{298}^\circ)/T] \quad (3)$$

to calculate the enthalpy of reaction at 298.15 K for each equilibrium point. The values for the Gibbs energy functions, $(G_T^\circ - H_{298}^\circ)/T$, for the other phases were taken from the tables of Robie *et al.* (1979) as were the $\Delta H_{f,298}^\circ$ values of SiO_2 , CO , and CO_2 used to reduce the calorimetric and the two different reaction enthalpies to the common basis, reaction (1). The different values of $\Delta H_{r,298}^\circ$ are shown in Figure 3. The mean value of the enthalpy change for reaction (1) is $-4.72 \pm .71$ kJ, if we assume that tridymite is the silica phase. The data point of Williams (1971) at 925°C was excluded in deriving this mean value because of its extreme deviation (≈ 6 kJ) from all the other values. The calorimetric ΔH° was given a weight of 8 because it was based on 8 separate measurements (King, 1952).

The equilibrium data are in reasonable agreement and lead to a value for $\Delta H_{f,298}^\circ$ of fayalite of -1478.17 ± 1.30 kJ/mol, which together with our entropy value gives $\Delta G_{f,298}^\circ = -1378.98 \pm 1.35$ kJ/mol. Although the new $\Delta H_{f,298}^\circ$ value for fayalite is about 1.19 kJ/mol less negative than the calorimetric value of -1479.36 kJ/mol (King, 1952 as corrected by Hemingway and Robie, 1977), the two values are in agreement, within the limits of the calorimetric $\Delta H_{f,298}^\circ$ measurement. In Table 3, we give values for the thermodynamic properties of fayalite obtained in this investigation for temperatures between 298.15 and 1400 K.

Using our new thermodynamic data for fayalite, we can now consider the equilibria for reactions involving magnetite (Fe_3O_4) as an additional phase, *e.g.*,

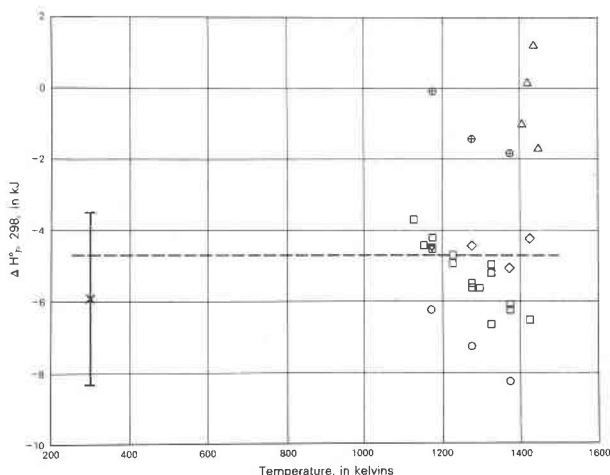
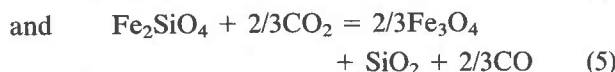


Fig. 3. Third law calculation of $\Delta H_{r,298}^\circ$ versus temperature for the reaction $2\text{Fe} + \text{SiO}_2 + 2\text{CO}_2 = \text{Fe}_2\text{SiO}_4 + 2\text{CO}$. Open circles, Cirilli (1946); open squares, Lebedev and Levitskii (1962); open diamonds, Schwerdtfeger and Muan (1966); open triangles, Kitayama and Katsura (1968); inverted open triangles, Schenck, Franz and Laymann (1932). The \oplus are calculated from the emf measurements of Taylor and Schmalzried (1964) for the reaction $2\text{Fe} + \text{SiO}_2 + \text{O}_2 = \text{Fe}_2\text{SiO}_4$. The \times was calculated from the hydrofluoric acid solution calorimetric values of ΔH obtained by (King 1952) and Hemingway and Robie (1977). The dashed line is the average value for $\Delta H_{r,298}^\circ$ adopted.

Table 3. Molar thermodynamic properties of Fe_2SiO_4 (fayalite) at high temperatures. Formula weight = 203.778 g/mol.

