ELECTRICAL AND THERMAL PROPERTIES OF IRON OXIDE.

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FURTHER data on electrical resistance and thermo-electric power of specimens of iron oxide, both Fe_2O_3 and Fe_3O_4, together with data on thermal conductivity of Fe_2O_3, have become available since the publication of a report on the subject from this laboratory in July, 1916.[1] Thermo-electric power and resistance data have now been carried to the melting point of the oxides studied, approximately 1520° C., four hundred degrees higher than was possible with the earlier apparatus.

Two methods of preparation were employed resulting in specimens of quite different physical behavior. The first method and that employed in the previous work consisted in first fusing a quantity of Fe_2O_3 in an arc furnace thus producing, as chemical analysis showed, a solid mass of Fe_3O_4. This was ground to an almost impalpable powder, compressed by means of a hydraulic press, baked at a bright red heat for one hour or more and then ground to the form desired, usually a rod some 15 mm. long by 6 sq. mm. cross-section. The tips of the specimen were melted by means of an oxy-hydrogen flame and platinum, platinum-rhodium thermo-junctions wires "frozen" in. The second method of preparation consisted in working the molten oxide into the form and size desired and fusing in the platinum junction wires as the specimen solidified.

Chemical analysis showed the specimens prepared by the first method to have completely reverted, after the baking process, to Fe_2O_3. At room temperature the resistance of specimens so prepared is beyond 10^7 ohms. The specimens prepared by fusion without baking show a resistance of but one or two ohms at room temperature The specimens prepared by the first method are comparatively stable, the data being approximately reproducible, run after run (see Fig. 2). (These specimens could as well have been prepared by direct compression of the original Fe_2O_3 and baking without the fusing and resultant reduction. It was not known at this time, however, that the subsequent baking caused the reversion to Fe_2O_3.) The specimens prepared by the second method, that is, the Fe_3O_4 specimens, are unstable, heating even to three or four hundred degrees causing a large permanent increase in resistance on

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[1] PHYS. REV., N. S., Vol. VIII., No. 1, p. 12 (1916).

cooling. Heating to 1400° C. causes a permanent radical change, the specimen behaving thereafter in all respects like the baked specimens (Fe_2O_3). Chemical analysis of such a specimen showed an oxidation to Fe_2O_3. The data for the fused unbaked specimens are therefore very rough and not reproducible. The curves for these specimens however serve to show the radical difference electrically between Fe_3O_4 and Fe_2O_3 (see Figs. 3 and 4).

Correction to a Previous Report.

As a result of the chemical analyses carried on in connection with the present work it is desired to here indicate a correction to a previous report, namely that on "Resistance and Thermo-Electric Relations in Iron Oxide," published in the Physical Review, N. S., Vol. VIII., No. 1, July, 1916. The specimens there reported upon are now known to have been Fe_2O_3 rather than, as stated, Fe_3O_4. The specimens were Fe_3O_4 at the start but the present work has shown that the baking in air at a bright red heat always oxidizes the specimen completely to Fe_2O_3.

Methods and Results with Fe_2O_3.

The specimen, prepared by fusion and baking as explained above, was placed in the end of a small quartz tube of about one cm. inside diameter, about the end of which were wound two turns of No. 20 platinum wire (*xx'*). The quartz tube containing the specimen and the wires (*xx'*) was placed in the center of a platinum-wound tubular furnace and resistance measurements taken by a fall of potential method as indicated in the previous paper.[1] To get thermo-electric power a temperature gradient was established along the specimen by sending current through the wires *xx'*. As soon as equilibrium was established the thermo-electric power was observed. The heater circuit (*xx'*) was then opened and, when temperature equality was reëstablished along the specimen, the resistance observations were repeated as a check on the first readings. The readings are thus seen to be simultaneous to the extent that it is possible to get simultaneous observations of two properties, one of which requires a uniform temperature, the other a temperature gradient. From five to ten minutes were required for the establishment of equilibrium conditions in the above cases.

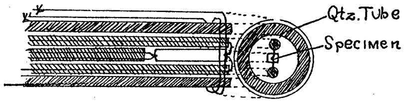

Fig. 1.

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[1] Loc. cit.

