

thors. The crystallographic observations are in qualitative agreement with the heat of solution data presented here. Thus, one would predict a regular relationship from lanthanum through gadolinium since these chlorides are iso-structural. Erbium and ytterbium chlorides would not be expected to fall on a line with the lighter rare earths because of the change from hexagonal to monoclinic structures. That ytterbium chloride breaks back sharply toward the straight line through the light rare earths is in qualitative agreement with the sudden change in volume of the unit cell observed by Carter.<sup>17</sup>

The total hydration energy of the chloride ion at infinite dilution is the same for the series of compounds studied in this work. For this reason, the differences in the heats of solution of the anhydrous chlorides at infinite dilution are a measure of the differences in lattice energies of the crystals and

total hydration energies of the cations. On the basis of the lanthanide contraction, one would predict that the lattice energy would increase positively for the seven hexagonal rare earth chlorides. Since the heats of solution increase negatively for the same group, it is seen that the differences in total hydration energies are greater than the differences in lattice energies. The same observation is true in the case of erbium and ytterbium. A quantitative measure of these differences will be possible once the lattice energies have been calculated.

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[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

## High Temperature Heat Contents of Calcium and Magnesium Ferrites

By K. R. BONNICKSON

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High temperature heat content measurements of two calcium ferrites ( $\text{CaFe}_2\text{O}_4$  and  $\text{Ca}_2\text{Fe}_2\text{O}_5$ ) and magnesium ferrite ( $\text{MgFe}_2\text{O}_4$ ) were conducted throughout the temperature range 298–1850°K. The heat of fusion of  $\text{CaFe}_2\text{O}_4$  was determined as 25,870 cal./mole at 1510°K., and that of  $\text{Ca}_2\text{Fe}_2\text{O}_5$  as 36,110 cal./mole at 1750°K. The compound  $\text{MgFe}_2\text{O}_4$  has two transformations in the crystalline state—a heat capacity peak at 665°K. and an isothermal transformation at 1230°K. involving a heat absorption of 350 cal./mole.

Interoxidic compounds of the commoner metals have not been studied extensively by thermodynamic means, and in many instances thermodynamic data are entirely lacking. This paper presents the results of high temperature heat content measurements in the range 298–1850°K. for two calcium-iron-oxygen compounds ( $\text{CaFe}_2\text{O}_4$  and  $\text{Ca}_2\text{Fe}_2\text{O}_5$ ) and one magnesium-iron-oxygen compound ( $\text{MgFe}_2\text{O}_4$ ). No previous, similar data exist for any of these substances.

### Materials

The compound  $\text{CaFe}_2\text{O}_4$ <sup>1</sup> was prepared from reagent grade ferric oxide and calcium carbonate. A stoichiometric mixture was repeatedly heated, for several hours each time, at temperatures between 1000 and 1210°. The material was ground, mixed and analyzed, and the composition adjusted as necessary between heats. The final product contained 74.05% ferric oxide and 26.05% calcium oxide, as compared with the theoretical 74.01 and 25.99%. The X-Ray diffraction pattern agreed with that in the A.S.T.M. catalog.

The compound  $\text{Ca}_2\text{Fe}_2\text{O}_5$ <sup>2</sup> also was prepared from reagent grade ferric oxide and calcium carbonate. A stoichiometric mixture was formed into pellets and heated repeatedly, for several hours each time, at temperatures between 850 and 1230°. Between heats, the substance was ground, mixed, analyzed, composition adjusted, and repelletized. The final product contained 58.71% ferric oxide and 41.27% calcium oxide, as compared with the theoretical 58.74 and 41.26%. The X-ray diffraction pattern agreed with the A.S.T.M. catalog.

(1) This substance was prepared and analyzed by R. E. Lorenson, Minerals Thermodynamics Branch, Bureau of Mines.

(2) This substance was prepared and analyzed by C. J. O'Brien, Minerals Thermodynamics Branch, Bureau of Mines.

