[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE]

THE HEAT CAPACITIES AT LOW TEMPERATURES OF "FERROUS OXIDE," MAGNETITE AND CUPROUS AND CUPRIC OXIDES[1]

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The thermodynamic properties of the important and interesting substances "ferrous oxide," magnetite and cuprous and cupric oxides, have been the subject of an enormous amount of experimental investigations and of an even greater amount of speculation. No attempt will be made here to review the accumulated data relating to the equilibria of these oxides with oxygen and the corresponding metals; most of the data are only approximations which fail to agree. The measurements presented here leave something to be desired with regard to ferrous oxide, which has never yet been prepared pure in quantities greater than a gram, and with regard to the entropy of cuprous oxide, which has at the lowest temperatures at which measurements were made, 75°K., the abnormally high heat capacity of over 8 calories per mole.

Materials.—A sample of crude ferrous oxide, kindly supplied by the Fixed Nitrogen Research Laboratory, was separated magnetically according to the method of Wyckoff and Crittenden.[3] The analysis, according to the method of Sims and Larsen,[4] which agrees with theirs as well as could be expected, was as follows: total iron, 77.24%; free iron, 0.80%; ferrous iron, 68.46%; and ferric iron (by difference), 7.98%. If we assume that all of the ferric oxide is combined with ferrous oxide as magnetite, Fe_3O_4, the material contained free iron, 0.80%; ferrous oxide, 83.05%; and magnetite 16.15%. Although Wyckoff and Crittenden conclude, as a result of their crystallographic measurements, that the purity of the material was much greater, large errors in the analysis do not seem probable in view of the care used to prevent oxidation during dissolution of the sample.

Although many attempts to secure pure ferrous oxide have been made, none has been successful, if we except those of Hilpert and Beyer,[5] Wöhler and Balz,[6] and Wöhler and Günther,[7] who prepared samples of 98–100% purity, but only in quantities of less than 1 g. Attempts to produce larger quantities are now being made in this Laboratory, but so far with indifferent

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[3] Wyckoff and Crittenden, THIS JOURNAL, **47**, 2876 (1925).

[4] Sims and Larsen, *Ind. Eng. Chem.*, **17**, 86 (1925).

[5] Hilpert and Beyer, *Ber.*, **44**, 1608 (1911).

[6] Wöhler and Balz, *Z. Elektrochem.*, **27**, 406 (1921).

[7] Wöhler and Günther, *ibid.*, **29**, 276 (1923).

success. One embarrassing characteristic, as found by Chaudron,[8] is that the reaction $4FeO = Fe + Fe_3O_4$ tends to take place below 570°, so that all preparations made above that temperature must be cooled to room temperature as rapidly as possible. Such a procedure is objectionable because a quenched material has internal strains which cause variations from the thermodynamic properties of the stable form.

The magnetite, from the deposit at Mineville, N. Y., was kindly lent for these measurements by Dr. Sosman of the Geophysical Laboratory of the Carnegie Institution of Washington. The ore was similar to that used by Sosman and Hostetter,[9] whose analysis was: Fe_3O_4, 99.0%; Fe_2O_3, 0.63%; and impurities, largely quartz, 0.37%. A correction was made for the heat capacity of the quartz.

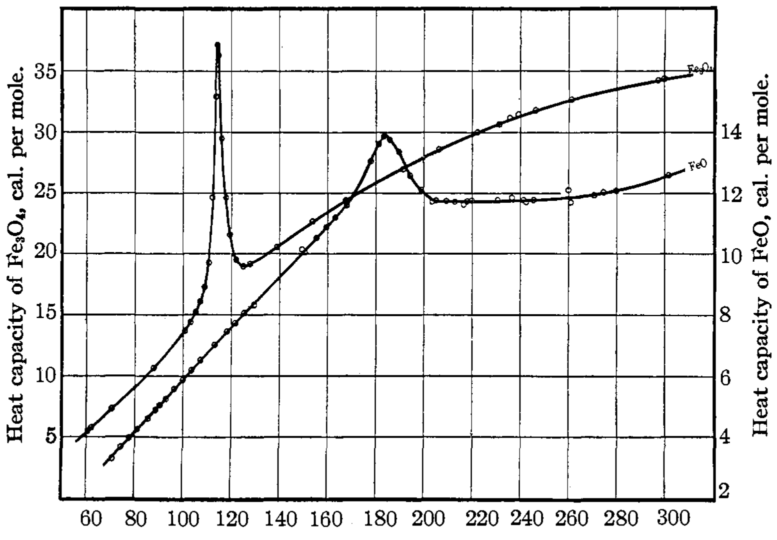

Fig. 1—The molal heat capacities of FeO and Fe_3O_4.

