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THE THERMAL CONDUCTIVITY OF FIRE-CLAY AT HIGH TEMPERATURES

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UNIVERSITY OF ILLINOIS
ENGINEERING EXPERIMENT STATION

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THE THERMAL CONDUCTIVITY OF FIRE-CLAY AT HIGH TEMPERATURES

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CONTENTS

METHODS AND RESULTS OF INVESTIGATION

I. INTRODUCTION [1]

The problem of thermal conductivity has for a long time furnished a favorite field of research for the physicist.[2] In reviewing the investigations of the past, many experiments, forming gradual approaches to a solution of this problem, will be found on record.[3] Nearly all of these experiments, however, were made at temperatures between that of melting ice, and steam at atmospheric pressure, and in no instances were even moderately high temperatures reached.[4] These experiments show that the chief difficulties have been the obtaining and maintaining of a high temperature, the determination of the quantity of heat conducted through the material, and the measurement of the correct temperature gradient in the specimen under test. Fortunately for present-day investigations, the electric heating coil and the thermocouple enable us to solve these problems with comparative ease and with a high degree of accuracy.

Although the investigation described in this bulletin was undertaken in the attempt to solve a specific problem,—the thermal conductivity of fire-clay at high temperatures,—the method developed will no doubt be of interest in other lines of work where the question of thermal conductivity is of importance. For instance, in all problems of refrigeration, this is a factor of the greatest importance. In the construction of cold storage buildings, a convenient method for test-

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[1] The investigation described in this bulletin was conducted in the Physical Laboratory of the University of Illinois by W. L. Egy, a research fellow of the Engineering Experiment Station. Its inception is due to Dr. J. K. Clement, and to him also is due the credit for the selection of the general method. Dr. A. P. Carman, Professor of Physics, advised Mr. Egy concerning the later phases of the investigation.

[2] See "The Conductivity, Porosity and Gas Permeability of Refractory Materials," by S. Wolagdine and A. L. Queneau, in Electro-Chemical and Metallurgical Industry, Sept., 1909, p. 383; Oct., 1909, p. 433. It is a singular coincidence that after many years in which no work was done upon this subject, two attempts should be made independently and practically at the same time.

[3] E. H. Hall, Phys. Rev., Vol. X, p. 277. June, 1900. Holborn & Wien, Zeitsch. Ver. Deutsch. Ingen., Vol. 40, 1896. Lees & Chorlton, Phil. Mag., Vol. 41, p. 495, Sec. 5, 1896. G. Glage, Ann. d. Physik., Vol. 323, p. 904, Dec., 1905. C. Niven, Roy. Soc. Proc., Vol. 76 A, p. 34, April 22, 1905. Tait, Trans. Roy. Soc. Edin., Vol. 28, p. 717, 1879.

[4] An account has recently been published of some very excellent work done by Dr. Wilhelm Nusselt on the "Thermal Conductivity of Heat Insulators." Some of his measurements were made at temperatures as high as 550° C. See Engineering, Vol. 87, pp. 1, 2, Jan. 1, 1909.

ing the various building materials would be of great value, although, of course, working at low temperatures would present a somewhat different problem.[1]

The primary object of these investigations in determining the thermal conductivity of fire-clay was to obtain information concerning the loss of heat through the walls of boiler furnaces. It is a well-known fact that considerable heat escapes through the walls of furnaces, but no idea of the amount of this heat has heretofore been obtained by direct methods. Nor do we have any definite knowledge of the effect of this heat, which passes through the walls, upon the different materials of which they are composed. While the engineer knows that the thicker the wall, the less heat is lost, he does not know how far he will be justified in increasing the thickness of the wall, until he has secured accurate data of the quantity of heat lost in this way.

To illustrate,—knowing the thermal conductivity, *K*, of brick, the dimensions of the furnace, and the inside and outside temperatures of the walls, the quantity of heat transmitted through them may readily be calculated. Taking the specific case of a 210 H. P. Heine boiler at the University of Illinois, when working under full load,—the area of walls exposed to the hot gases is about 364 sq. ft., and the thickness of the same about 20 in. The average temperature of the inside of this area is approximately 1400° F., and of the outside, 150°F. If we now take the value of K as found for that test-piece which was nearest like the brick in the setting, that is, $K = .0026$, (See Curve No. 2), and calculate the heat conducted through the walls we have, using *c. g. s.* units,

$$Q = .0026 \, \frac{.555\,(1400-150)}{2.54\,(20)} \, 929\,(364) \times 3600$$

(See formula 1, page 4.)

$$Q = 43{,}400{,}000 \text{ calories per hour}$$
$$\text{or } 172{,}000 \text{ B. t. u. per hour}$$

This is about 1.6 per cent of the total heat generated. These figures are only approximations, but they show that with careful measurements, the heat lost through the various parts of the walls may be calculated directly.

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[1] The conductivity of the substances in the earth's crust is of interest to geologists. The British Association for the Advancement of Science had a committee working for seven years to determine the conductivity of some of the rocks in the British Isles. (Herschel, Lebour, and Dunn, Rep. Brit. Assn., Vol. 49, 1879.)

II. PRINCIPLES OF THERMAL CONDUCTIVITY

A brief resumé of the principles of thermal conductivity follows: The quantity of heat, Q', flowing through a given wall is proportional to the difference in temperature, $T_1 - T_2$, of the two faces. For a given difference in temperature, Q' is inversely proportional to the thickness, r. The heat flowing through a section of the wall will, of course, be proportional to the area, A, of that section. Q' is necessarily proportional also to the time, t, over which measurements are taken. Using these principles,

$$Q' = K \frac{T_1 - T_2}{r} At \dots\dots\dots\dots (1)$$

K is a constant for the given substance at any temperature, and is called the internal thermal conductivity or simply the thermal conductivity of that material. If Q is expressed in calories; $T_1 - T_2$ in centigrade degrees; A, in square centimeters; r, in centimeters; and t, in seconds, K will be in *c. g. s.* units.

If we consider a lamina of infinitesimal thickness, dr, the difference in temperature between its faces being dT, for a time, dt,

$$Q' = K \frac{T - (T + dT)}{dr} Adt = -KA \frac{dT}{dr} dt \dots\dots (2)$$

The expression $\frac{dT}{dr}$ is called the temperature gradient at the point in question, or in other words, the change in temperature per unit thickness.

$$\text{From equation (2)} \quad K = -\frac{Q}{A} \frac{dr}{dT} \dots\dots\dots\dots (3)$$

where Q is the heat flowing across the area A in unit time.

From the above expression, it may be seen that in order to determine the thermal conductivity of a substance, it is necessary to measure the quantity of heat flowing through a unit area, and the temperature gradient. The most accurate method of measuring Q, is to generate a known quantity of heat by means of an electric heating circuit, in such a manner that all the heat generated must flow through the substance to be tested. If a constant quantity of heat is generated until conditions have reached an equilibrium, then the quantity of heat conducted through the material per second must be equal to the quantity generated per second. This method may be used with a heating coil either in a hollow sphere or in a long cylinder. The latter form was chosen for these tests because of the experimental difficulties arising in the former.

In using this method, the assumption is made that there will be no escape of the heat longitudinally at the middle of the cylinder; that is, the exact amount of heat generated by a centimeter length of the coil, taken at the middle, must flow out through the corresponding circular section of just one centimeter thickness. To avoid errors from this cause, the length of the cylinder must be several times greater than its diameter.

The test-pieces were made into cylinders about 40 cm. in length and 12 cm. in diameter, with a hole through the center about 3.5 cm. in diameter for the reception of the heating coil. Four longitudinal holes about 3 mm. in diameter were made, in which thermocouples could be placed for the measurement of the temperature.