The compound  $\text{MgFe}_2\text{O}_4$ <sup>1</sup> was prepared from reagent grade ferric oxide and magnesia. A stoichiometric mixture, in pellet form, was heated repeatedly for periods of several hours in the temperature range 900 to 1,300°, the treatment between heats being the same as for the calcium compounds. The final product contained 79.74% ferric oxide, 20.22% magnesia and 0.14% silica. (Theoretical contents of ferric oxide and magnesia are 79.84 and 20.16%.) The X-ray diffraction pattern agreed with the A.S.T.M. catalog.

### Measurements and Results

Previously described apparatus and methods<sup>3</sup> were used in the high temperature heat content measurements. The samples were enclosed in platinum-rhodium capsules during the measurements, the heat contents of the capsules having been determined by separate experiments. The furnace thermocouple was calibrated frequently against the melting point of pure gold. The results are expressed in defined calories (1 cal. = 4.1840 abs. joules) per mole. Molecular weights accord with the 1951 International Atomic Weights,<sup>4</sup> and all weighings were reduced to vacuum. The experimental heat content results are listed in Table I and plotted in Fig. 1.

According to the existing phase diagram for the  $\text{CaO-Fe}_2\text{O}_3$  system,<sup>5</sup> the compound  $\text{CaFe}_2\text{O}_4$  melts incongruently over a range of temperature. There is some evidence in the present results of beginning

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

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

(5) R. B. Sosman and H. E. Merwin, *J. Wash. Acad. Sci.*, **6**, 534 (1916).

TABLE I  
EXPERIMENTAL HEAT CONTENTS ABOVE 298.16°K. (CAL./MOLE)

$T_f$ °K.	$H_T - H_{298.16}$	$T_f$ °K.	$H_T - H_{298.16}$	$T_f$ °K.	$H_T - H_{298.16}$
CaFe <sub>2</sub> O <sub>4</sub> (mol. wt. 215.78)					
411.3	4,220	1333.7	43,870	1566.2	79,130(b)
549.3	9,880	1385.5	46,560	1573.3	80,460(b)
650.9	14,050	1406.0	47,750	1574.4	79,800(b)
726.1	17,220	1429.7	48,300	1593.9	80,980(b)
846.8	22,310	1462.6	50,590	1616.3	83,700
909.1	25,070	1504.6	64,320(a)	1652.0	85,590
1038.2	30,600	1529.7	74,970(a)	1702.1	88,490
1131.7	34,700	1549.3	78,650(b)	1805.3	94,080
1229.0	39,130				
Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub> (mol. wt. 271.86)					
376.5	3,695	1107.0	45,250	1652.3	77,850
478.3	9,100	1202.7	50,850	1703.9	80,950
597.7	15,620	1260.1	54,060	1751.8	118,940
731.5	23,500	1338.9	58,650	1752.1	118,380
788.3	26,560	1409.0	62,780	1766.8	120,070
912.9	33,960	1441.0	64,650	1793.0	122,090
1014.1	39,920	1483.6	67,280	1810.3	123,400
1033.7	40,660	1606.7	74,180	1837.6	125,320
MgFe <sub>2</sub> O <sub>4</sub> (mol. wt. 200.02)					
362.6	2,290	795.7	21,530	1246.7	42,340
473.8	6,770	861.1	24,490	1261.6	42,970
500.6	7,900	908.6	26,760	1310.7	45,120
569.6	11,060	938.4	27,770	1364.8	47,450
628.4	13,680	1002.8	30,910	1379.1	48,060
640.5	14,270	1063.1	33,630	1392.8	48,800
648.4	14,710	1119.0	36,150	1395.5	48,810
657.8	15,200	1180.2	39,090	1430.8	50,360
661.1	15,240	1193.8	39,610	1441.6	50,870
702.6	17,310	1213.5	40,650	1608.1	58,490
703.3	17,350	1227.5	41,300	1703.0	63,210
703.7	17,410	1231.8	41,670	1827.1	69,310

of melting as low as 1,463°K., and melting is not complete at 1,530°K. (Note results labeled a in Table I.) Five determinations (labeled b in Table I) in the temperature range 1,573 to 1,594°K. are discordant by about 1.3% on the average; either there was some lack of equilibrium, or the substance was not completely melted. These five points were given no weight in drawing the curve for the liquid in Fig. 1 or in subsequent treatment of the data. Because of the incongruent melting range, the melting temperature has been taken rather arbitrarily at an intermediate value of 1,510°K. The heat of fusion at this temperature is 25,870 cal./mole, and the entropy of fusion is 17.13 cal./deg. mole.