TEMP. K	$(H_f^\circ - H_{298}^\circ)/T$ J/(mol·K)	S_f° J/(mol·K)	$-(G_f^\circ - H_{298}^\circ)/T$ J/(mol·K)	C_p° J/(mol·K)	ΔH_f° kJ/mol	ΔG_f° kJ/mol
298.15	0.000	151.00	151.00	132.90	-1478.17	-1378.98
UNCERTAINTY		0.20	0.20		1.30	1.35
400	36.525	193.00	156.48	152.20	-1477.08	-1345.23
500	60.754	228.15	167.40	162.30		
600	78.257	258.36	180.10	168.89	-1473.63	-1280.01
700	91.586	284.79	193.20	174.09	-1472.07	-1247.91
800	102.192	308.34	206.15	178.77	-1471.34	-1215.97
900	110.956	329.67	218.71	183.37	-1470.39	-1184.08
1000	118.432	349.23	230.80	188.09	-1471.07	-1152.25
1100	124.989	367.39	242.40	193.08	-1473.24	-1120.23
1200	130.882	384.41	253.53	198.39	-1473.27	-1088.19
1300	136.292	400.51	264.22	204.09	-1469.71	-1056.31
1400	141.350	415.86	274.51	210.20	-1466.23	-1024.68

Reaction (4) is the QFM buffer reaction used to control the oxygen partial pressure in mineral equilibrium studies, and has been studied by Eugster (1957), Wones and Gilbert (1969), Hewitt (1978), and Chou (1978).

Gronvold and Sveen (1974) have suggested on the basis of the arguments of Anderson (1956) and the equilibrium data of Rau (1972) that Fe_3O_4 probably has a zero-point entropy, S_0° , of $\approx 3.4 \text{ J}/(\text{mol}\cdot\text{K})$. To test this possibility, we have used our new data on fayalite and data from the tables of Robie and others (1979) for the other phases to calculate the equilibrium constant for the QFM buffer reaction. The equilibrium curves of Wones and Gilbert (1969), Hewitt (1978), and Chou (1978) are shown in Figure 4, together with our two calculated curves. The curve calculated assuming that $S_0^\circ = 0$ for magnetite lies near that of Hewitt (1978) but has a somewhat greater slope.

From the equation of Wones and Gilbert (1969), we calculate the entropy change for reaction (4) at 1000 K = $170.4 \pm 10 \text{ J}/(\text{mol}\cdot\text{K})$, and from Hewitt's (1978) equation, we calculate $\Delta S_{r,1000}^\circ = 167.1 \pm 10 \text{ J}/(\text{mol}\cdot\text{K})$. The calorimetrically determined value for $\Delta S_{r,1000}^\circ$ is $164.1 \pm 3.0 \text{ J}/(\text{mol}\cdot\text{K})$ if we assume that magnetite has no zero-point entropy, and is $157.1 \text{ J}/(\text{mol}\cdot\text{K})$ if we assume that magnetite has a zero-point entropy of $3.4 \text{ J}/(\text{mol}\cdot\text{K})$. It therefore seems fair to conclude that the equilibrium and calorimetric measurements on the QFM buffer reaction do not support Anderson's (1956) model for a residual entropy in magnetite at 0 K.

Let us assume that Hewitt's (1978) curve is the correct one, and that the major part of the difference between the calculated (calorimetric) curve and his curve arises from the value of $\Delta G_{f,T}^\circ$ for

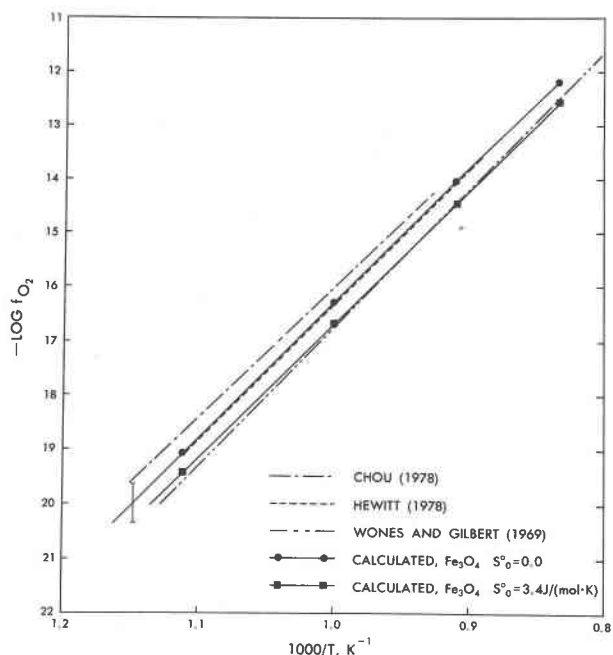


Fig. 4. Comparison of various experimental determinations of the equilibrium $2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2 = 3\text{Fe}_2\text{SiO}_4 + \text{O}_2$ with that calculated from thermodynamic data.