Applying equation 3 to the case of a cylinder, the heat, Q, generated by 1 cm. length of the coil in unit time is expressed by

$$Q = \frac{.2394 \quad EI}{l} \quad \text{calories}$$

where E represents volts, I, amperes, and l, the length of the coil in centimeters. The constant, .2394, is the reciprocal of the mechanical equivalent of a calorie expressed in joules or watts. The area perpendicular to the flow of heat at a distance r from the axis is $2\pi r$ per unit length. Substituting for Q and A in equation 3

$$K = -\frac{.2394 \quad EI}{2\pi lr} \cdot \frac{dr}{dT} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Assuming that K is constant between the temperatures T_1 and T_2 and integrating

$$K = \frac{.2394}{2\pi l} \cdot \frac{EI}{T_1 - T_2} \log \; (r_2/r_1) \ldots\ldots\ldots (5)$$

where T_1 and T_2 are the temperatures at points distant r_1 and r_2, respectively, from the axis. For any given values of r_1 and r_2, the only variables in this equation are EI, the electrical watts dissipated in the coil, and $T_1—T_2$, the difference in temperature between r_1 and r_2. Thus our expression may be reduced to

$$K = C \frac{EI}{T_1 - T_2} \qquad \text{.............(6)}$$

where

$$C = \frac{.2394 \log (r_2/r_1)}{2\pi l}$$

III. DESCRIPTION OF THE APPARATUS

Cylinders.—The cylinders tested were made by the Laclede-Christy Clay Products Company, St. Louis, Missouri. Twelve test-pieces were obtained, made up from four different mixtures, which were marked *A, B, 1* and *3.*

Those marked *A* were of a dark reddish-brown color and contained no gravel. The structure appeared similar to sandstone. After heating in the test, these pieces were cracked in a great many places. The pieces marked *B* were also of a reddish-brown color, but were of medium coarse structure. They contained very small pieces of white gravel throughout the mass. Those marked *1* were a little coarser than the *B* cylinders and were brown in color. They contained a very small amount of gravel. Cylinders *3* were almost white and very coarse. They contained a large amount of gravel.

One cylinder of each composition was tested at temperatures ranging from 400° C. to 800° C. or 900° C. The remaining pieces were tested at only one temperature. One of the cylinders, marked *1,* could not be tested because the holes in it for the insertion of the thermocouples were not deep enough.

Furnace.—Fig. 2 shows a longitudinal section of the furnace ready for use. *aa* is the test-piece. This was surrounded by a larger cylinder, *bb,* of fire-clay, in order to get uniform radiation from *aa,* and also to maintain higher temperatures. Coverings, *cc,* were placed over each end to prevent loss of heat in this direction. The whole was supported by an open framework of strap iron. A thermocouple was placed in each of the holes, *D* and *F.*

Heating Coil.—The heating coil was made of pure nickel wire about 1.8 mm. in diameter, wound nine turns to the inch upon a ½-in. porcelain electric insulator tube. Commercial insulator tubes 20 in. long were taken for this purpose and the enlarged end cut off, leaving

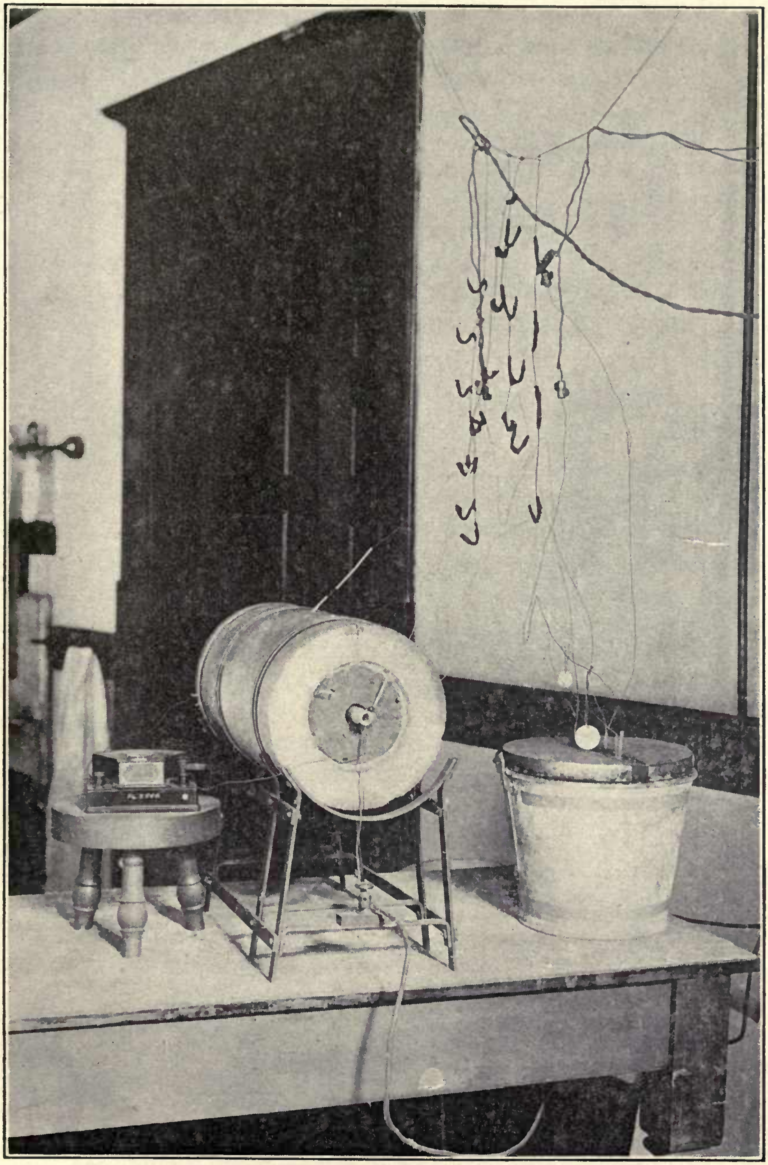


FIG. 1 TEST-PIECE SURROUNDED BY FIRE-CLAY JACKET—ALSO SHOWING THERMOCOUPLES IN PLACE

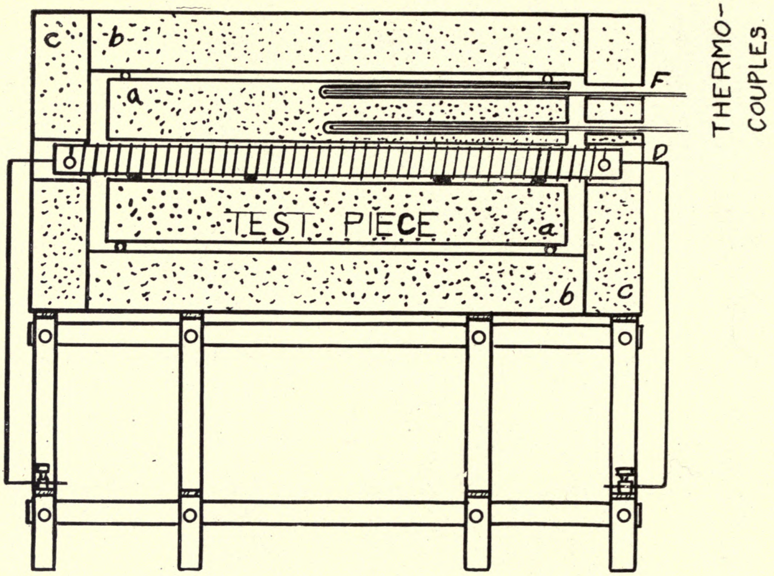


FIG. 2 SECTION OF FURNACE

them 18 or 19 in. long. Small holes were chipped in the ends of each tube, and the ends of the wire pulled tightly through these holes, thus holding the wire in place. The holes were 16⅛ in. apart, allowing 145 turns of wire, or an equivalent length of 40.9 cm. Potential leads were fastened to the power wire where it emerged from the insulator, by winding one end of a piece of smaller wire tightly about it. The place where this connection was made had a rather high temperature, so nickel was used to prevent any thermo-electric effect at the junction.