The compound Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> also melts incongruently according to the phase diagram.<sup>5</sup> In the present work there was no evidence of melting below 1704°K., and melting was complete at 1752°K. In treating the data, the melting point is taken as 1750°K. The heat of fusion is 36,110 cal./mole, and the entropy of fusion is 20.63 cal./deg.-mole.

The compound MgFe<sub>2</sub>O<sub>4</sub> has two transformations in the crystalline state, at 665° and at 1230°K. The 665°-transformation appears to involve a heat capacity peak rather than an isothermal heat absorption. The heat capacity at 298°K. is

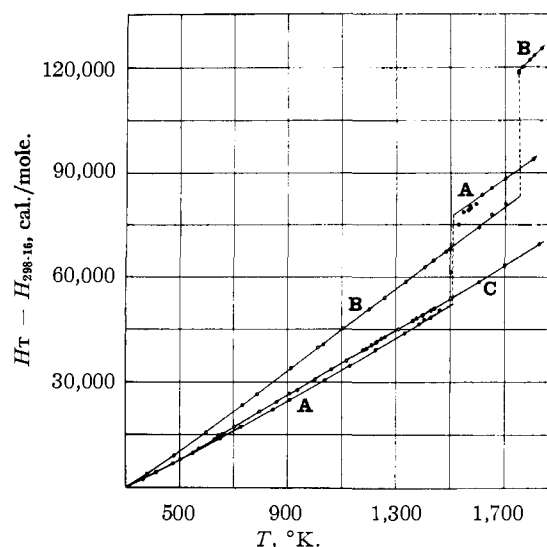


Fig. 1.—High temperature heat contents: curve A, CaFe<sub>2</sub>O<sub>4</sub>; curve B, Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>; curve C, MgFe<sub>2</sub>O<sub>4</sub>.

34.35 cal./deg.-mole<sup>6</sup> and between 298° and 665°K. it increases rapidly to a calculated value of 50.7 cal./deg.-mole. At 665°K., or just above this temperature, it falls abruptly to 45.40 cal./deg.-mole and then remains virtually constant to 1230°K. At the 1230°-point there is an apparent isothermal heat absorption of 350 cal./mole. The heat capacity of the high temperature form is 41.4 cal./deg.-mole at 1230°K. and at higher temperatures it slowly increases to 50.1 at 1800°K. It is interesting to note that the heat content of crystalline MgFe<sub>2</sub>O<sub>4</sub> is higher than that of crystalline CaFe<sub>2</sub>O<sub>4</sub> at temperatures above about 510°K., which is at least partly a consequence of the transformations in MgFe<sub>2</sub>O<sub>4</sub>.

Table II contains smooth values of the heat

TABLE II  
HEAT CONTENTS (CAL./MOLE) AND ENTROPIES (CAL./DEG.-MOLE) ABOVE 298.16°K.