The observations, of course, give the thermo-electric power for the oxide against platinum. This was found to be negative for the lower ranges and, at 400° C., of the magnitude of 600 micro-volts per degree. The sign was determined by means of the rule stated in a previous paper,[1] viz., if current flows from the oxide to platinum across the hot junction, the oxide is said to be negative to platinum, and the E.M.F. is taken as negative.

Resistance measurements were plotted in accordance with the equation[2]

$$\text{Log}_{10}\, WT^{3/2} = A\,\frac{1}{T} + B.$$

W is the resistance (specific resistance was not determined). T is the temperature on the absolute scale; A and B are constants.

Observations in the past have shown considerable variation on successive runs in both resistance and thermo-electric power values. In order to study these changes on successive heatings, a series of runs were taken on the same specimen, the specimen not being mechanically disturbed in any way during the whole series of observations. Four runs were thus obtained, each run starting at a higher temperature than the preceding. Observations were taken with descending temperature steps. The data are shown graphically (Fig. 2). Simultaneous resistance and thermo-electric power runs are shown plotted together.

The transformation previously reported[3] at 710–730° C. is confirmed by both resistance and thermo-electric power lines on every run. The thermo-electric power line is straight up to the transformation point, but beyond that temperature steadily and consistently deviates, showing two reversals in sign. A second, very marked, reversible transformation is revealed at 1320° C. by the behavior of both the resistance and thermo-electric power lines. An inversion point for Fe_2O_3 at 1250–1350° C. has been reported by Kohlmyer[4] on evidence obtained from cooling curves. Kohlmyer also reports an inversion at 1028–1035° C. This latter point was not corroborated by the present data.

The variations in the different runs are probably due to the dissociation and recombination of oxygen on heating and cooling the specimen. The amount of recombination on each occasion depends probably upon the rapidity of cooling.

In the previous paper[5] a relation was thought to be indicated between

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[1] PHYS. REV., N. S., Vol. III., No. 3, p. 207.

[2] For discussion of this equation see previous paper, PHYS. REV., N. S., Vol. VIII., No. 1, p. 12.

[3] Loc. cit.

[4] E. J. Kohlmyer, Metallurgie, 6, 323–325 (1909).

[5] Loc. cit.

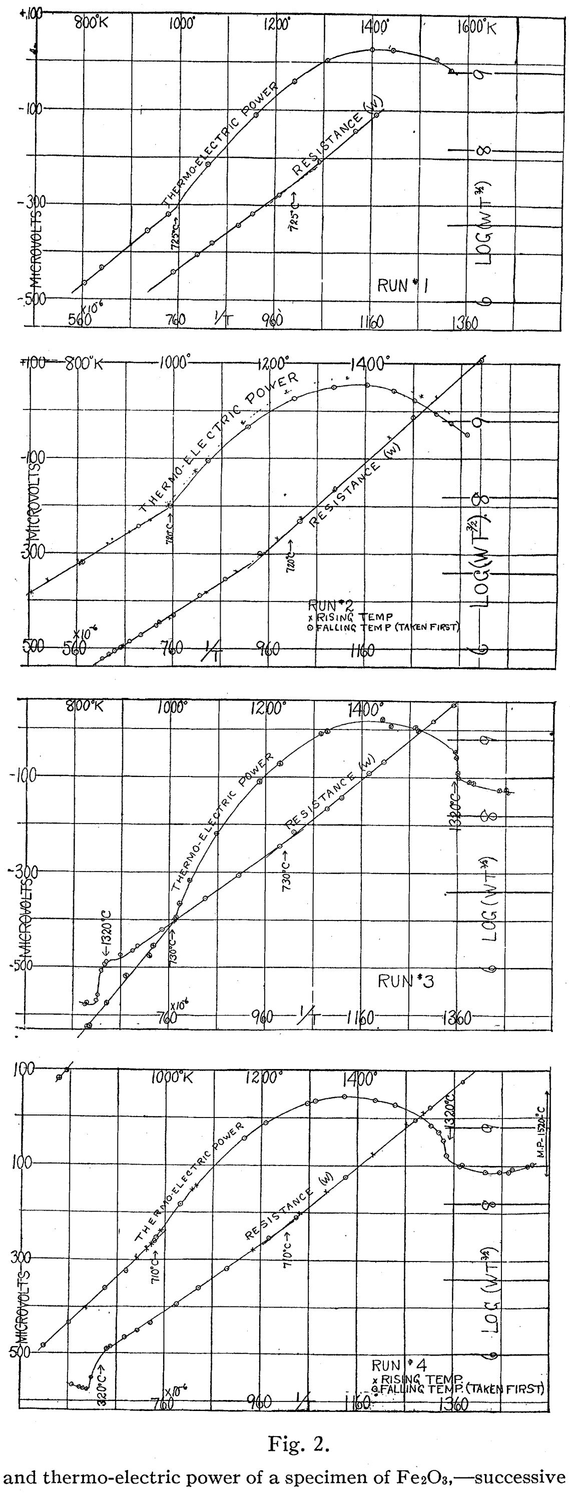

Fig. 2.