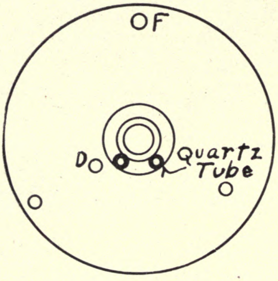


FIG. 3

The coil was at first supported in the cylinder by two small pieces of quartz tubing at each end (see Fig. 3). At the higher temperatures, however, the insulator softened and sagged down in the middle, and two additional pieces of quartz were placed under it, each one-third the distance from either end. The holes in the end of the furnace were packed with asbestos to prevent the escape of heat. The heating coil was made a few turns longer than the test-piece to prevent cooling of the ends.

IV. Method of Measurements

The current was measured by a Weston direct-reading portable standard millivoltmeter and shunt. The current was taken from 110-volt mains and was regulated by means of two large rheostats, as in the calibration work, (Appendix). As it was necessary to maintain the current constant to one-tenth of an ampere for several hours at a time, and the line voltage varied considerably, a storage battery was placed across the mains as shown in Fig. 4. By means of another resistance, the current from the mains was adjusted to a few amperes less than that flowing through the furnace. In this way only a few amperes were drawn from the battery and its voltage remained constant through a considerable change of the line voltage. This was not always sufficient, however, for satisfactory operation.

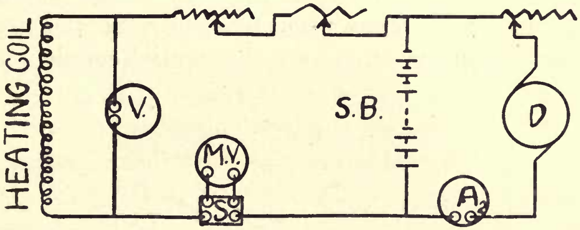


Fig. 4

The voltage drop through the coil was measured by a Weston portable voltmeter, the smallest division of which corresponded to one volt. The temperature coefficient of nickel is very large, and the resistance of the wire varied considerably with the temperature. As the turns at the end of the coil were somewhat cooler than those in the middle, their resistance was less, and the average voltage drop per centimeter for the whole coil would be less than the drop per centimeter of the central portion. As the average value was used in the calculations, an error would thus be introduced. This was compensated for, by having the potential leads connected to the heating circuit, as stated above, outside the insulator, thus adding to the potential drop across the actual 145 turns, the drop in the wire from the last turn to the point of connection.

The temperatures were measured by platinum—platinum-rhodium thermocouples, made by Heraus, in Germany, and calibrated by the melting-point method described in the Appendix. The couples were also calibrated in opposition as a differential couple. This was done by placing both couples in a quartz tube in a large piece of iron and heating the iron up to about 1100° C., taking the reading of the differential couple at various temperatures. The couples were placed in the small holes (D, F, Fig. 2) in the test-piece far enough so that the junctions were midway between the ends. The two wires were insulated from each other by placing very small porcelain tubing over the platinum-rhodium wire.

The electromotive force of the couples was measured by a Wolff potentiometer and a galvanometer, as in the calibration (See Appendix). Each couple was read separately and then the two were connected in opposition and read as a differential couple. The relation

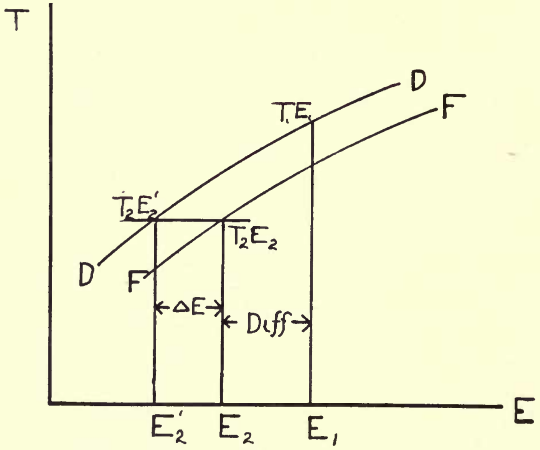


FIG. 5

between this reading and the corresponding difference in temperature is obtained as follows:

Let us call these readings Diff. Let the curve *DD* (Fig. 5) represent the relation between temperature and electromotive force for couple *D*, and curve *FF*, that for couple *F*. Let E_1 and E_2 be the readings of couples *D* and *F*, respectively. The curve *DD* is expressed by the equation,

$$T_1 = A + BE_1 + CE_1^2$$

and $$T_2 = A + BE'_2 + C\,(E'_2)^2$$

then $$T_1 - T_2 = B\,(E_1 - E'_2) + C\,[E_1^2 - (E'_2)^2]$$

now $$E'_2 = E_2 - \triangle E$$

and $E_1 = E_2 + \text{Diff.}$ ("Diff" is the reading of the differential). Substituting for E_1 and E'_2 above,

$$T_1 - T_2 = B\,(\text{Diff} + \triangle E) + C\,(\text{Diff} + \triangle E)\quad(E_1 + E_2 - \triangle E.$$

$\triangle E$ is negligible in comparison with $(E_1 + E_2)$ and may be dropped from the last factor.

Manipulation.—The arrangement of the potentiometer circuits is shown in Fig. 6. From the ice bath the couples were connected to two "single-pole double-throw" switches (1 and 2) which were mounted on the same base. Throwing switch No. 1 to the left and No. 2 to the right, couple *D* could be read. Reversing No. 2 placed *F* in the circuit. With both switches to the right, the two couples were connected in the circuit in opposition, in their proper order, since *D* was the hotter couple and therefore had the higher electromotive force.

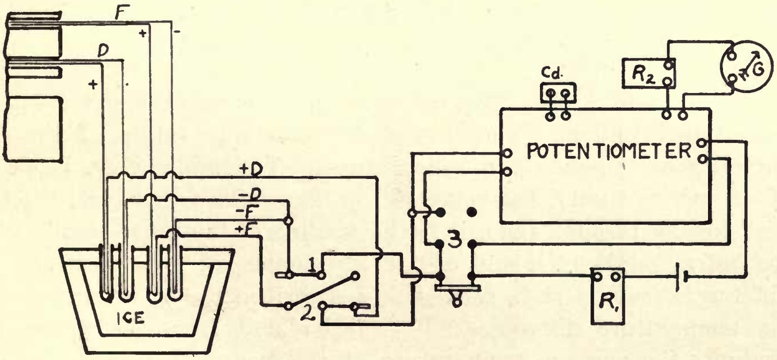


Fig. 6 Potentiometer Circuit

The statement was made above that the heat which was generated at the middle of the coil flowed out along radial lines. This was tested by moving the outer couple *F* (Fig. 2), back and forth in a longitudinal direction and noting the reading in the various positions. This operation showed that the temperature was constant to 0.3° C. for a distance of 6 or 7 cm. from the middle. As no heat will flow along constant temperature lines, there could be no longitudinal flow of heat in the 12 or 14 cm. in the middle of the test-piece, and hence the assumption is allowable.

