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Heat Capacities at Low Temperatures and Entropies at 298.16° K. of Calcium and Magnesium Ferrites

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Heat capacity measurements of calcium ferrite ($CaFe_2O_4$), dicalcium ferrite ($Ca_2Fe_2O_5$) and magnesium ferrite ($MgFe_2O_4$) were conducted throughout the temperature range 51 to 298°K. Calcium ferrite has an anomalous heat capacity between 150 and 200°K. The entropies of the calcium ferrites at 298.16°K. are 34.7 ± 0.2 and 45.1 ± 0.3 cal./deg. mole, respectively, for $CaFe_2O_4$ and $Ca_2Fe_2O_5$. Because of randomness in its crystal structure, the entropy of magnesium ferrite cannot be definitely evaluated at present; however, the entropy increment between 0 and 298.16°K. is 28.3 ± 0.2 cal./deg. mole.

Introduction

Thermodynamic values are seriously lacking for many of the interoxidic compounds of the common metals, and thermodynamic calculations involving these substances have been conducted largely with empirically estimated data. This paper reports the results of heat capacity measurements in the temperature range 51 to 298°K. and the entropies at 298.16°K. for two calcium ferrites ($CaFe_2O_4$ and $Ca_2Fe_2O_4$) and magnesium ferrite ($MgFe_2O_4$—magnesium–iron spinel). No previous similar data exist for these substances. However, high temperature heat content measurements in the range 298–1,850°K. were published recently by Bonnickson[1] of this Laboratory.

Heat Capacity Measurements and Results

The samples used in this work are identical with those described by Bonnickson.[1] His paper gives the methods of preparation, the results of chemical analysis, and the results of X-ray diffraction.

The heat capacity measurements were made with previously described[2] apparatus and techniques, using samples having the following masses: 240.82 g. of monocalcium ferrite, 235.23 g. of dicalcium ferrite and 244.89 g. of magnesium ferrite. The measured values, expressed in defined calories (1 cal. = 4.1840 abs. joules), appear in Table I. Molecular weights were computed from the 1951 International Atomic Weights.[3]

TABLE I

HEAT CAPACITIES

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
		$CaFe_2O_4$ (mol. wt., 215.78)			
52.99	3.458	159.83	25.34	195.63	30.32
56.73	4.061	161.86	25.84	197.44	30.46
60.89	4.822	164.20	26.19	200.50	30.78
65.35	5.701	165.55	26.33	206.15	31.37
69.81	6.570	166.51	26.44	216.04	32.36
74.42	7.495	168.42	26.73	228.40	33.40
80.11	8.672	170.27	27.04	237.14	33.95
84.04	9.509	172.76	27.38	245.81	34.46
94.62	11.78	175.74	27.77	256.00	34.98
105.31	14.03	179.87	28.32	266.30	35.41
114.23	15.95	183.47	28.89	276.19	35.90
124.50	18.05	186.25	29.29	286.53	36.33
135.79	20.30	187.92	29.46	296.08	36.65
146.13	22.32	191.39	29.83	298.16	(36.72)
155.88	24.30	194.45	30.16		
		$Ca_2Fe_2O_5$ (mol. wt., 271.86)			
53.29	6.139	115.15	21.33	216.27	38.52
57.16	7.012	124.54	23.39	230.81	40.12
61.71	8.166	135.95	25.79	238.04	40.84
66.48	9.367	145.94	27.78	245.80	41.65
71.15	10.54	156.09	29.64	255.71	42.57
75.76	11.68	165.90	31.38	266.41	43.53
80.26	12.86	175.88	33.02	275.94	44.37
85.17	14.09	185.97	34.54	286.17	45.22
94.75	16.47	195.88	35.91	296.09	45.92
105.70	19.08	206.34	37.22	298.16	(46.10)
		$MgFe_2O_4$ (mol. wt., 200.02)			
53.10	2.594	114.71	12.31	216.37	27.15
57.59	3.123	124.78	14.06	227.94	28.41
62.42	3.778	136.07	15.99	237.25	29.32
67.54	4.514	145.69	17.59	245.87	30.14
71.98	5.159	155.51	19.12	256.51	31.06
76.44	5.838	165.97	20.69	266.57	31.93
80.89	6.542	175.79	22.11	276.25	32.72
85.40	7.290	185.65	23.46	286.62	33.51
94.72	8.851	196.01	24.75	296.10	34.18
105.45	10.68	206.64	25.98	298.16	(34.35)

Dicalcium ferrite and magnesium ferrite gave entirely normal heat-capacity curves. On the other hand, as may be seen from Fig. 1, monocalcium ferrite shows anomalous behavior in the temperature range 150 to 200°K. This behavior does not produce a heat capacity peak but does alter markedly the slope of the heat capacity curve. Two series of measurements in this region are seen to be in satisfactory agreement, showing that the phenomenon is reproducible. Such a marked effect could hardly be ascribed to impurities (which total only a minor amount) and it is believed, therefore, that it is definitely attributable to the monocalcium ferrite.