The cupric oxide was made by heating No. 28 copper wire in a muffle at 700° until oxidation was apparently complete. Analysis by reduction with hydrogen showed 79.90 and 79.91% copper, whereas the theoretical percentage is 79.89; this corresponds to 0.60% cuprous oxide, but the sample was completely soluble in 4% sulfuric acid without the deposition of metallic copper. The wire was probably completely converted to cupric oxide, but contained the residual impurities of the original copper.

The cuprous oxide was prepared from the cupric oxide by decomposition at about 0.002 mm. pressure in a silica tube, as described by Maier.[10]

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[8] Chaudron, *Ann. chim. phys.*, [9] **16**, 271 (1921).

[9] Sosman and Hostetter, THIS JOURNAL, **38**, 812 (1916).

[10] Maier, *ibid.*, **51**, 194 (1929).

After heating at about 700° until a layer of cuprous oxide, which does not seriously attack fused silica ware below 1100°, had been formed on the outside, the temperature was raised to 1000° and maintained until no more oxygen was evolved. Reduction by hydrogen showed 88.82% of copper, which is the theoretical proportion.

In calculating the heat capacity of the ferrous oxide, it was assumed that the specific heat of the sample was the same as that of pure ferrous oxide. The magnetite and iron are in solid solution in the ferrous oxide, as is shown by the lack of magnetism of the sample and by the normal course of the heat capacity curve near 114°K., where the curve for pure magnetite shows a sharp maximum. Consequently a correction could not be made for the magnetite as if it were a separate phase, and although our knowledge of the properties of pure ferrous oxide may be none the greater, the procedure adopted seemed the only feasible one. Moreover, it seems improbable that the heat capacity of pure ferrous oxide at 25° is as high as 12.5, the value given, since the heat capacity of manganous oxide, 10.30, is very nearly that predicted by Kopp's law, 10.2.

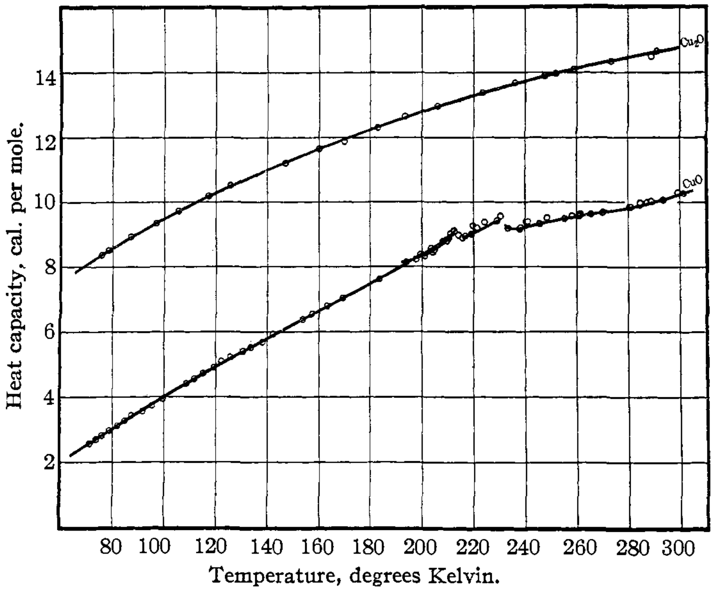

Fig. 2.—The molal heat capacities of Cu_2O and CuO.

In the following tables, heat capacities are expressed in gram calories (15°) per mole. One calorie is equal to 4.185 absolute joules. The calculations were made on the basis of O = 16, Cu = 63.57 and Fe = 55.84.

The measurements of the heat capacity of magnetite agree with those of Parks and Kelley[11] at the lowest temperatures, but gradually become

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[11] Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

