

Prior to the publication of the experimental heat capacity data, we had made an attempt to calculate the heat capacity curve. For this purpose we had estimated $\theta = 106$, $a = 8.9 \times 10^{-3}$ and $b = 6 \times 10^{-3}$. These parameters are somewhat in error, particularly the last one, and as a result the heat capacity curve was rather poorly reproduced below 80°K., where the heat capacity is most sensitive to θ , and especially above 180°, where it is most sensitive to the value of b . In the range 89–180°, the deviations were of the order of 1–4%.

Thermodynamic Functions for Some Reactions of Cyclooctatetraene

Another possibility for checking the structural basis of a vibrational assignment exists in the thermodynamic functions as determined from chemical equilibria. Unfortunately the same situation that gives rise to equivalent entropy values for the D_4 and D_{2d} structures operates to make it possible to explain experimental values of the free-energy and other thermodynamic quantities equally well on the basis of either structure. Regardless of this fact, the calculated values of these quantities may be of use in connection with the reactions of cyclooctatetraene, and we have therefore calculated equilibrium constants and related functions for several gas reactions involving the molecule.

The values of ΔH_f° , ΔS_f° and ΔF_f° for the formation of cyclooctatetraene from its elements in their standard states at various temperatures are listed in Table III. These values were obtained from the heat of formation of liquid cyclooctatetraene⁴ at 298.16°K., the heat of vaporization⁵ at 298.16°K. (10.3 ± 0.075 kcal./mole) and the heats of formation and entropies of graphite and hydrogen in their standard states.¹⁴

(14) American Petroleum Institute Project 44, U. S. National Bureau of Standards, Washington 25, D. C., "Selected Values of Chemical Thermodynamic Properties."

TABLE III
THERMODYNAMICS OF FORMATION OF CYCLOOCTATETRAENE VAPOR

T, °K.	ΔH_f° , kcal.	ΔF_f° , kcal.	ΔS_f° , e.u.
298.16	71.12	88.40	-57.96
400	69.75	94.53	-61.95
500	68.68	100.82	-64.28
600	67.84	107.36	-65.87
700	67.13	114.05	-67.03
800	66.70	120.75	-67.56
900	66.32	127.56	-68.03
1000	66.18	134.33	-68.15

The equilibrium constants for some vapor-phase cyclooctatetraene reactions are given in Table IV. K_1 is the constant for the formation of one mole of cyclooctatetraene from four moles of acetylene, K_2 for formation from one mole of benzene and one mole of acetylene, and K_3 for isomerization to styrene. The necessary thermodynamic quantities for Table IV were obtained for acetylene and benzene from reference 14, and for styrene from Beckett and Pitzer.¹⁵

TABLE IV
EQUILIBRIUM CONSTANTS FOR SOME CYCLOOCTATETRAENE REACTIONS

T, °K.	K_1	$10^4 K_2$	K_3
298.16	7.1×10^{81}	40.7	2.24×10^{27}
400	3.55×10^{64}	11.5	4.47×10^{20}
500	2.95×10^{48}	5.37	5.13×10^{16}
600	5.01×10^{37}	3.27	1.26×10^{14}
700	9.55×10^{19}	2.29	1.74×10^{12}
800	1.58×10^{14}	1.74	6.61×10^{10}
900	5.25×10^9	1.51	5.25×10^9
1000	1.39×10^6	1.35	6.77×10^8

(15) Beckett and Pitzer, *THIS JOURNAL*, **68**, 2313 (1946).

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High-temperature Heat Contents of Ferrous Oxide, Magnetite and Ferric Oxide¹

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High-temperature heat-content measurements of ferrous oxide, magnetite and ferric oxide were conducted from 298.16°K. to the respective temperatures, 1784, 1825 and 1757°K. One heat-capacity anomaly was found for magnetite and two for ferric oxide. The heat of fusion of ferrous oxide ($\text{Fe}_{0.947}\text{O}$) was determined. A table of heat content and entropy increments above 298.16°K. is given and heat content equations are derived.