Entropies at 298.16°K.—The entropy increments for the measured temperature range, 51 to 298.16°K., were obtained by Simpson-rule integration of C_p against log T plots. The extrapolated entropy increments below 51°K. were calculated from the following empirical combinations of Debye and Einstein functions, which fit the measured

$$CaFe_2O_4: D\left(\frac{249}{T}\right) + 3E\left(\frac{355}{T}\right) + 3E\left(\frac{595}{T}\right) \quad (1.0\%,\ 51\text{–}125°K.)$$

$$Ca_2Fe_2O_5: D\left(\frac{175}{T}\right) + 3E\left(\frac{284}{T}\right) + 3E\left(\frac{610}{T}\right) + 2E\left(\frac{547}{T}\right) \quad (1.4\%,\ 51\text{–}225°K.)$$

$$MgFe_2O_4: D\left(\frac{278}{T}\right) + 2E\left(\frac{375}{T}\right) + 2E\left(\frac{579}{T}\right) + 2E\left(\frac{796}{T}\right) \quad (0.8\%,\ 51\text{–}125°K.)$$

(1) K. R. Bonnickson, THIS JOURNAL, **76**, 1480 (1954).

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

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

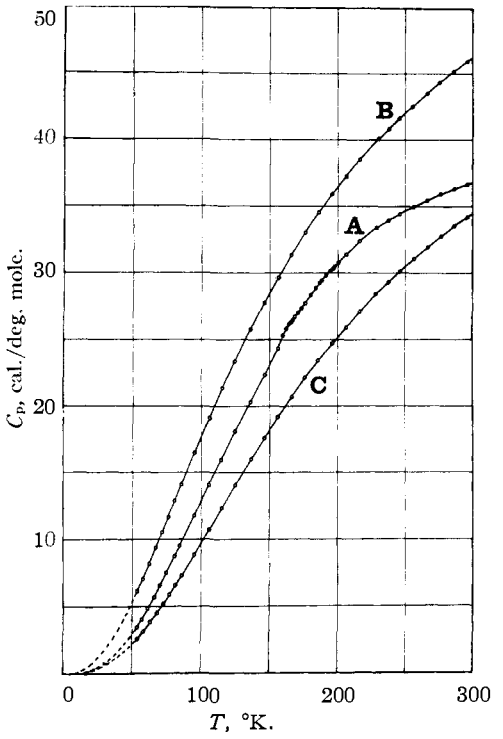

Fig. 1.—Heat capacities: A, $CaFe_2O_4$; B, $Ca_2Fe_2O_5$; C, $MgFe_2O_4$.

heat capacity data within the deviation limits and over the temperature ranges given in parentheses.

The results of the entropy calculations are in Table II. Uncertainties have been assigned by considering the error in the measured portion (above 51°K.) as ±0.3% and that in the extrapolated portion (below 51°K.) as ±5%. Experience has shown this method of assigning uncertainties to be on the conservative side, that is, the actual uncertainty generally is less than that assigned.

TABLE II

ENTROPIES AT 298.16°K. (CAL./DEG. MOLE)

	$CaFe_2O_4$	$Ca_2Fe_2O_5$	$MgFe_2O_4$
$S^0_{51.00}$ (extrap.)	1.16	2.50	0.86
$S^0_{298.16} - S^0_{51.00}$ (meas.)	33.58	42.61	27.41
$S^0_{298.16}$	34.7 ± 0.2	45.1 ± 0.3	28.3 ± 0.2

Magnesium ferrite has been shown by Barth and Posnjak[4] to be a spinel of the variate class. Half of the iron atoms fill the available tetrahedral sites in the crystal lattice. The other half are in the octahedral sites and irregularly mixed with magnesium atoms.[5] Thus the crystal structure has some degree of randomness, not determinable either from the present work or from X-ray diffraction, and not considered in Table II. Assumption of complete randomness in the arrangement of the magnesium and half of the iron atoms would require the addition of $2R \ln 2 = 2.75$ cal./deg. mole to the value for magnesium ferrite in Table II, making $S^0_{298.16} = 31.0$, which is the maximum possible value. Because of the tendency toward localized electrical neutralization in crystals, it is likely that a lesser degree of randomness prevails. If it is assumed that each FeO_4^{-5} tetrahedron is exactly electrically neutralized, calculation shows that the addition of $R \ln 3/2 = 0.81$ to the value for magnesum ferrite in Table II would be required, making $S^0_{298.16} = 29.1$, which probably is about the minimum possible value. Some support for the latter value possibly may be inferred from the work of Bonnickson[1] who found a reversible, non-isothermal transformation in magnesium ferrite terminating at 665°K. It is not possible to evaluate accurately the entropy change for this transformation but it appears to be about 2 cal./deg. mole. It may be postulated, but not proved, that complete randomness prevails above 665°K. and that ordering occurs in the region just below 665°K. to the extent required for exact electrical neutralization of each FeO_4^{-5} tetrahedron. No absolutely definite choice of entropy value for magnesium ferrite is possible at present. Such considerations do not apply to the two calcium ferrites as there is no evidence for randomness in their structures.

Using entropies of the oxides listed by Kelley,[6] in conjunction with values in Table II, there are obtained the following entropies of formation from the constituent oxides at 298.16°K.: $CaFe_2O_4$, 3.7 ± 0.6; $Ca_2Fe_2O_5$, 4.6 ± 0.7 cal./deg. mole.

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(4) T. F. W. Barth and E. Posnjak, *Z. Krist.*, **82**, 325 (1932).

(5) R. W. G. Wyckoff, "The Structure of Crystals," Suppl. to Second Edition, Reinhold Publ. Corp., New York, N. Y., 1935, p. 69.

(6) K. K. Kelley, U. S. Bur. Mines Bull. 477 (1950).