Resistance and thermo-electric power of a specimen of Fe_2O_3,—successive runs on the same specimen. The resistance lines are plotted to the scales indicated to the right and along the bottom. The thermo-electric power lines follow the scales indicated to the left and at the top.

(Q) the electron heat of dissociation (proportional to the slope of the resistance line) and the slope of the thermo-electric power line, viz., that an increase in (Q) meant a decrease in the rate of change of thermo-electric power and vice versa. The present data does not bear out this idea but rather indicates no simple relation between these quantities.

METHODS AND RESULTS WITH Fe_3O_4.

Specimens prepared by fusion without subsequent baking were found upon analysis, as before stated, to be pure Fe_3O_4. These specimens were ground to approximately the same size as the baked specimens and upon them the same electrical measurements were made. Since oxidation goes on more and more rapidly as temperature rises, clear-cut, definite results on temperature variation of the property under study are not possible without control of the oxygen pressure. Certain general information however can be obtained. The Fe_3O_4 specimens are characterized by low resistance (one or two ohms at room temperature), with negative temperature coefficient, the resistance dropping to two or three tenths of an ohm at 1200° C. The resistance curves (see Figs. 3 and 4) usually indicate a transformation between 600° and 800° C. On cooling from 1400° C. the resistance increases rapidly and if the heating has been sufficiently prolonged (one hour or more) the specimen then behaves in all respects like Fe_2O_3. The resistance on cooling to room

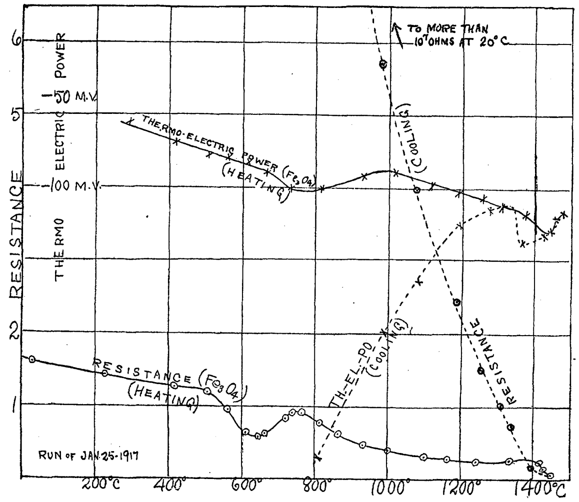

Fig. 3.

Resistance and thermo-electric power of a specimen of Fe_3O_4 (showing oxidation at 1400° C. to Fe_2O_3). Resistance is plotted directly against temperature.

temperature may be anything between the initial value of one or two ohms and 10^7 or more ohms depending upon the degree of oxidation. Specimens which showed the complete change to the behavior of Fe_2O_3 specimens were found on chemical analysis to have the corresponding composition, namely 70.0 per cent. iron. Approximately the same thermo-electric power line was obtained with four different specimens. The relation is indicated by two straight lines differing slightly in slope, the transition from one to the other occurring between 700° and 800° C. The values of thermo-electric power are small corresponding to the low resistance of the specimen. After prolonged heating the line becomes the typical thermo-electric power line for Fe_2O_3. Figures (3) and (4) show resistance and thermo-electric power changes on heating, for two specimens of Fe_3O_4. The dotted lines indicate the behavior on cooling.