The general method of operation was to start the furnace with a rather large current, about 25 amperes, and gradually reduce this, as the furnace approached the temperature desired. This took from three to five hours for the lower temperatures. The storage battery would then be placed in the circuit (see Fig. 4) and the current kept constant for two or three hours more. When the outer couple, *F*, showed a temperature constant to one-tenth of a degree, indicating equilibrium conditions, readings were taken. The voltage and current readings were taken before and after the temperature readings, in order to be sure there was no change. The temperature readings were taken in the order, *D*, *F*, *D*, (*D*-*F*), and *D*. It will be noticed by referring to Fig. 6, that only one change of either switch No. 1 or No. 2 is necessary to change from any one of the above readings to the next in order. Each cylinder, at the close of the tests on it, was broken across the middle, and r_1 and r_2 carefully measured in the plane in which the temperature readings had been taken.

V. RESULTS

Tables 1 to 4 show the readings and results obtained from the first four cylinders. The curves also show the values of the conductivity at the different temperatures. The tables give, in order, (from left to right), the voltage drop across the furnace *E;* the current flowing through the coil *I*; the reading of the inner couple (*D*); the outer couple *(F),* and of the two connected in opposition as a differential couple *Diff.,* corrected as described above, in micro-volts; the temperature difference, $T_{\text{diff.}}$, calculated from the differential reading; the average temperature of the two couples and the conductivity, *K*. The readings are arranged in the order of increasing temperatures, although they were not taken in this order in every case. It will be noticed that the conductivity of the two coarser fire-clays was constant, while that of the other two which were of finer structure increased with the temperature.

Table 5 gives the comparative values of the different cylinders in the order in which they were tested. The particular value given for each of the first four was so chosen as to be near the temperature at which the later pieces of the same composition were tested.

The accuracy of the values for K in this work is limited to the accuracy in measuring r_1 and r_2. The temperature readings are certainly accurate to 1.0° C., and very probably to 0.5° C. The voltage and current readings are accurate to one per cent. An error may be introduced in the values of r_1 and r_2 because of the uncertainty of the position of the thermo-junction in the hole. If the couple were touching one side of the hole, it would take the temperature of that side, while r_1 and r_2 were always measured to the center of the holes. This error, however, would be a constant factor for the tests on any cylinder, since the couples were never disturbed after they were once placed in a cylinder, until the completion of the tests on that piece. Thus the comparative values of K for any given specimen at different temperatures would not be affected by the values of r_1 and r_2.

The greatest error is caused by changes of current through the furnace. The supply voltage changed a great deal, and the batteries used were not large enough to maintain the current constant at all times. If the current should change just before a reading was taken, the temperatures would not correspond to the other readings, though they might not be changing at the time. The variation between cylinders of the same composition is probably due to a difference in porosity. An investigation of the effect of porosity as well as composition of substances would, no doubt, lead to more definite results, in regard to a comparison of fire-clays.

TABLE 1

Mark	r_1	r_2	E	I	D	F	Diff	T_{diff}	$T_{ave.}$	K
B	23.5	58.0	27.6	15.4	3677	2067	1597	170.9	362.4	.00209
..	....	....	33.6	17.2	4595	2470	2116	223.9	430.6	.00217
..	....	....	35.2	17.8	5325	2990	2319	242.6	494.2	.00217
..	....	....	38.8	18.7	5928	3257	2657	276.1	537.8	.00221
..	....	....	40.9	19.1	6541	3634	2889	297.3	586.6	.00221

TABLE 2

Mark	r_1	r_2	E	I	D	F	Diff	T_{diff}	$T_{ave.}$	K
3	33.8	52.0	30.1	17.8	3700	2919	781	81.3	406.5	.00264
..	....	....	36.3	19.8	4687	3621	1066	108.4	493.2	.00266
..	....	....	36.0	19.8	4729	3667	1063	108.0	497.7	.00265
..	....	....	40.0	20.9	5423	4164	1261	126.0	557.5	.00266
..	....	....	40.9	21.1	5514	4232	1285	128.1	565.4	.00270
..	....	....	43.9	21.7	6023	4540	1485	146.3	605.7	.00261
..	....	....	46.3	22.0	6587	4991	1601	155.4	655.2	.00267
..	....	....	47.3	22.3	6626	4992	1635	158.6	657.1	.00263
..	....	....	50.6	22.5	7208	5402	1809	172.9	704.6	.00264

TABLE 3

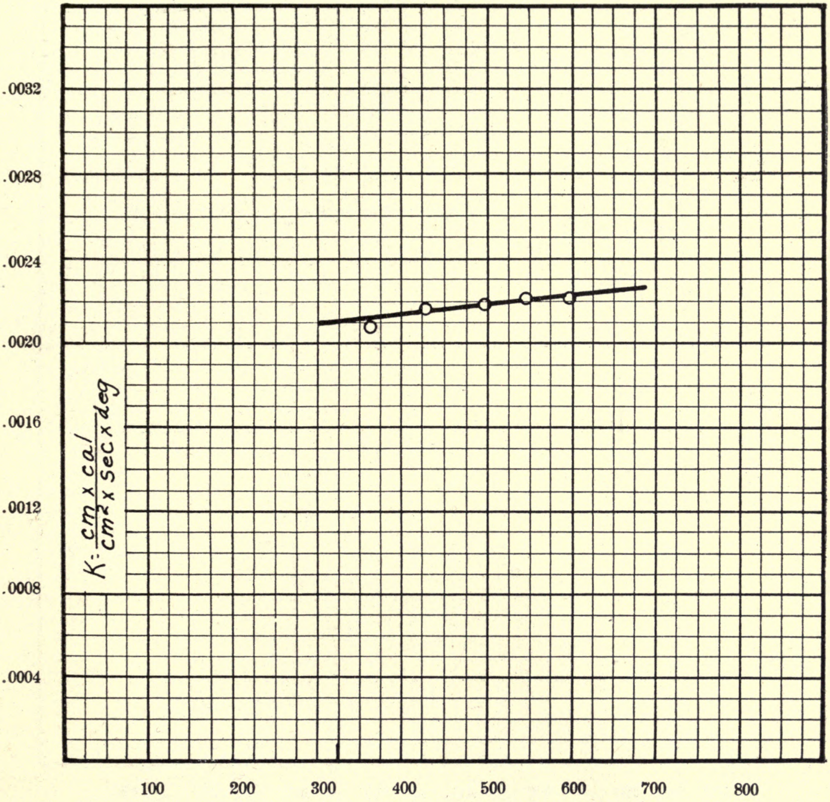
Mark	r_1	r_2	E	I	D	F	Diff	T_{diff}	$T_{ave.}$	K
A	33.3	66.0	39.2	19.9	5197	3190	2001	203.3	496.2	.00245
..	....	....	43.8	19.0	5827	3664	2164	216.4	551.6	.00245
..	....	....	45.5	20.7	6347	3958	2387	236.0	591.7	.00254
..	....	....	49.7	20.4	6924	4232	2693	263.0	633.0	.00246
..	....	....	51.7	20.3	7279	4480	2800	271.0	662.1	.00247
..	....	....	52.7	20.2	7301	4512	2795	270.4	664.7	.00251
..	....	....	52.8	20.5	7377	4598	2782	268.5	672.6	.00251
..	....	....	59.7	20.8	8337	5032	3305	312.4	738.0	.00252
..	....	....	61.0	21.0	8399	5069	3336	314.9	742.6	.00259
..	....	....	61.8	20.6	8591	5191	3403	319.7	757.2	.00254

TABLE 4

Mark	r_1	r_2	E	I	D	F	Diff	T_{diff}	$T_{ave.}$	K
1	23.9	49.3	29.6	16.8	3572	2697	876	91.6	388.2	.00366
..	....	....	34.8	18.4	4547	3386	1159	118.5	474.0	.00364
..	....	....	42.6	20.5	6031	4335	1678	165.7	596.7	.00355
..	....	....	45.2	21.2	6430	4583	1847	180.7	627.4	.00358
..	....	....	54.3	22.8	8085	5640	2449	230.2	756.5	.00362