TABLE I

THE MOLAL HEAT CAPACITY OF "FERROUS OXIDE," *viz.*, THE HEAT CAPACITY OF 71.84 G. OF THE SAMPLE

Run no.	T, °K.	C_p	Run no.	T, °K.	C_p	Run no.	T, °K.	C_p
1	301.8	12.56	17	125.4	8.036	33	177.8	13.02
2	70.7	3.296	18	129.5	8.318	34	181.0	13.59
3	74.1	3.662	19	150.6	10.04	35	183.2	13.86
4	77.5	3.952	20	155.3	10.51	36	185.7	13.75
5	81.0	4.254	21	159.5	10.87	37	189.5	13.35
6	85.5	4.594	22	163.4	11.19	38	194.1	12.57
7	88.5	4.882	23	168.0	11.59	39	198.8	12.09
8	90.1	5.042	24	205.0	11.75	40	203.3	11.70
9	93.0	5.252	25	209.3	11.73	41	217.9	11.72
10	96.3	5.574	26	212.8	11.70	42	230.5	11.77
11	99.8	5.866	27	216.5	11.60	43	236.5	11.84
12	103.4	6.174	28	219.9	11.75	44	241.3	11.77
13	107.1	6.488	29	242.5	11.70	45	261.0	11.69
14	113.0	6.984	30	245.5	11.76	46	270.7	11.93
15	118.2	7.440	31	260.0	12.09	47	274.6	12.02
16	121.6	7.720	32	149.3	10.12	48	279.8	12.09

TABLE II

THE MOLAL HEAT CAPACITY OF MAGNETITE

Run no.	T, °K.	C_p	Run no.	T, °K.	C_p	Run no.	T, °K.	C_p
1	297.3	34.28	12	110.4	19.25	23	153.7	22.63
2	299.7	34.39	13	112.0	24.62	24	167.5	24.36
3	60.5	5.495	14	113.6	32.92	25	191.4	26.98
4	62.0	5.771	15	114.7	36.27	26	206.2	28.59
5	70.5	7.331	16	115.9	29.49	27	222.1	30.00
6	87.6	10.63	17	117.6	24.58	28	235.7	31.18
7	100.7	13.67	18	119.4	21.52	29	239.2	31.45
8	103.0	14.38	19	121.8	19.48	30	231.3	30.67
9	105.1	15.20	20	124.8	18.95	31	246.0	31.81
10	107.0	16.09	21	127.5	19.16	32	261.1	32.68
11	108.8	17.27	22	138.9	20.53			

Fe_3O_4 (110°K.) = Fe_3O_4 (125°K.). $\Delta H = 361.4$

TABLE III

THE MOLAL HEAT CAPACITY OF CUPROUS OXIDE

Run no.	T, °K.	C_p	Run no.	T, °K.	C_p	Run no.	T, °K	C_p
1	147.0	11.22	8	236.1	13.70	15	75.9	8.366
2	159.9	11.66	9	247.6	13.93	16	78.4	8.519
3	170.0	11.89	10	259.0	14.12	17	87.0	8.935
4	182.9	12.32	11	252.1	13.98	18	96.9	9.355
5	192.9	12.67	12	273.5	14.36	19	105.3	9.721
6	206.1	12.98	13	289.1	14.50	20	117.0	10.18
7	223.5	13.40	14	291.0	14.66	21	125.6	10.51

less as the temperature rises, finally reaching a difference of 5.8% at 25°. Part of the difference is accounted for by a correction for the quartz in

TABLE IV

THE MOLAL HEAT CAPACITY OF CUPRIC OXIDE

Run no.	T, °K.	C_p	Run no.	T, °K.	C_p	Run no.	T, °K.	C_p
1	71.3	2.580	25	224.4	9.378	49	201.1	8.344
2	73.7	2.710	26	237.9	9.211	50	204.5	8.503
3	75.8	2.824	27	241.1	9.402	51	208.1	8.792
4	78.7	2.974	28	248.7	9.517	52	211.6	9.016
5	81.8	3.123	29	258.3	9.578	53	216.0	8.913
6	84.8	3.272	30	130.7	5.418	54	219.2	9.030
7	88.2	3.437	31	133.7	5.531	55	228.8	9.415
8	91.7	3.574	32	138.1	5.704	56	246.0	9.336
9	95.2	3.739	33	153.8	6.389	57	261.2	9.589
10	99.5	3.972	34	157.2	6.564	58	280.6	9.852
11	108.5	4.416	35	163.0	6.802	59	284.9	9.910
12	111.6	4.560	36	169.2	7.054	60	289.1	10.03
13	115.2	4.725	37	183.5	7.637	61	293.6	10.06
14	119.2	4.934	38	211.1	8.918	62	204.7	8.532
15	122.2	5.113	39	217.0	8.955	63	209.7	8.800
16	125.5	5.215	40	230.5	9.566	64	212.6	9.117
17	142.1	5.941	41	240.7	9.379	65	229.4	9.418
18	199.5	8.383	42	281.2	9.849	66	233.5	9.183
19	203.5	8.578	43	284.9	9.985	67	238.2	9.185
20	210.1	8.880	44	287.5	10.01	68	261.5	9.636
21	212.3	9.138	45	299.4	10.28	69	265.7	9.616
22	214.4	8.976	46	301.6	10.27	70	271.4	9.684
23	219.9	9.274	47	193.8	8.154			
24	221.3	9.215	48	197.6	8.239			

the magnetite, which they did not make, and part by a correction for loss of heat during the measurements.