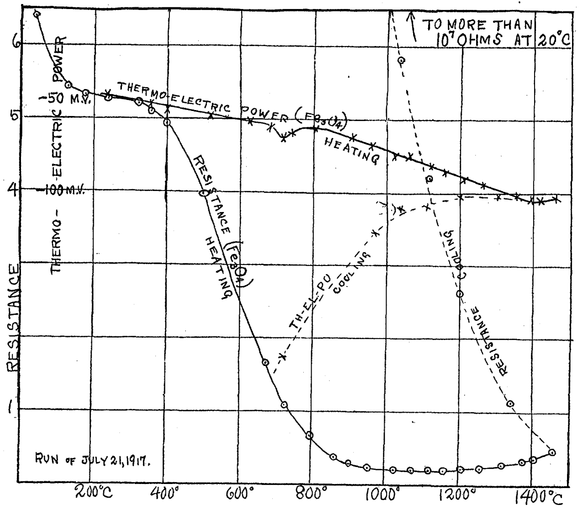

Fig. 4.

Resistance and thermo-electric power of a specimen of Fe_3O_4 (showing oxidation at 1400° C. to Fe_2O_3). Resistance is plotted directly against temperature.

Recent observations of Sosman and Hostetter[1] have shown the possibility of solid solution in the system Fe_2O_3–Fe_3O_4 with all gradations of ferrous iron from zero to 33.33 per cent. A more exact study of the effect on the electrical resistance of the dissociation of oxygen, or the variation of ferrous content, at a given temperature, is now being attempted.

Thermal Conductivity of Fe_2O_3.

Very little is known concerning the change of thermal conductivity with temperature in the case of the so-called "variable" conductors of

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[1] Am. Chem. Jour., Vol. XXXVIII., No. 4, Apr., 1916.

which iron oxide is a type. Even in the case of metals, data over wide temperature ranges are quite meager. Therefore a study of the thermal conductivity of iron oxide seemed to offer interesting possibilities of information in this field. By the method described below it has been found possible to obtain results through a temperature range of about 1000 degrees. These results though admittedly rough are thought to be significant. The absolute values are not of great importance since they depend somewhat upon the density and composition of the particular specimen and these factors are determined largely by the mode of preparation and the heat treatment. The law of temperature change however is significant since it is probably not effected by the uncertainty as to whether all the values are high or all low.

Powdered Fe_3O_4, prepared by fusing pure Fe_2O_3 in a carbon arc, was compressed in an iron cylinder The iron cylinder was 16.0 cm. long, 5.8 cm. outside diameter, 3.38 cm. inside diameter. At the center of the cylinder was held an iron rod, one cm. in diameter, and wrapped in several thicknesses of paper. This rod was allowed to pass through a hole in the piston used with the hydraulic press and in this way the oxide was compressed about it. After compression the whole arrangement was heated to a bright red heat and the iron rod easily withdrawn owing to the charring of the paper covering. This left a hole through the center of the solidly packed oxide core extending the length of the specimen. The central hole was designed to carry a heating coil (see Fig. 5). This heating coil was of nichrome wire and was wound on the inside of a quartz tube which was of such diameter as to fit the hole closely. Junction wires of platinum and platinum-10 per cent. rhodium were placed at *A*, *B*, *C* and *D* (Fig. 5). The wires for *A* and *B* were run through the central hole between the oxide and the quartz tube. The fit was so tight that the junction enlargements were believed to be tightly pressed against the inner surface of the oxide. Junctions *C* and *D* reached the outer surface of the oxide through holes in the iron casing. These holes were plugged with alundum cement. In order that a radial heat flow from the central portion might be reasonably certain, the oxide and

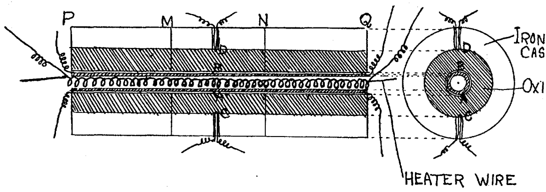

Fig. 5.

its iron casing were sawed through at M and N and then bolted together again. A contact of this sort offers a high resistance to the flow of heat across it. The length of this central section was 4.94 cm. The input of energy into the section MN was obtained by measuring the current and the potential drop through the heater, multiplying the pd. by 0.309, the ratio of the length of the central section (MN) to the entire length (PQ). The quartz tube containing the heating wires was packed with powdered aluminum oxide to eliminate convection. The outer iron casing was covered with about 5 mm. of alundun cement in which were embedded the junction wires leading to D and C. This whole arrangement was then slipped into the center of another iron cylinder approximately twice as long as PQ and of such diameter as to fit the specimen closely. The outside of this cylinder was also covered with a layer of alundum cement and in this was embedded a winding of nichrome ribbon running the whole length. Ordinary asbestos packing completed the construction.