magnetite used to obtain the calculated curve. At 1000 K, the difference between the two curves corresponds to 0.70 kJ in ΔG_r° . This difference is within the uncertainty assigned to the value for magnetite (Robie *et al.*, 1979). Also we note that Hewitt's equation itself has an uncertainty of $\pm 0.1 \text{ log units}$, which at 1000 K means $\pm 1914 \text{ joules}$. Considerable uncertainties also are associated with the ΔG_f° values for quartz and fayalite. In fact, the error band associated with the calorimetric calculation ($\pm 0.35 \text{ log units}$) would include the curves presented by Hewitt (1978), Wones and Gilbert (1969), and Chou (1978). The JANAF values for magnetite should not be used because they were calculated without access to the more accurate heat capacity and entropy data of Gronvold and Sveen (1974) and Westrum and Gronvold (1969), or to the more recent equilibrium studies of Rau (1972).

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References

- Anderson, P. W. (1956) Ordering and antiferromagnetism in ferrites. *Physical Review*, 102, 1008–1013.
- Barker, F., Wones, D. R., Sharp, W. N., and Desborough, G. A. (1975) The Pikes Peak batholith, Colorado front range, and a model for the origin of the Gabbro-anorthosite-syenite-potassic suite. *Precambrian Research*, 2, 97–160.
- Bowen, N. L., Schairer, J. F., and Posnjak, E. (1933) The system $\text{Ca}_2\text{SiO}_4\text{--Fe}_2\text{SiO}_4$. *American Journal of Science*, XXV, 273–297.
- Chou, I-Ming (1978) Calibration of oxygen buffers at elevated P and T using the hydrogen fugacity sensor. *American Mineralogist*, 63, 690–703.
- Cirilli, V. (1946) Studio dell' equilibrio di riduzione con ossido di carbonio degli ossidi di ferro in presenza di silice. *Gazzetta Chimica Italiana*, 76, 331–338.
- de Boor, C. (1979) A practical guide to splines. Springer-Verlag, New York.
- Eugster, H. P. (1957) Heterogeneous reactions involving oxidation and reduction at high pressures and temperatures. *Journal of Chemical Physics*, 26, 1760.
- Finch, C. B., Clark, C. W., and Kopp, O. C. (1980) Czochralski growth of single-crystal fayalite (Fe_2SiO_4) under controlled oxygen fugacity conditions. *American Mineralogist*, 65, 381–389.
- Gronvold, F., and Svein, A. (1974) Heat capacity and thermodynamic properties of synthetic magnetite (Fe_3O_4) from 300 to 1050 K: Ferrimagnetic transition and zero-point entropy. *Journal of Chemical Thermodynamics*, 6, 859–872.
- Hazen, R. M. (1977) Effects of temperature on the crystal structure of ferromagnesian olivine. *American Mineralogist*, 62, 286–295.
- Hemingway, B. S., and Robie, R. A. (1977) Enthalpies of formation of low albite ($\text{NaAlSi}_3\text{O}_8$), and NaAlO_2 : Revised values for ΔH_f° and ΔG_f° of aluminosilicates. *Journal of Research of the U.S. Geological Survey* 5, 413–429.
- Hewitt, D. A. (1978) A redetermination of the fayalite-magnetite-quartz equilibrium between 650 and 850°C. *American Journal of Science*, 278, 715–724.
- Kelley, K. K. (1941) The specific heats at low temperatures of ferrous silicate, manganous silicate, and zirconium silicate. *Journal of the American Chemical Society*, 63, 2750–2752.
- King, E. G. (1952) Heats of formation of manganous metasilicate (rhodonite) and ferrous orthosilicate (fayalite). *Journal of American Chemical Society*, 74, 4446–4448.
- Kitayama, K., and Katsura, T. (1968) Composition of fayalite and its standard free energy of formation. *Japanese Journal of Physical Chemistry*, 41, 525–528.
- Kondo, H., and Miyahara, S. (1963) Magnetic properties of some synthetic olivines. *Journal of the Physical Society of Japan*, 18, 305.
