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High Temperature Heat Contents of Magnesium Orthosilicate and Ferrous Orthosilicate

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High temperature heat content measurements of magnesium orthosilicate and ferrous orthosilicate were conducted over the temperature range from 298.16°K. to 1808 and 1724°K., respectively. The temperature and heat of fusion of ferrous orthosilicate were evaluated. A table of smoothed heat content and entropy increment data above 298.16°K. was constructed, and heat content equations were derived.

Introduction

Magnesium orthosilicate (forsterite) and ferrous orthosilicate (fayalite) are of considerable metallurgical and geochemical interest. These compounds occur extensively in furnace slags and are important constituents of some basic rock minerals, principally the olivines. Low temperature heat capacity data in the range 51° to 298°K. have been reported for both substances.[1,2] No high temperature heat content data for magnesium orthosilicate have been reported. The previous studies of ferrous orthosilicate by Esser, Averdieck and Grass[3] in the temperature range 273–1473°K. and by Roth and Bertram[4] in the range 293–1161°K., are incomplete and in poor agreement with each other.

This paper reports heat content measurements covering the range from 298.16 to 1808°K. for magnesium orthosilicate and from 298.16 to 1724°K. for ferrous orthosilicate, including a considerable portion of the liquid range of the latter compound, so that its heat of fusion is obtained.

Materials and Method

The sample of magnesium orthosilicate was prepared by R. E. Lorenson, Bureau of Mines, Berkeley, Calif., from highly pure silica and reagent grade magnesium oxide. A stoichiometric mixture of the two oxides was pressed into pellets and heated to 1300°. The product was ground to −200-mesh, analyzed and the necessary adjustment made in the composition. The sample was then moistened, dried slowly and heated for periods totaling 10 hours at 1400–1480° and 10 hours at 1480–1500°, with several intervening grindings to −200-mesh. The final product contained 42.60% silica and 57.51% magnesium oxide, as compared with the theoretical 42.70 and 57.30%, respectively. The X-ray diffraction pattern agreed with that given in the A.S.T.M. catalog.

The ferrous orthosilicate was a portion of the sample used by Kelley,[1] whose paper may be consulted for a description of the method of preparation. The analysis, as reported in that paper, gave 54.5% iron and 29.5% silica, as compared with the theoretical values, 54.81% iron and 29.49% silica.

Measurements were made by the "dropping" method, using apparatus and experimental procedures described previously.[5,6] The samples were enclosed in platinum-rhodium alloy capsules, the heat contents of which were determined by separate experiments. The capsule containing the ferrous orthosilicate was evacuated of air, filled with helium, and sealed gas-tight by pinching shut and welding the capsule neck. The neck of the capsule containing the magnesium orthosilicate was merely pinched shut. During the course of the measurements the furnace thermocouple was calibrated frequently at the melting point of pure gold.

Results and Discussion

The experimentally determined heat contents, expressed in defined calories (1 cal. = 4.1840 abs. joules) per mole, are listed in Table I and are plotted against temperature in Fig. 1. Molal weights are computed according to the 1951 International Atomic Weights.[7]

TABLE I

MEASURED HEAT CONTENTS ABOVE 298.16°K. (CAL./MOLE)

T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
Mg_2SiO_4 (mol. wt. 140.73)					
398.1	3,015	1008.6	26,500	1406.4	43,760
489.3	6,145	1073.3	29,180	1495.8	47,790
606.9	10,440	1120.1	31,220	1595.4	52,260
707.2	14,290	1213.1	35,200	1698.4	56,790
813.3	18,480	1320.2	39,840	1807.6	61,890
913.1	22,540				
Fe_2SiO_4 (mol. wt. 203.79)					
395.1	3,230	1191.2	37,090	1480.9	69,020[a]
492.5	6,920	1206.2	37,830[b]	1494.4	73,920
597.0	11,050	1288.7	41,740	1509.5	74,760
694.6	15,100	1370.3	45,730	1526.5	75,820
800.2	19,570	1390.5	46,940[a]	1578.2	78,960
896.6	23,790	1406.4	48,440[a]	1625.7	81,680
987.1	27,720	1426.8	50,220[a]	1675.7	84,400
1087.7	32,340	1452.4	53,840[a]	1723.7	86,970
1104.7	33,050				

The results for magnesium orthosilicate are completely regular, no evidence of any anomaly in the heat capacity being encountered in the temperature range studied.

The heat content of ferrous orthosilicate increases regularly to 1370.3°K. The five values labeled (a) in Table I show premelting phenomena; at 1480.9°K. fusion appears to have been about 80% complete. The values obtained in the liquid range, at 1494.4°K. and above, show an average deviation of only 0.1% from a linear relationship. One run at 1206.2°K., labeled (b) in Table I, made after the sample had been completely melted, checks within 0.1% the previous runs in the solid range. Determinations above 1723.7°K. were precluded because of the attack of the molten sample on the capsule. The melting point, the temperature at which fusion is complete, is taken as 1490°K., and the heat of fusion at this temperature is 22,030 cal./mole.