$T_f$ °K.	CaFe <sub>2</sub> O <sub>4</sub>		Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>		MgFe <sub>2</sub> O <sub>4</sub>	
	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$
400	3,940	11.35	4,870	14.01	3,860	11.10
500	7,900	20.18	10,210	25.92	7,870	20.03
600	11,950	27.57	15,800	36.10	12,270	28.04
665	....	....	....	....	15,600(α)	33.31
665	....	....	....	....	15,600(β)	33.31
700	16,090	33.95	21,490	44.87	17,190	35.64
800	20,310	39.58	27,250	52.56	21,730	41.70
900	24,600	44.63	33,060	59.41	26,270	47.05
1000	28,950	49.22	38,890	65.55	30,810	51.83
1100	33,360	53.42	44,730	71.12	35,350	56.16
1200	37,820	57.30	50,580	76.21	39,890	60.11
1230	....	....	....	....	41,250(β)	61.23
1230	....	....	....	....	41,600(γ)	61.51
1300	42,340	60.92	56,430	80.89	44,630	63.91
1400	46,920	64.31	62,280	85.22	49,000	67.15
1500	51,540	67.50	68,130	89.26	53,520	70.27
1510	52,000(c)	67.80	....	....	....	....
1510	77,870(l)	84.93	....	....	....	....
1600	82,810	88.11	73,980	93.04	58,190	73.28
1700	88,300	91.44	79,830	96.58	63,000	76.20
1750	....	....	82,760	98.28(c)	....	....
1750	....	....	118,870	118.91(l)	....	....
1800	93,790	94.58	122,580	121.00	67,960	79.03
1850	....	....	126,290	123.04	....	....

(6) From unpublished measurements of E. G. King, Minerals Thermodynamics Branch, Bureau of Mines.

content and entropy increments above 298.16°K. The latter were calculated by the method of Kelley.<sup>7</sup>

The following equations represent the heat content results within the average limits and for the temperature intervals indicated in parentheses.

$$\text{CaFe}_2\text{O}_4(\text{c}): H_T - H_{298.16} = 39.42T + 2.38 \times 10^{-3}T^2 + 3.66 \times 10^{-5}T^{-1} - 13,194; (0.3\%; 298-1510^\circ\text{K}.)$$

$$\text{CaFe}_2\text{O}_4(\text{l}): H_T - H_{298.16} = 54.90T - 5030; (0.1\%; 1510-1800^\circ\text{K}.)$$

$$\text{Ca}_2\text{Fe}_2\text{O}_5(\text{c}): H_T - H_{298.16} = 59.24T + 11.68 \times 10^5T^{-1} - 21,580; (0.5\%; 298-1750^\circ\text{K}.)$$

$$\text{CaFe}_2\text{O}_5(\text{l}): H_T - H_{298.16} = 74.20T - 10,980 (0.1\%; 1750-1850 \text{ K}.)$$

$$\text{MgFe}_2\text{O}_4(\alpha): H_T - H_{298.16} = 21.06T + 22.29 \times 10^{-3}T^2 - 8261; (1.2\%; 298-665^\circ\text{K}.)$$

$$\text{MgFe}_2\text{O}_4(\beta): H_T - H_{298.16} = 45.40T - 14,590; (0.1\%; 665-1230^\circ\text{K}.)$$

$$\text{MgFe}_2\text{O}_4(\gamma): H_T - H_{298.16} = 25.67T + 6.79 \times 10^{-3}T^2 - 247; (0.1\%; 1230-1800^\circ\text{K}.)$$

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

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[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

## The Compressibility of Liquid Normal Hydrogen from the Boiling Point to the Critical Point at Pressures up to 100 Atmospheres<sup>1</sup>

BY HERRICK L. JOHNSTON, WILLIAM E. KELLER AND ABRAHAM SOLOMON FRIEDMAN

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A description is given for an apparatus used to determine equation of state data for liquids at low temperature. Measured values of  $\bar{P}$  vs.  $V$  isotherms of normal liquid  $\text{H}_2$  are tabulated for seven temperatures between 20.38 and 32.58°K. The data have been replotted as isochores, the straight-line character of which can be adequately described by  $P = A_v + B_vT$  with  $B_v = -7.11 + 437(1/V)$ ; values of  $A_v$  and  $B_v$  are given at integral values of the specific volume. Comparison of experimental results with calculations based on two proposed models for liquids are made and the agreement is found to be unsatisfactory.