TABLE 5

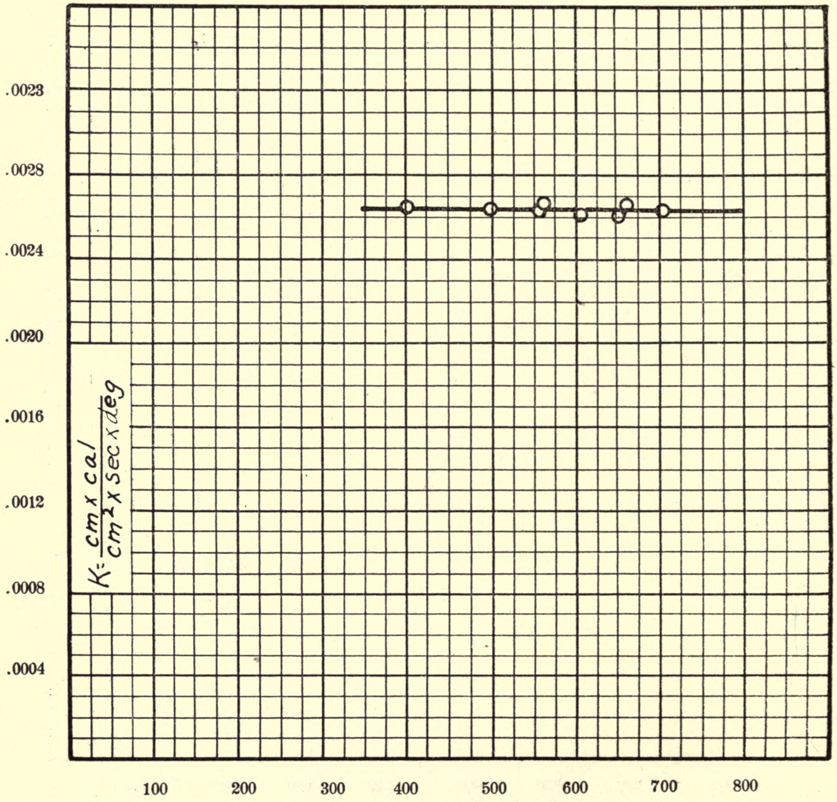
	Mark	r_1	r_2	E	I	D	F	Diff	T_{diff}	$T_{ave.}$	K
1	B	23.5	58.0	40.9	19.1	6541	3634	2889	297.3	587	.00221
2	3	33.8	52.0	50.6	22.5	7208	5402	1809	172.9	705	.00264
3	A	33.3	66.0	52.7	20.2	7301	4512	2795	270.4	665	.00257
4	1	23.9	49.3	54.3	22.8	8085	5640	2449	230.2	757	.00362
5	3	31.0	48.4	42.0	20.5	5633	4429	1205	119.6	581	.00299
6	A	29.0	56.0	54.0	20.1	8170	5414	2756	259.6	749	.00256
7	3	27.0	49.5	57.0	19.7	8556	6001	2558	237.5	795	.00267
8	1	30.0	51.0	60.5	20.1	8318	5888	2433	227.1	770	.00265
9	B	32.0	51.5	63.0	19.0	8823	6716	2210	202.1	891	.00263
10	B	27.5	46.0	44.0	20.3	6535	4638	1900	185.5	635	.00231
11	A	26.5	61.5	45.0	20.1	7483	4623	2860	275.4	679	.00257



TEMPERATURE IN CENTIGRADE DEGREES

CURVE NO. 1

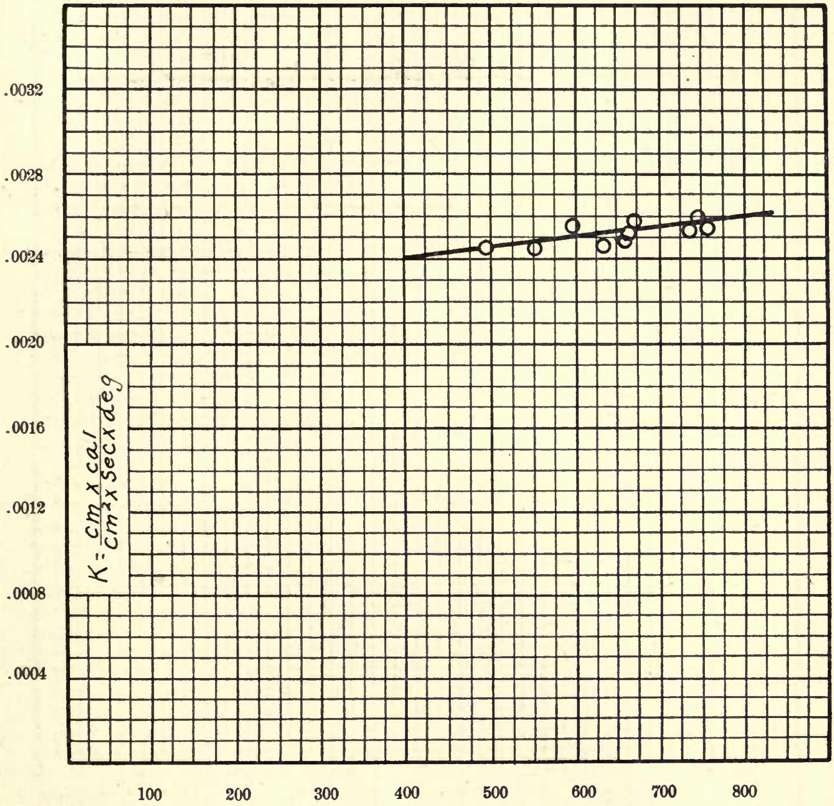
FIG. 7



Temperature in Centigrade Degrees

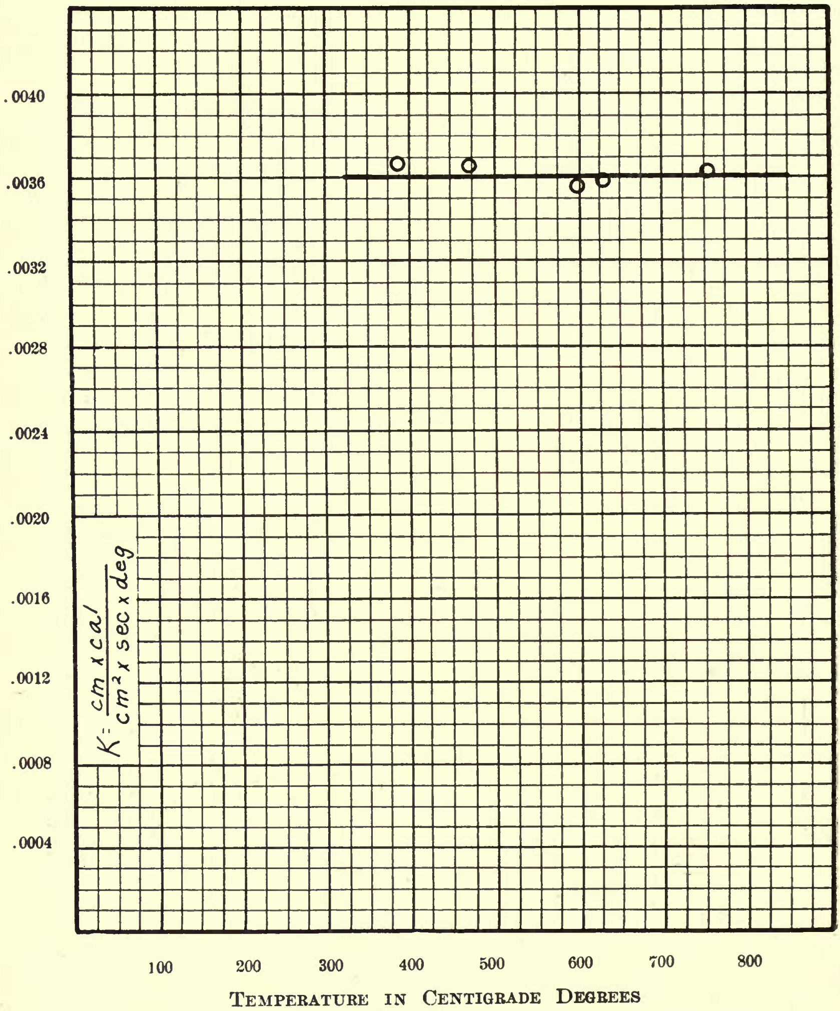
Curve No. 2

Fig. 8



Curve No. 3

Fig. 9



Curve No. 4

Fig. 10

APPENDIX

The use of thermocouples for measuring high temperatures is no longer a novelty in physical investigations, but the details of the calibration are not generally accessible. Hence the exact method of calibration used in this work has been described at considerable length in this Appendix.