Introduction

Despite the great importance of the oxides of iron, high-temperature heat-content data have not been available for ferrous oxide above 1173°K., for magnetite above 1273°K. or for ferric oxide above 1097°K. The only previous work on ferrous oxide is that of White,² who made determinations at only two temperatures, 973 and 1173°K. Magnetite was studied by Esser, Averdick and Grass,³

Roth and Bertram,⁴ Weiss and Beck,⁵ and Weiss, Piccard and Carrard.⁶ Brown and Furnas,⁷ Kolosowsky and Skoulski,⁸ and Roth and Bertram⁴ measured ferric oxide. The results for the latter two substances contain large discrepancies.

This paper reports the results of high tempera-

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

(5) Weiss and Beck, *Arch. sci. phys. nat.*, **25**, 529 (1928).

(6) Weiss, Piccard and Carrard, *ibid.*, **42**, 378 (1916); **43**, 22, 113, 199 (1917).

(7) Brown and Furnas, *Trans. Am. Inst. Chem. Eng.*, **18**, 309 (1926).

(8) Kolosowsky and Skoulski, *Bull. soc. chim. France*, **47**, 136 (1930).

(1) Not subject to copyright.

(2) White, *THIS JOURNAL*, **55**, 1047 (1933).

(3) Esser, Averdick and Grass, *Arch. Eisenhüttenw.*, **6**, 298 (1933).

ture heat content measurements of ferrous oxide, magnetite and ferric oxide from 298°K. to the respective temperatures, 1784, 1825 and 1757°K.

Materials

Preparation of a suitable sample of ferrous oxide presents difficulties. It is known from the work of Jette and Foote⁹ and Darken and Gurry¹⁰ that the stoichiometric composition (FeO) does not exist as a thermodynamically stable, single-phase substance. The maximum iron content of the ferrous oxide phase found by the former workers corresponds to Fe_{0.948}O and by the latter to Fe_{0.953}O. Evidence favors vacant iron spaces in the lattice rather than extra oxygen in the interstices. At temperatures below 833°K., ferrous oxide is unstable with respect to iron and magnetite. It is necessary, therefore, to prepare the substance at high temperatures and to quench through the range from 833° to room temperature rapidly enough to prevent disproportionation. At room temperature and somewhat above, the rate of transformation is very low.

The method of preparation finally adopted was that of Blue and Claassen,¹¹ in which equivalent quantities of magnetite and iron are heated at the same temperature, *in separate containers*, in a closed system under a pressure of a few mm. of water vapor. The water vapor acts upon the iron to produce hydrogen which, in turn, reduces magnetite and reforms water. Thus, water vapor serves to transfer oxygen from the magnetite to the iron, and as the process continues the materials in the two containers approach each other in composition.

In the present work, three batches of about 130 g. each were made. Only material produced from the magnetite side was retained for use in the measurements. The original amounts of magnetite and iron were such as to yield products having near the maximum iron content of the ferrous oxide phase as mentioned above. A silica-glass outer container was used, and alundum thimbles separated the solid reactants. The temperature employed was 1150°K., and the heating periods ranged from 4.9 to 9.3 days for the three batches. Quenching was accomplished by plunging the silica-glass container and its contents at about 950°K. into a bath of stirred, iced brine. Careful examination and chemical analyses showed the three batches to be virtually identical, and they were subsequently combined and thoroughly mixed.

The final product analyzed 76.60% iron, 23.18% oxygen (loss in weight on complete reduction by hydrogen) and 0.17% silica. The iron:oxygen ratio corresponds to Fe_{0.947}O. The X-ray diffraction pattern showed no lines other than those of the ferrous oxide phase. Tests for metallic iron by the mercuric chloride method of Morris¹² were negative. The substance was only slightly magnetic, indicating at most only a negligible residuum of magnetite.