The specimen could be heated uniformly to any desired temperature up to 1050° C. Tests when the inner heater wires were carrying no current gave uniform and steady temperatures after about five hours' heating. The criterion was simply that all four junctions should read alike. The final observations for thermal conductivity were made after both the outside furnace and the inner heater current had been on for some six to eight hours. Readings were begun after about five hours' heating and then taken every half hour, the last two or three readings usually being constant and indicating steady conditions.

The method above described is similar to that employed by Angell[1] in measuring heat conductivity of nickel and aluminum merely in that the shape of the specimen was cylindrical. In detail the methods are quite unlike.

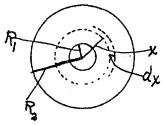

Fig. 6.

In order to compute (k), the thermal conductivity, the input of energy into the section (MN) was equated to the radial flow across this section. This is expressed by the equation

$$\frac{PdI}{J} = k \cdot 2\pi x \cdot l \frac{dT}{dx}. \qquad (1)$$

Pd is the potential drop across the specimen (length MN); I, the current; J, the mechanical equivalent of heat; k, the thermal conductivity; l, the length of the specimen (MN)(= 4.94 cm.); dT/dx, the temperature gradient at the distance x from the center; r_1, the radius of the hole (= .536 cm.); r_2, the outer radius of the oxide (= 1.69 cm.).

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[1] M. F. Angell, "Thermal Conductivity at High Temperatures," Phys. Rev., Vol. XXXIII., No. 5, p. 421 (1910).

Equation (1) may be written

$$\frac{PdI}{2\pi kJl}\int_{r_1}^{r_2}\frac{dx}{x}=\int_{T_1}^{T_2}dT$$

and upon integration gives

$$k=\frac{PdI}{2\pi Jl(T_2-T_1)}\log_e\left(\frac{r_2}{r_1}\right). \tag{2}$$

The table accompanying will serve to indicate the degree of accuracy of the results. The average of the readings of A and B was taken as the temperature of the inner surface; that of C and D, of the outer surface. Even when very large temperature gradients were used, such as 133° in one case, 76° in another, the values were found to be in good agreement with results obtained with much smaller temperature gradients (40° or thereabout). This is regarded as indicating the essential correctness of the results. The justification for considering the average of the inner junctions as giving the correct temperature of the inner surface, and the average of the outer junctions as giving the correct temperature of the outer surface is found in the general line-up of the points as shown on the curve (Fig. 7). Unless the averages gave pretty closely the correct values such consistent behavior would be hard to account for. Some uncertainty necessarily exists concerning the exact composition of the oxide at each temperature at which measurements were made. Chemical analysis at the close of the work showed 70.0 per cent. iron, the exact percentage required for Fe_2O_3. Since heating for some eight hours was found necessary for steady conditions before thermal conductivity could be measured, and since the first measurements were made at the upper temperatures (1047°, 905° C., etc.) there can be very little doubt that the oxide was at least very closely of the composition Fe_2O_3 throughout the observations. The indication of a linear relation between thermal conductivity and temperature for the class of materials exemplified by iron oxide is regarded as the significant part of this work. The data were taken in the order given in the table.

The remarkable difference here brought out between the behavior of electrical and thermal conductivity, the former increasing rapidly according to an exponential law, the latter slowly according to a linear relation, indicates probably a different mechanism involved in these two effects. The behavior of electrical conductivity is explained by Königsberger[1] as due to the increase in the number of free electrons with rising temperature. An indication of the relative number of free electrons is given by the thermionic emission from bodies of this class. For glowing lime

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[1] J. Königsberger, Jahrbuch d. Radioaktivität, Vol. II., p. 84, 1914.

Data for Thermal Conductivity of Fe_3O_4.