METHOD FOR CALIBRATING THERMOCOUPLES FOR HIGH TEMPERATURE MEASUREMENTS

Since, as a rule, no two thermocouples have the same electromotive force, and since the electromotive force of any couple is appreciably changed by the action of metallic and possibly other vapors at high temperatures, it is necessary to calibrate the couples from time to time. The method described is that known as the *melting point* or *Frankenheim* method.[1] The couple, surrounded by a closed porcelain or fused silica tube, is immersed in the melted metal, and the furnace allowed to cool slowly. Readings of the electromotive force taken at regular intervals will show a steady decrease until the freezing point is reached, remain constant until the metal is nearly all solidified, and will then fall off again. Knowing the temperature at which the metal melts, we can thus determine the value of the electromotive force of the thermocouple corresponding to a definite temperature. Obtaining a number of points in this way by using different metals, a curve may be drawn through them showing the relation between the electromotive force and the temperature for that particular couple.

The Furnace.—Frequent use of this method demands a furnace which may be quickly and readily heated up and easily controlled. The furnace used in this work was a vertical furnace with an inside diameter of 2⅜ in. and a depth of 6 in. (see Fig. 11). The coil, which was of pure nickel wire about .072 in. in diameter, was first wound in one layer upon a collapsible wooden arbor. The wires were tied together by several longitudinal threads to keep them from springing out when the arbor was removed. A covering of paste, formed of water and a patent mixture, called "magnesite,"[2] was then applied. After the paste had dried, the coil was placed in a cylinder (also of a magnesite compound) 6¼ in. long and just large

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[1] (Holborn & Day), Amer. Jour. Science, Vol. 160, p. 171.

[2] Obtained from Harbison and Walker Refractories Company, Pittsburg.

enough to contain it. The outside diameter was about 4½ in. The arbor was then removed, leaving the coil on the inside of the furnace, which had also been coated with the magnesite paste. This in turn was placed upon a fire-clay disc and surrounded by a cylinder of the same material,[1] the whole being covered with another fire-clay disc, usually in two pieces. The outside dimensions of the whole were about 8 in. in diameter and 9½ in. in height. The space between the magnesite cylinder and the surrounding one of fire-clay was filled loosely with calcined magnesia.[2]

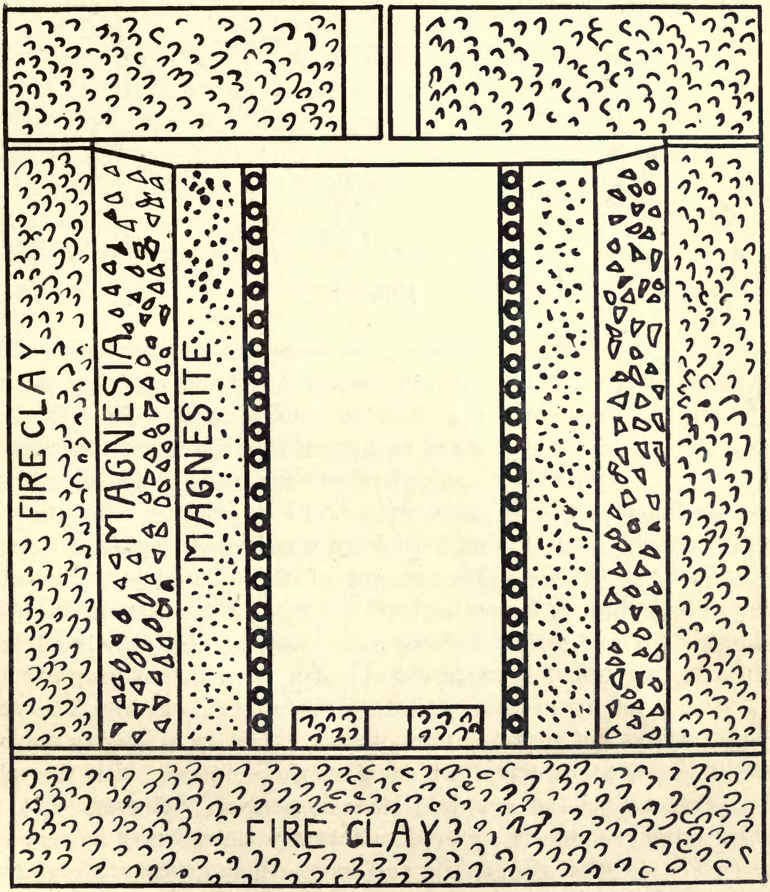

Fig. 11

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[1] Obtained from Dental Manufacturing Company, Buffalo, N. Y.

[2] Obtained from Eimer and Amend, New York City.

To avoid delay, in certain stages of the work, a furnace was used with a cylinder of magnesite instead of fire-clay. This was not so satisfactory, because more heat was lost through the magnesite than through the fire-clay; heavier currents were, therefore, required to maintain the necessary temperatures. With the furnace as described above, a temperature of 1000° C. could be obtained in less than two hours with a current of 25 amperes; and it could be maintained with 19 or 20 amperes.

Heating Circuit.—The arrangement of the heating circuit is shown in Fig. 12. The current was obtained from 110-volt continuous current mains and was regulated by two large Cutler-Hammer rheostats or "theatre dimmers." One of these had a current-carrying capacity of 125 to 50 amperes and a resistance of 4 ohms. The other was specially made and had a fixed resistance of 4 ohms, with 30 amperes carrying capacity, which could be short circuited, and also had a variable resistance of 6 ohms, with 30 to 10 amperes capacity. The low resistance rheostat permitted very small adjustments of current.

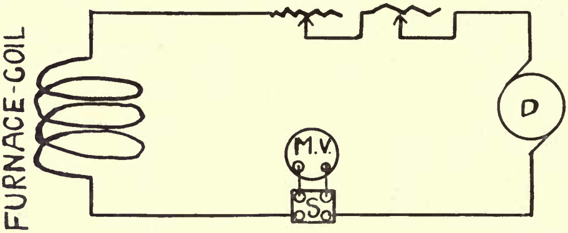

FIG. 12

Graphite Crucibles.—The charge of metal used was placed in graphite crucibles to a depth of at least 2 in. Fig. 13 shows the shape and size of these vessels. Such crucibles may be purchased from supply houses, but it is preferable to turn them out of graphite rods because the purity of the graphite rod is more certain.[1] The exact dimensions are not specified nor are they necessary so long as they will contain a charge of metal which is large compared with the silica tube surrounding the couple. It is important, however, that the inside of the crucible be tapered so that the charge may be removed. The covers are also of graphite and have a hole in the center for the insertion of the silica tube containing the thermocouple.

Thermocouples.—The thermocouples used in this work consisted

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[1] Acheson Graphite Co., Niagara Falls, N. Y.