(1) K. K. Kelley, THIS JOURNAL, **63**, 2750 (1941).

(2) K. K. Kelley, *ibid.*, **65**, 339 (1943).

(3) H. Esser, R. Averdieck and W. Grass, *Arch. Eisenhüttenw.*, **6**, 289 (1933).

(4) W. A. Roth and W. W. Bertram, *Z. Elektrochem.*, **35**, 297 (1929).

(5) J. C. Southard, THIS JOURNAL, **63**, 3142 (1941).

(6) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

(7) E. Wichers, THIS JOURNAL, **74**, 2447 (1952).

In Fig. 1 it is seen that the results of Esser, Averdieck and Grass[3] are consistently too high, deviating from the present data by amounts ranging from +26.5% at 373°K. to +1.8% at 1373°K., with an average deviation of +8.0% in this range. Their value at 1473°K. lies in the melting range of the compound. The data of Roth and Bertram[4] range from 3.0% low at 369°K. to 6.0% high at 968°K., with an average deviation of +2.8%, disregarding their highest result (at 1161°K.), which they indicate as faulty due to oxidation. Both of these previous studies were conducted on natural samples, which were reported as 95.6 and 97.8% pure, respectively.

Table II lists smooth values of the heat contents above 298.16°K. at even 100°-values of temperature for both compounds and at the melting point for ferrous orthosilicate. The matching entropy increments, calculated by the method of Kelley,[8] also are listed.

TABLE II

HEAT CONTENTS (CAL./MOLE) AND ENTROPY VALUES (CAL./DEG. MOLE) ABOVE 298.16°K.

	Mg_2SiO_4		Fe_2SiO_4	
T, °K.	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$
400	3,100	8.91	3,440	9.89
500	6,520	16.53	7,210	18.29
600	10,180	23.19	11,190	25.54
700	14,010	29.10	15,320	31.91
800	17,960	34.37	19,560	37.57
900	22,000	39.13	23,890	42.67
1000	26,130	43.48	28,310	47.33
1100	30,340	47.49	32,850	51.65
1200	34,630	51.22	37,510	55.71
1300	39,000	54.72	42,290	59.53
1400	43,450	58.02	47,190	63.17
1490			51,690(c)	66.28
1490			73,720(l)	81.06
1500	47,950	61.12	74,300	81.45
1600	52,470	64.04	80,050	85.15
1700	57,000	66.79	85,800	88.64
1800	61,540	69.38	91,550	91.93

(8) K. K. Kelley, U. S. Bur. Mines Bull. 476 (1949).

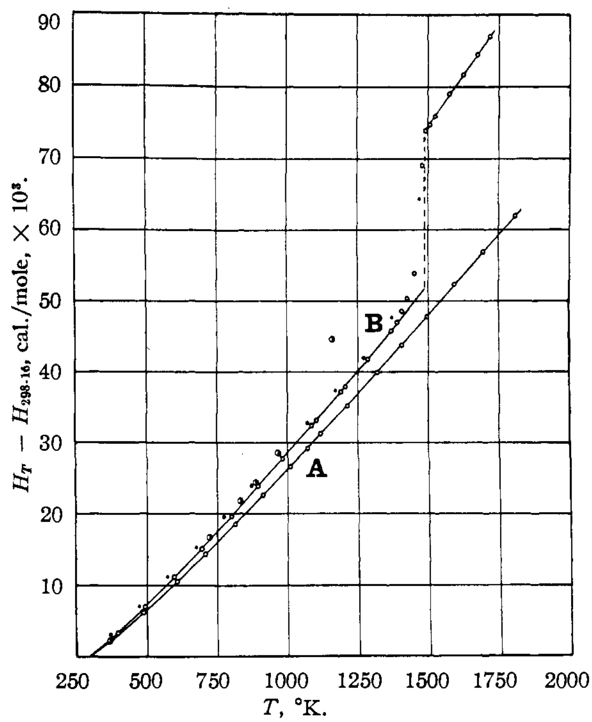

Fig. 1.—High temperature heat contents: curve A, Mg_2SiO_4; curve B, Fe_2SiO_4. (Open circles, this research; dots, Esser, Averdieck and Grass; half-shaded circles, Roth and Bertram).

The heat content data are represented by the following equations derived by the method of Shomate.[9] The temperature range of validity and the average deviation from the measured values are shown in parentheses.

Mg_2SiO_4(c): $H_T - H_{298.16} = 35.81T + 3.27 \times 10^{-3} T^2 + 8.52 \times 10^5 T^{-1} - 13,825$ (298–1808°K., 0.4%)

Fe_2SiO_4(c): $H_T - H_{298.16} = 36.51T + 4.68 \times 10^{-3} T^2 + 6.70 \times 10^5 T^{-1} - 13,549$ (298–1490°K., 0.2%)

Fe_2SiO_4(l): $H_T - H_{298.16} = 57.50T - 11,954$ (1490–1724°K., 0.1%)

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(9) C. H. Shomate, THIS JOURNAL, 66, 928 (1944).