### Introduction

No comprehensive investigation of the  $P$ - $V$ - $T$  properties of liquid hydrogen<sup>2</sup> has heretofore been undertaken. The most accurate information available has been that derived from Bartholomé's measurements<sup>3</sup> of the compressibility of liquid normal hydrogen at the boiling point (20.39°K.), at 18.24°K. and at 16.43°K., and from liquid-vapor density determinations of Mathias, Crommelin and Onnes.<sup>4</sup> The regions of temperatures above the boiling point and pressures above saturation have not been mapped. As part of this Laboratory's program for the determination of the properties of hydrogen, we have measured  $P$  vs.  $V$  isotherms for the liquid in that region. It is the purpose of this communication to describe the apparatus employed and to report experimental results.

**Apparatus.**—The general plan of the experiment includes the following measurements: (1) the temperature of a bomb containing a known volume of liquid hydrogen; (2) the pressure exerted on the liquid by gaseous hydrogen; and (3) the number of moles of liquid in the bomb corresponding to each pressure determination along each isotherm. An isotherm is determined by first filling the pipet to the highest pressure and then decreasing the pressure in stepwise fashion, measuring the number of moles of each decrement.

Figure 1 illustrates the cryostat assembly. The liquid under investigation is contained in the copper bomb, or pipet (A). Tests indicated that 200 atm. of internal pressure does not significantly deform the pipet. Within the pipet are four snug-fitting fins made from  $1/32$  in. sheet copper to ensure rapid thermal equilibration. The threaded

plug (B) and monel capillary (C) (0.012 in. inside diameter, 0.025 in. wall) were silver-soldered to the pipet in a helium atmosphere in order to prevent oxidation of the internal copper surfaces. D is a well for the junction of a copper-constantan thermocouple embedded 2 in. into the pipet wall. This well is filled with Wood's metal to maintain good thermal contact between couple and pipet.

In order to determine the level of liquid hydrogen and the thermal gradient along the capillary, control thermocouples are situated at 8-in. intervals along the length of the capillary. To make certain that the meniscus will never be far above the neck of the pipet a small, 4-watt heater-station is placed on the capillary 1 in. above the bomb. During the course of the experiments, however, the temperature of the capillary an inch or two above the pipet was always above the critical temperature of hydrogen, so that it was never necessary to use the heater.

Surrounding the pipet is a heavy-walled copper container (I) for the liquid hydrogen refrigerant. The vapor pressure of the refrigerant is so regulated between the normal boiling and critical pressures that the temperature of the bath determines the temperature of the isotherm being run. Control of the temperature is effected by manual adjustment of a set of four needle valves in parallel with the hydrogen gas outlet line (E). Vapor pressures of the coolant are read on a 300-lb. test gage having 1-lb. subdivisions, and pressures can be maintained within 0.25 p.s.i. of any desired value in the working range. This results in temperature control to within 0.02° under the most unfavorable conditions, and usually to within 0.01°. A 240-ohm, 60-watt manganin wire heater coiled around the outside of the copper container is used to raise the bath temperature.

The top of the refrigerant container, which is threaded and soft-soldered in place, is fitted with 12.5 mm. o.d. monel tubes to allow for the introduction of liquid hydrogen coolant and the escape of vapor. The inlet tube just above the container passes through a high pressure valve (F) operated from outside the cryostat; the outlet tube leads directly into the temperature control system. The pipet thermocouple is surrounded by a monel tube (H) so that the couple makes no direct contact with liquid hydrogen. The pipet itself is suspended in the container by a thick-walled monel tube (G), which also serves as a vacuum jacket around the capillary.

The outer vessel of this apparatus is a vacuum-tight copper cylinder (J) constructed so as to allow all the tubes leading to the refrigerant container to be vacuum-jacketed

(1) The essentials of the present report were presented at the Proceedings of the NBS Semicentennial Symposium on Low Temperature Physics, March, 1951.

(2) H. W. Woolley, R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **41**, 379 (1948).

(3) E. Bartholomé, *Z. physik. Chem.*, **B33**, 387 (1936).

(4) E. Mathias, C. A. Crommelin and H. K. Onnes, *Communs. Phys. Lab. Univ. Leiden*, No. 154b (1921).