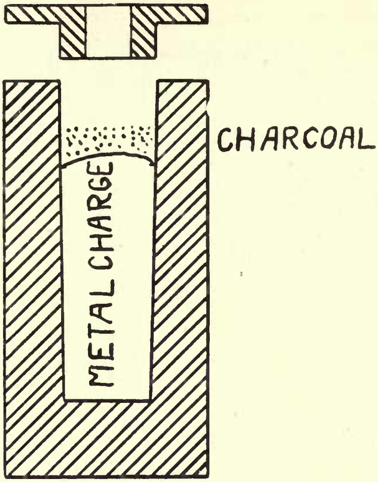

FIG. 13

of one wire of pure platinum and another of 90 per cent platinum and 10 per cent rhodium. The wires were each 0.6 mm. in diameter and 5 ft. long. The two wires were insulated from each other by pieces of very small porcelain tubing which were placed on the platinum-rhodium wire (see Fig. 14). The junction was then placed in a tube of fused silica, closed at the lower end. This tube, containing the wires and capillary porcelain tubing, was thrust into the melted metal to within about ⅝ in. from the bottom of the crucible.

The protecting tubes of fused silica [1] were about ¼ in. in diameter and long enough to extend well out of the furnace. They were supported by a tripod and clamp at the upper end. A broken tube may be readily closed at one end in an electric arc or an oxy-hydrogen flame. Silica tubes as small as 2 mm. inside diameter may be used for this work by dispensing with the porcelain tubing on the platinum-rhodium wire, and separating the wires with strips of mica. This arrangement has considerable advantage, enabling one to get a much better curve; a smaller charge of metal can also be used. It is, however, not advisable to use the smaller tubes where a number of couples are to be calibrated, and where time is of importance, as it is difficult to insert the wires in the tube and keep them separated.

Cold Junctions.—The other ends of the wires were soldered to copper wires and kept at 0° C. The arrangement of these junctions

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[1] Elmer and Amend, New York City.

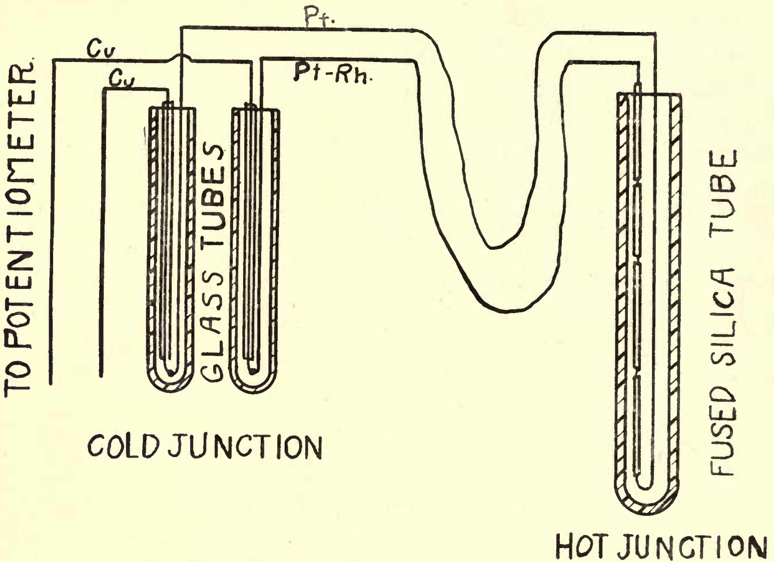

Fig. 14

(see Fig. 14), was similar to that of the hot junction except that glass tubing was used in the place of the quartz and porcelain. They were kept at the ice point by placing them through the lid of a double-walled bucket, which contained a mixture of ice and water. This bucket was packed with sawdust between the two walls.

Metals Used for Fixed Points.—The metals used for calibrating the couples were zinc in an oxidizing atmosphere, melting at 419° C.; silver in a reducing atmosphere, melting at 961.5° C.; and copper in a reducing atmosphere, melting at 1084° C. These values of their melting points are the ones found by Holborn and Day, 1900, and are at present accepted by the German Reichsanstalt. Later values found by Day and Clement are somewhat lower, being 418.5° ± .1; 958.3 ± .5; and 1081.0 ± .5 respectively.[1] The charges of silver and copper were covered with powdered charcoal which was of a very pure grade. This was done because the values given above for these two metals were obtained in a reducing atmosphere.

Other metals which may be used are cadmium, 322° C.; and gold 1063° C. The melting point of cadmium is somewhat low for a platinum-rhodium couple. Above 1100°, nickel melting at 1435°, iron melting at 1505°, and platinum melting at 1720°, may eventually

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[1] Amer. Jour. Science, Vol. XXVI, Nov., '08.