Ferric oxide was prepared from reagent-grade ferric chloride. Precipitation of ferric hydroxide was followed by repeated washing, filtering, drying at 450°K., grinding to -60 mesh, repeated leaching with hot water, and, finally, prolonged ignition at 1420°K. The product analyzed 69.86% iron, as compared with the theoretical 69.94%.

Magnetite was prepared from ferric oxide, made as indicated above, by heating for 8 hours at 1630°K. under high vacuum. The product contained 72.16% iron and 27.54% oxygen, as compared with the theoretical 72.36 and 27.64%, respectively. The principal impurity was 0.22% silica. The X-ray diffraction pattern showed only magnetite lines.

Measurements and Results

Measurements were made by the "dropping" method, using previously described apparatus.^{13,14} The samples were enclosed in platinum-rhodium alloy capsules, the necks of which were welded shut after evacuating and filling the pore space with he-

lium. The heat contents of the empty capsules were determined in separate experiments.

Frequent calibrations of the furnace thermocouple were made at the melting point of gold and a few at the melting point of palladium. Frequent checks of the over-all behavior of the apparatus were made by determining the heat content of a capsule filled with high-quality corundum.

The measured results, expressed in defined calories per mole, are listed in Table I and plotted in Fig. 1 (molecular weights accord with the 1949 International Atomic Weights).

TABLE I

HEAT CONTENTS ABOVE 298.16°K.					
T, °K.	$\frac{H_T - H_{298.16}}{\text{cal./mole}}$	T, °K.	$\frac{H_T - H_{298.16}}{\text{cal./mole}}$	T, °K.	$\frac{H_T - H_{298.16}}{\text{cal./mole}}$
Fe _{0.947} O (mol. wt. 68.89)					
339.8	501	975.1	8,600	1314	13,290
341.1	504	1044.3	9,505	1364	13,970
393.5	1,140	1048.4	9,570	1427	14,920
446.9	1,787	1122.0	10,610	1498	15,980
521.1	2,700	1197.6	11,640	1555	16,790
604.6	3,725	1265.1	12,580	1614	17,850
606.6	3,725	1273.6	12,650	1683	26,260
708.1	5,130	1274.2	12,680	1709	26,630
842.3	6,845	1294.7	13,000	1747	27,270
893.1	7,505	1299.2	13,050	1784	27,880
Fe ₂ O ₃ (mol. wt. 231.55)					
351.6	2,030	890.7	29,880	1338	51,590
444.8	5,890	929.4	31,950	1340	51,720
512.8	8,935	931.7	31,960	1414	55,280
617.3	13,890	981.5	34,430	1449	56,940
718.5	19,390	1000.0	35,370	1541	61,220
821.1	25,600	1017.5	36,150	1553	61,810
824.4	25,760	1025.8	36,620	1652	66,660
852.3	27,680	1044.8	37,570	1766	72,100
868.2	28,590	1122.4	41,250	1825	75,420
874.6	28,950	1239.7	46,930		
Fe ₂ O ₃ (mol. wt. 159.70)					
374.8	2,005	1054.1	25,910	1444	39,160
445.4	4,170	1075.8	26,720	1530	42,130
547.7	7,300	1095.9	27,380	1588	44,110
650.1	10,710	1109.9	27,940	1614	44,970
777.6	15,290	1155.8	29,350	1672	47,110
872.9	18,930	1171.3	29,940	1677	47,330
924.5	21,030	1203.4	30,980	1700	48,060
948.0	21,970	1283.6	33,690	1717	48,860
956.8	22,440	1305	34,390	1730	49,360
971.3	23,000	1329	35,290	1757	50,620
1002.0	24,100	1370	36,620		

The following procedures were adopted to minimize the possibility of decomposition of ferrous oxide into magnetite and iron. All determinations between 890 and 1270°K. were conducted by pre-setting the furnace at 1270°K. The sample was introduced and held at 1270° for at least one-half hour, and then the furnace temperature was lowered to the desired run temperature. Measurements above 1270 and below 845°K. were conducted by introducing the sample into the furnace preset at the run temperature. After each measurement, a magnetic test was made to determine whether the sample had been altered. No signifi-

(9) Jette and Foote, *Trans. A. I. M. E.*, **105**, 276 (1933).