- Lebedev, B. G., and Levitskii, V. A. (1962) Equilibrium of high temperature carbon monoxide reduction of iron orthosilicate. *Zhurnal Fizicheskoi Khimii*, 36, 630–632.
- Nafziger, R. H., and Muan, A. (1967) Equilibrium phase composition and thermodynamic properties of olivines and pyroxenes in the system MgO--FeO--SiO_2 . *American Mineralogist*, 52, 1364–1385.
- Orr, R. L. (1953) High temperature heat contents of magnesium orthosilicate and ferrous orthosilicate. *Journal of the American Chemical Society*, 75, 528–529.
- Rau, H. (1972) Thermodynamics of the reduction of iron oxide powders with hydrogen. *Journal of Chemical Thermodynamics*, 4, 57–64.
- Reinsch, C. H. (1967) Smoothing by spline functions. *Numerische Mathematik*, 10, 177–183.
- Robie, R. A., and Hemingway, B. S. (1972) Calorimeters for heat of solution and low-temperature heat capacity measurements. U.S. Geological Survey Professional Paper 755.
- Robie, R. A., Hemingway, B. S., and Fisher, J. R. (1979) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin 1452. (First published 1978; reprinted with corrections, 1979.)
- Robie, R. A., Hemingway, B. S. and Takei, H. (1982) Heat capacities and entropies of Mg_2SiO_4 , Mn_2SiO_4 , and Co_2SiO_4 between 5 and 380 K. *American Mineralogist*, 67, 470–482.
- Robie, R. A., Hemingway, B.S., and Wilson, W. H. (1976) The heat capacities of Calorimetry Conference copper and muscovite $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$, pyrophyllite $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$, and illite $\text{K}_3(\text{Al}_7\text{Mg})(\text{Si}_{14}\text{Al}_2)\text{O}_{40}(\text{OH})_8$ between 15 and 375 K and their standard entropies at 298.15 K. *Journal of Research of the U.S. Geological Survey*, 4, 631–644.
- Robie, R. A., Hemingway, B. S., and Wilson, W. H. (1978) Low-temperature heat capacities and entropies of feldspar glasses and anorthite. *American Mineralogist*, 63, 109–123.
- Santoro, R. P., Newnham, R. E., and Nomura, S. (1966) Magnetic properties of Mn_2SiO_4 and Fe_2SiO_4 . *Journal of Physics and Chemistry of Solids*, 27, 655–666.
- Schenck, R., Franz, H., and Laymann, A. (1932) Gleichgewicht-untersuchungen über die Reduktions-, Oxydations- und kohlungsvorgänge beim eisen XI. *Zeitschrift für Anorganische und Allgemeine Chemie*, 206, 124–151.
- Schwerdtfeger, K., and Muan, A. (1966) Activities in olivine and pyroxenoid solid solutions of the system Fe--Mn--Si--O at 1150°C; Transactions of the Metallurgical Society of the AIME, 236, 201–210.
- Smyth, J. R. (1975) High temperature crystal chemistry of fayalite. *American Mineralogist*, 60, 1092–1097.
- Taylor, R. W., and Schmalzried, H. (1964) The free energy of formation of some titanates, silicates, and magnesium aluminate from measurements made with galvanic cells involving solid electrolytes. *Journal of Physical Chemistry*, 68, 2444–2449.
- Wager, L. R., and Deer, W. A. (1939) Geological investigations in east Greenland III. The petrology of the Skaergaard intrusion, Kangerdlugssuaq East Greenland. *Meddelelser om Grønland*, 105, 1–352.
- Westrum, E. F., Jr., and Gronvold, F. (1969) Magnetite (Fe_3O_4). Heat capacity and thermodynamic properties from 5 to 350 K, low-temperature transition. *Journal of Chemical Thermodynamics*, 1, 543–557.
- Williams, R. J. (1971) Reaction constants in the system $\text{Fe--Mg--SiO}_2\text{--O}_2$ at 1 atm between 900° and 1300°C: Experimental results. *American Journal of Science*, 270, 334–360.
- Wones, D. R., and Gilbert, M. C. (1969) The fayalite-magnetite-quartz assemblage between 600° and 800°C. *American Journal of Science*, 267-A, 480–488.