A plot of the heat content–temperature curve shows that the heat capacity never becomes infinite, but reaches a maximum of 37.1 at 114.15°K. The maximum is undoubtedly due to a change in the magnetic properties.

The first 46 points for cupric oxide, determined in October, 1926, were satisfactory below 200°K., but the measurements made above that temperature were inaccurate because the current through the resistance thermometer varied, due to the rapidly changing temperature of the room. In April of this year it was decided to repeat the measurements above this temperature. Fig. 3 shows all of the points between 180 and 270°K. taken at both times, with numbers corresponding to those in Table IV. It was surprising to find that two discontinuities in the heat capacity curve existed within a narrow range of temperature, and that the runs of the first series were not as inconsistent as was at first supposed. According to expectations the heat capacity in the neighborhood of 220°K. varied with the history of the sample, as will be seen by a comparison of the first and second series. The former was taken after cooling to liquid-air temperatures and heating step by step, and the latter after cooling to 190°K. and proceeding in the same manner, beginning with Run 47, and to 200°K., beginning with Run 62. It may be noted, however, that similar experiments[12] with mangano-manganic oxide and manganese dioxide showed the heat capacity of each of these substances to be independent of its history. Some preliminary measurements of the heat capacity of magnetite, made with an unsatisfactory calorimeter—later discarded—led to the conclusion that its history likewise did not affect this quantity. It will be noted that for manganous oxide, manganese dioxide, and magnetite the discontinuities of the heat capacity curves were very large in comparison with those of cupric oxide, and apparently took place with much greater ease and rapidity.

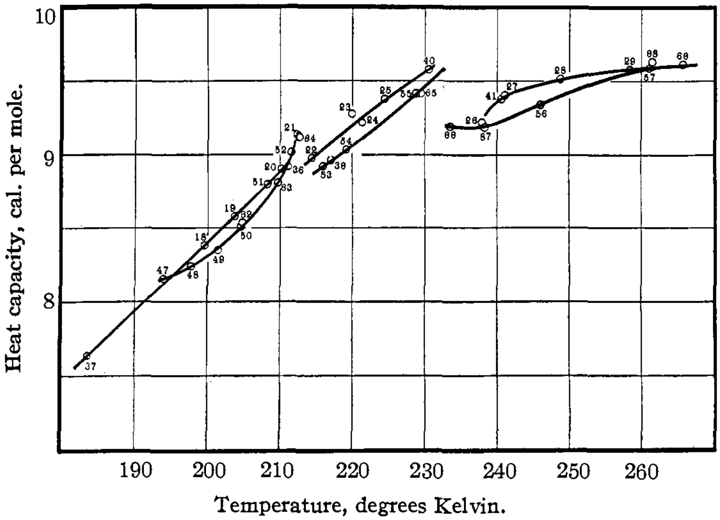

Fig. 3.—The molal heat capacity of CuO.

The Calculation of Entropy.—Obviously no sum of the theoretical equations so far devised, representing heat capacity as a function of the temperature, can be made to fit the data for ferrous oxide, magnetite and cupric oxide. However, if the upper and lower portions of the curve on the C_p-log T axes are connected by a curve representing the probable values of C_p, if no maximum were present, a combination of theoretical curves can be made to represent the interpolated curve with considerable accuracy and the entropy at some temperature below the interpolation can be calculated from the theoretical function.

In the following the Debye function is represented by $D(\beta\nu/T)$, and the Einstein function by $E(\beta\nu/T)$. For ferrous oxide the interpolation is rather large—from 89 to 282°K. The function

$$C_v = D\left(\frac{311}{T}\right) + E\left(\frac{387}{T}\right) + E\left(\frac{1265}{T}\right)$$

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[12] Millar, This Journal, **50**, 1875 (1928).

reproduces the lower portion of the experimental curve and the interpolation within 0.1% to 200°, and within 0.5% to 250° K. The total entropy at 25° is 12.7. Although this value exceeds the entropy of iron—6.71, calculated by Lewis, Gibson and Latimer[13]—more than the entropy of a monoxide usually exceeds that of the metal, yet it was found[12] that the entropy of manganous oxide was 14.92, whereas that of metallic manganese has been found by the above authors to be 7.3. The value for FeO, $S^\circ_{298} = 12.7$, is probably accurate within 2 units.