(10) Darken and Gurry, *This Journal*, **67**, 1398 (1945); **68**, 798 (1946).

(11) Blue and Claassen, *ibid.*, **71**, 3830 (1949).

(12) Morris, *Bur. Mines R. I.*, 3824 (1945).

(13) Southard, *This Journal*, **63**, 3142 (1941).

(14) Kelley, Naylor and Shomate, *Bur. Mines Tech. Paper*, 686 (1946).

cant changes occurred, except during the measurements at 521.1, 604.6, 606.6 and 708.1°K. In each of these instances, the sample was regenerated into its original condition by heating for one-half hour at 1270°K. and quenching with Dry Ice.

The heat-content curve of crystalline ferrous oxide shows no abnormality except a more than usual scattering of the above designated points in the region of rapid disproportionation. White's² two determinations, at 973.7 and 1173.6°K., respectively, are in excellent agreement with the present work when calculated upon the same basis, the deviations being only 0.29 and 0.02%, respectively.

Four closely concordant points in the liquid range of ferrous oxide were obtained. The heat of fusion is 7,490 cal./mole, in good agreement with the "best" value of Darken and Gurry,¹⁰ 7,300 cal. The melting point is taken as 1,650°K., the liquidus temperature for $\text{Fe}_{0.947}\text{O}$ according to Darken and Gurry.

The heat-content data for magnetite show a magnetic anomaly around 880°K., corresponding to a maximum in heat capacity. The heat capacity rises sharply in the transition range and then falls abruptly to a persisting, virtually constant value. It was found convenient in subsequent treatment of the data to assign an arbitrary transition temperature of 900°K., this being about the temperature at which the transformation is substantially complete.

Comparison with previous data for magnetite shows that those of Weiss and Beck⁵ are in best agreement with the present results, the average deviation being 0.8% and the plus and minus deviations balancing. The other results are low by amounts ranging from 1.7% for Roth and Bertram's⁴ data to 4.3% for Weiss, Piccard and Carrard's⁶ data for synthetic material.

The melting point of magnetite was not reached in the present work. Darken and Gurry¹⁰ give 1870°K. as the melting point and 33,000 cal./mole as the heat of fusion.

TABLE II

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

T	$\text{Fe}_{0.947}\text{O}$		Fe_3O_4		Fe_2O_3	
	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$
400	2,120	3.48	3,990	11.48	2,750	7.91
500	2,440	6.23	8,320	21.12	5,770	14.64
600	3,700	8.53	13,060	29.75	9,010	20.54
700	4,980	10.50	18,340	37.88	12,460	25.85
800	6,280	12.23	24,260	45.77	16,130	30.75
900	7,590	13.78	30,550(α)	53.18	20,030	34.34
900	30,550(β)	53.18
950	22,060(α)	37.54
950	22,220(β)	37.71
1000	8,920	15.18	35,350	58.24	24,020	39.55
1050	25,820(β)	41.31
1050	25,820(γ)	41.31
1100	10,280	16.47	40,150	62.81	27,500	42.87
1200	11,670	17.68	44,950	66.99	30,870	45.80
1300	13,080	18.81	49,750	70.83	34,250	48.51
1400	14,520	19.88	54,550	74.39	37,650	51.03
1500	15,980	20.88	59,350	77.70	41,070	53.39
1600	17,460	21.84	64,150	80.80	44,540	55.63
1650	18,210(c)	22.30
1650	25,700(l)	26.84
1700	26,510	27.32	68,950	83.71	48,100	57.79
1800	28,140	28.26	73,750	86.45	51,880	59.95