A.	*B.*	*C.*	*D.*	Temp. Difference.	Average Temp.	Energy Input (Watts).	*k.*
1,064°	1,072°	1,026°	1,024°	43°	1,047°	18.91	.00390
918	934	887	883	41	905	15.16	.00335
732	734	675	663	65	701	18.37	.00255
849½	849½	798	792	54½	822	18.45	.00300
861	863	812	806	53	835	18.45	.00309
880	881	831	825	52½	854	18.75	.00317
895	898	847	842	52	870	18.75	.00320
308	310	173	175	133	242	22.57	.00149
282	281	217	216	65	258	11.28	.00154
439	441	388½	385½	53	415	11.30	.00189
536	539	491	489	47½	515	11.50	.00214
616	619	576	572	43½	595	11.37	.00232
677	681	640	636	41	658	11.50	.00251
645	647	605	602	42½	624	11.42	.00239
668	674	635	630	39½	651	11.28	.00249
729	731	694	688	39	711	11.33	.00258
735	738	701	695	38½	718	11.30	.00260
750	755	720	709	38	734	11.50	.00269
777	781	746	738	37	759	11.60	.00279
855	860	828	822	32½	842	11.53	.00314
193	201	120	122	76	159	11.15	.00130

the law of electron emission is an exponential one of the same type as that expressing the change of electrical conductivity with temperature.[1] Thermal conductivity therefore seems to bear no simple relation to the number of free electrons.

A very interesting phenomenon brought out by the curve is the break at 720° C. corresponding very well with the break in the resistance and thermo-electric power lines at that temperature.

Summary.

The work here reported is an extension of previous research on electrical resistance and thermal electromotive forces in the oxides of iron. The methods have been improved, the measurements of the two properties have been made more nearly simultaneous and have been extended to the melting point of the oxides (1520° C.).

The chemical composition of the specimens has been investigated and the difference in the electrical behavior of the two oxides, Fe_2O_3 and Fe_3O_4, shown.

A correction to a previous report has been indicated.

The previously reported transformation for Fe_2O_3 at 710°–730° C. is verified. The thermo-electric line below this point is again shown to be

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[1] H. A. Wilson, Phil. Trans. A., Vol. CCII., p. 243, 1903.

straight, while above this point the more extended data indicate a very different law, a maximum positive value being reached in the neighborhood of 1125° C., the values thereafter decreasing to zero and then becoming negative, thus showing two reversals in sign. A transformation at 1320° C. probably involving some change in structure is clearly indicated by the behavior of the thermo-electric line in this region.

The electrical resistance in the case of Fe_2O_3 is found to obey the exponential law suggested by Königsberger for substances of this class and is plotted to the corresponding logarithmic equation. When so plotted the two transformations revealed by the thermo-electric power lines are strikingly corroborated.

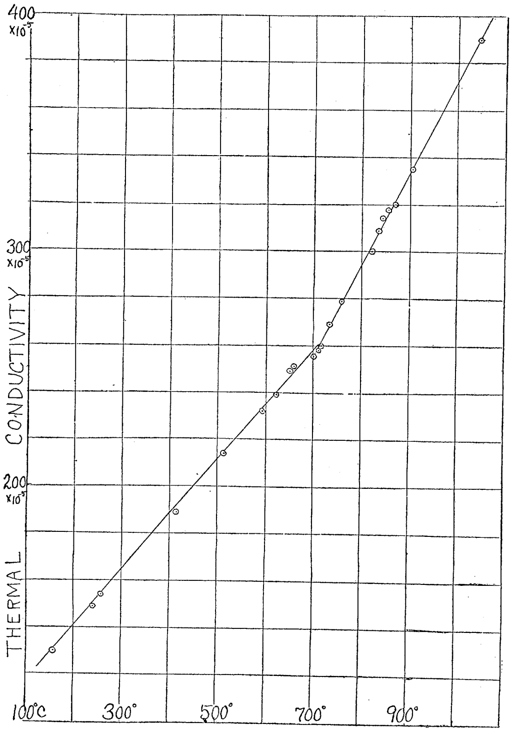

Fig. 7.

Thermal conductivity and temperature (Fe_2O_3).

The electrical resistance and thermo-electric power of Fe_3O_4 as a function of temperature is reported upon. Owing to change in composition (oxidation) which occurs on heating, the pure temperature variation is masked, but a wide difference from the behavior of Fe_2O_3 is shown.

Values of thermal conductivity of Fe_2O_3 up to 1050° C. have been obtained. The change of thermal conductivity with temperature is found to be a linear one. The data are shown graphically by two straight lines intersecting at approximately 720° C., the transformation point previous brought out by the resistance and thermo-electric power lines.

The work was performed in large part in the summer of 1916 under a grant from the Carnegie Institution of Washington.

CORNELL UNIVERSITY,
September, 1917.