The interpolation under the peak in the curve representing the heat capacity of magnetite extends from 93 to 158°K. The function

$$C_v = 3D\left(\frac{346}{T}\right) + 4E\left(\frac{574}{T}\right)$$

represents the interpolation and the data above and below within 0.1% to room temperature. Calculation from the Debye function gives $S^\circ = 0.969$ at 44.7°K., and graphical integration above that temperature gives for Fe_3O_4, $S^\circ_{298} = 34.69$. Parks and Kelley[11] give 35.1, of which only 0.17 unit is due to their higher values of the heat capacity near room temperature. The agreement is excellent in view of the difficulty which they must have experienced in using the method of Lewis and Gibson[14] to obtain the entropy at 90°K., the lowest temperature at which they made a measurement, which is almost within the irregular portion of the curve. The present value is probably correct to 0.2 entropy unit.

An accurate calculation of the entropy of cuprous oxide is impossible, since the heat capacity is still over 8 at the lowest temperature. Furthermore, the four lowest points seem too high. The temperature scale may be in error at the lower end, although no uncertainty was anticipated before the calculation of the heat capacity, or these points may lie on the upper portion of an irregularity in the curve. However, the data can be well represented by the function $D(92/T) + E(235/T) + E(825/T)$, which represents the data within 0.3% up to room temperature, with the exception of the four lowest points. Calculation from the Debye function gives $S^\circ = 1.83$ at 25.1°K., and for Cu_2O, $S^\circ_{298} = 21.7 \pm 1.0$. It is hoped that the heat capacity of cuprous oxide at much lower temperatures will be obtained at a later date and thus permit a more satisfactory calculation of its entropy.

For cupric oxide the interpolation extends from 135 to 288°K. The function $D(443/T) + E(671/T) + E(1265/T)$ represents the data and the interpolation within 0.1% to 126° K., and within 0.5 to 224°K. The entropy calculated from the Debye function is 0.69 at 76.2°, and graphical integration over the remaining range gives for CuO, $S^\circ_{298} = 9.75 \pm 0.05$.

No reliable determinations of the heats of formation of the oxides of

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[13] Lewis, Gibson, and Latimer, This Journal, **44**, 1008 (1922).

[14] Lewis and Gibson, *ibid.*, **39**, 2554 (1917).

iron have been made. Since such measurements will, it is hoped, be made in this Laboratory at a later date, calculations of the free energy of these substances will be deferred.

Although the data for the oxides of copper are of sufficient accuracy to permit calculations of their free energies, their consideration is most profitable in connection with the measurements of the e.m.f. of cells reported in the paper by Maier.[10]

Summary

The heat capacities of "ferrous oxide" and of cuprous and cupric oxide have been measured from 70 to 300°K., and of magnetite from 60 to 300°K.

Their entropies are:

	FeO	Fe_3O_4	Cu_2O	CuO
S°_{298}	12.7 ± 2.0	34.69 ± 0.2	21.7 ± 1.0	9.75 ± 0.05

Berkeley, California

NOTES

A Simple Apparatus for the Determination of Carbon Dioxide.—The following method has been worked out for the accurate determination of carbon dioxide in limestone. The originality, we believe, lies in the simplification of the apparatus and in the arrangement to minimize contamination with atmospheric carbon dioxide.

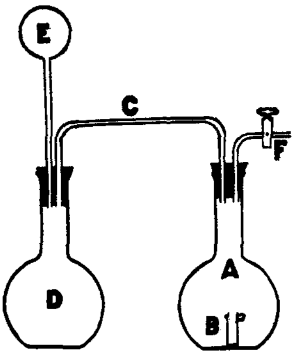

Fig. 1.

No special apparatus is required; two ordinary 1-liter Pyrex flasks, a small rubber balloon, two rubber stoppers and some large glass tubing are all that is necessary.

Chromic acid is used to liberate the carbon dioxide, and this is absorbed in a carefully standardized solution of barium hydroxide. The excess barium hydroxide is then titrated with standard hydrochloric acid, using phenolphthalein as indicator.

Procedure.—Set up the apparatus as shown in the figure and make sure that it is air tight. Weigh out 0.1000 g. of carbonate into B, place 100 cc. of a 1% aqueous solution of chromic anhydride in A and 50 cc. of water in D. Heat the contents of both A and D to boiling, remove both flames and add 25 cc. of a 0.2 *N* barium hydroxide solution to D. Carefully lower the bottle B containing the charge into A with a copper wire without letting the acid come in contact with the carbonate. Quickly stopper both A and D, which are thus connected by the tube C. Shake flask A to overturn B, place D in cold water and boil the contents of A. The balloon E serves as a safety valve, pressure regulator and pressure indicator. After boiling