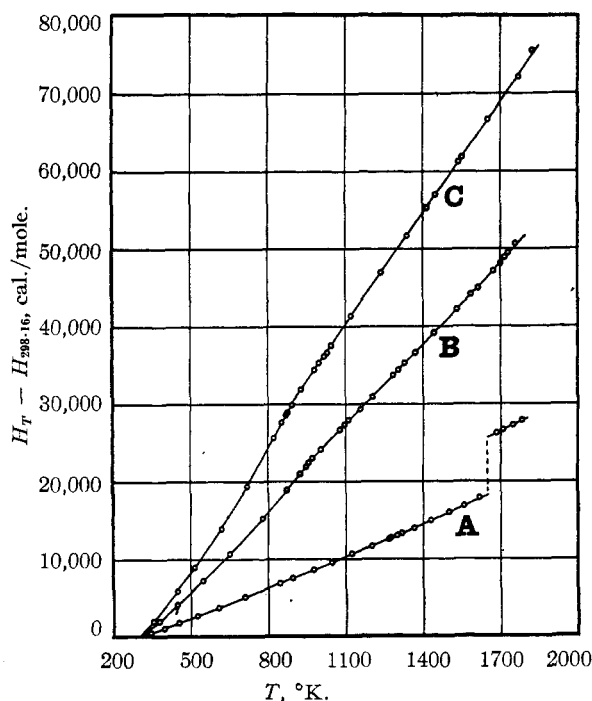


Fig. 1.—Molal heat contents: A, $\text{Fe}_{0.947}\text{O}$; B, Fe_2O_3 ; C, Fe_3O_4 .

Ferric oxide shows two anomalies, presumably of magnetic nature, at about 950 and 1050°K., respectively. Both appear to involve maxima in the heat-capacity curves rather than isothermal heats of transformation. However, in fitting the data with equations, it was found advantageous to treat them as if there were a small heat effect (160 cal./mole) at the 950°-point.

The ferric oxide results of Roth and Bertram⁴ are in only fair agreement with the present values, the average deviation being 1.5%. The data of Brown and Furnas⁷ and Kolossowsky and Skoulski⁸ are too uncertain to warrant comparison.

Table II gives heat content and entropy increments at even temperature intervals and at transformation points, for convenience in making thermodynamic calculations.

The following heat-content relationships are valid within the average deviations and temperature ranges shown in parentheses

$$\text{Fe}_{0.947}\text{O}(c): H_T - H_{298.16} = 11.66T + 1.00 \times 10^{-3}T^2 + 0.67 \times 10^5 T^{-1} - 3790 \quad (298 - 1650^\circ\text{K.}, 0.3\%)$$

$$\text{Fe}_{0.947}\text{O}(l): H_T - H_{298.16} = 16.30T - 1200 \quad (1650 - 1800^\circ\text{K.}, 0.1\%)$$

$$\text{Fe}_3\text{O}_4(\alpha): H_T - H_{298.16} = 21.88T + 24.10 \times 10^{-3}T^2 - 8666 \quad (298 - 900^\circ\text{K.}, 0.6\%)$$

$$\text{Fe}_3\text{O}_4(\beta): H_T - H_{298.16} = 48.00T - 12,650 \quad (900 - 1800^\circ\text{K.}, 0.2\%)$$

$$\text{Fe}_2\text{O}_3(\alpha): H_T - H_{298.16} = 23.49T + 9.30 \times 10^{-3}T^2 + 3.55 \times 10^5 T^{-1} - 9021 \quad (298 - 950^\circ\text{K.}, 0.1\%)$$

$$\text{Fe}_2\text{O}_3(\beta): H_T - H_{298.16} = 36.00T - 11,980 \quad (950 - 1050^\circ\text{K.}, 0.1\%)$$

$$\text{Fe}_2\text{O}_3(\gamma): H_T - H_{298.16} = 31.71T + 0.88 \times 10^{-3}T^2 - 8446 \quad (1050 - 1750^\circ\text{K.}, 0.1\%)$$

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