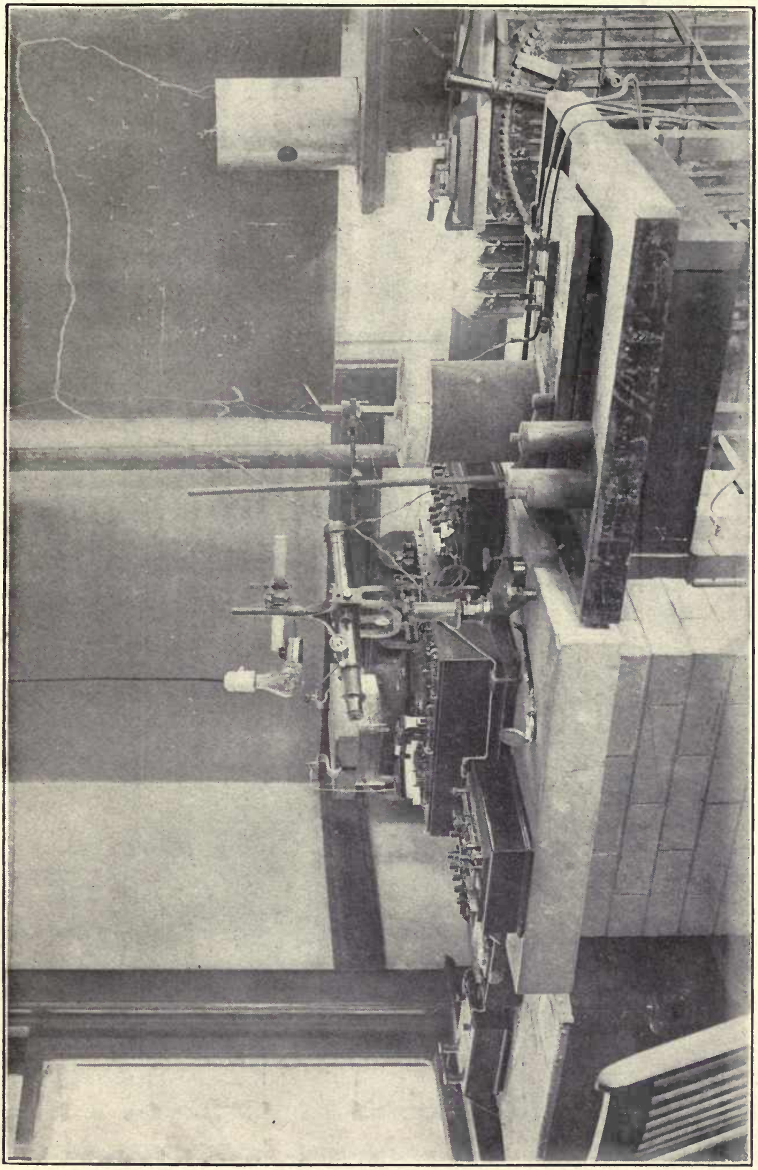

FIG. 15 SHOWING CALIBRATION FURNACE AND POTENTIOMETER

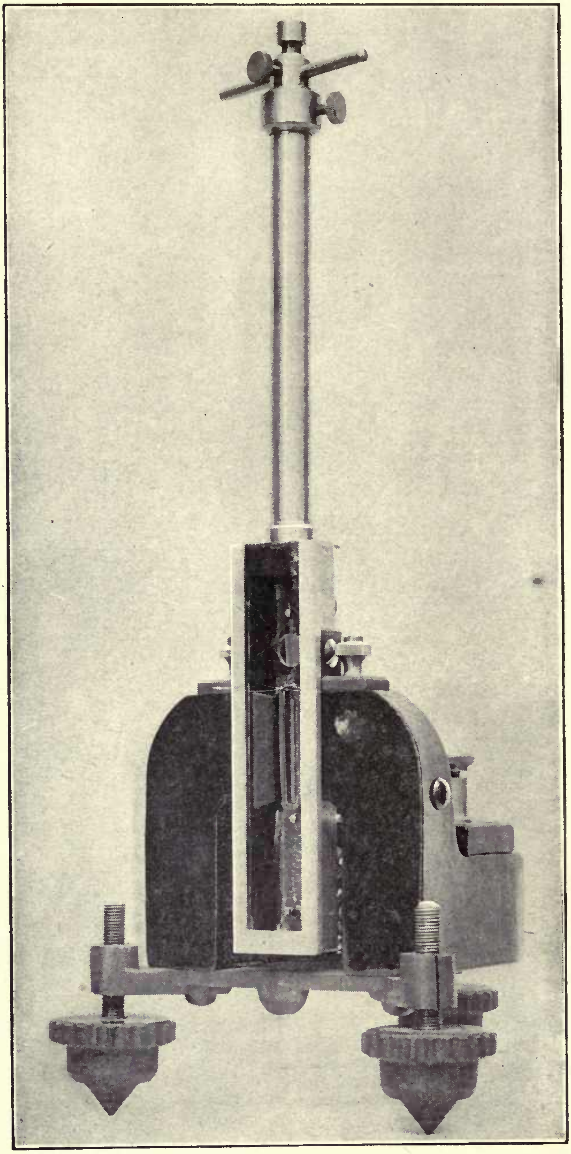

Fig. 16 Special Galvanometer Made for Use with Thermocouples

be available for fixed points, although it is not advisable to use any point above the copper point until the gas thermometer scale has been established above 1100°. A number of metals are unavailable for getting a fixed point on account of under-cooling.

It is of importance that the metals used for fixed points be of the highest purity, since any impurity alters the melting point.

Typical Set of Readings.—Below is given a typical set of readings taken with couple *F* (see p. 10), at the zinc melting point. The readings are in micro-volts or .000001 volt. The first column was taken with 8 amperes flowing through the furnace. After the zinc had solidified, the current was increased to 17.5 amperes, and as the zinc melted, the readings in column two were taken. The readings were taken regularly at intervals of 30 seconds.

8 Amperes		17.5 Amperes	
3461		3404	
3440		3412	
3431		3415	
3430		3418	
3429	Freezing Point 419° C.	3421	
3429		3423	
3429		3425	
3429		3426	
3429		3427	
3429		3428	
3429		3428	
3428		3429	Melting Point 419° C.
3428		3429	
3426		3435	
3420		3460	
3414		3490	
3400			

It may readily be seen from these curves that the transition points can be fixed better from the cooling curves than from the melting curves, because the bend of the curve is sharper and the flat part of the curve is better defined. Hence the cooling curve is the one used. It is much more definite and may be repeated, while the heating curve is often a little below the actual temperature, due to the lag in the charge and conduction of heat by the tubes.

Potentiometer and Galvanometer.—The electromotive force of the couples was measured with a Wolff potentiometer and galvanometer; a combination of the compensation and galvanometer methods being used (see Fig. 17). The Wolff box was connected in series with an adjustable resistance, R_1, of a little over 5000 ohms, and a single storage cell. As the resistance of the potentiometer was 15 000 ohms, the current could then be adjusted to exactly .0001 ampere. This was done by connecting a standard cell, (*Cd.*), of 1.0197 volts, across a resistance in the box of 10 197 ohms, and adjusting the series resistance, R_1, until the galvanometer, *G*, showed no deflection on closing the circuit. A reading of one ohm on the box then corresponded to .0001 volt or 100 micro-volts. As the smallest divisions of the box are 0.1 ohm, this gave a sensibility of 10 micro-volts, or about 1° C.

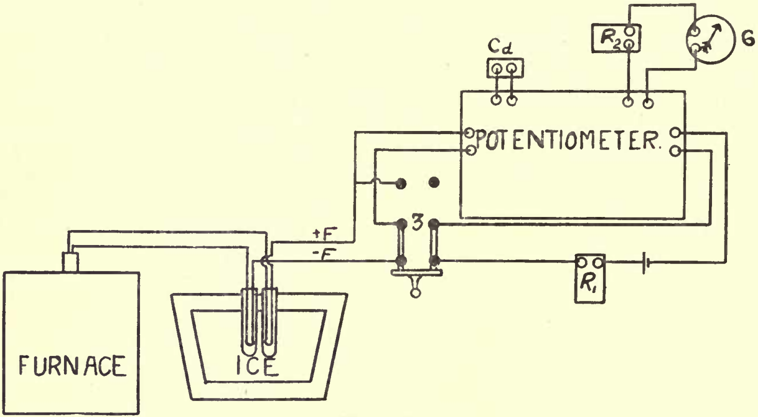

Fig. 17

The galvanometer[1] had a period of four seconds on open circuit and a sensibility of 2.85 micro-volts or 210 megohms. Its resistance was 230 ohms. It was used with a telescope and scale at a distance of about 150 centimeters.

A small resistance, R_2, was connected in series with the galvanometer, and this was adjusted so that the last dial on the Wolff box corresponded to a deflection of ten divisions of the scale. This increased the sensibility of the apparatus tenfold, as one scale division thus corresponded to 1 micro-volt or about 0.1° C. This adjustment was accomplished by first closing the battery circuit, setting the

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[1] D'Arsonval type made especially for this work by Leeds & Northrup Co.

potentiometer on zero, and short-circuiting the thermocouple circuit. Such a value of R_2 could then be found that a movement of one division of the next to the last dial on the box, would give a deflection of exactly one hundred scale divisions. Of course as the setting of the box is increased or diminished, R_2 would have to be decreased or increased a corresponding amount, to keep the sensibility constant.

Scale and Telescope.—The scale used with the galvanometer had divisions about 0.6 mm. in length. One half of the scale was marked with red and was numbered from 800 at the end to 1000 or 0 at the center. The other half was black and was numbered from 0 at the center to 200 at the other end. The galvanometer was so connected that deflections toward the black figures indicated an addition to the potentiometer reading, and those toward the red figures a subtraction from it. The advantage of having the red scale read backwards, that is from 1000 to 800, is that negative deflections are already subtracted when read. For example, a negative deflection of 15 divisions would read 985. This, besides being a great convenience, also reduces to a minimum the chance of error in subtracting the galvanometer reading from that of the potentiometer.

Telescope.—The telescope used was a Hartmann and Braun instrument with horizontal and vertical tangent screw adjustments. These adjustments are a great convenience, the horizontal adjustment for setting the scale to zero being almost a necessity.

Manipulation.—When readings were to be taken at regular intervals as in the above set, the current was first adjusted, as described above, by comparison of the potentiometer with the standard cell. The galvanometer was then short-circuited through the Wolff box by the "double-pole double-throw" switch shown in Fig. 17. In the position shown, this switch closes the main potentiometer circuit with the storage cell, with the right hand blade, and connects the thermocouple to the potentiometer with the left hand blade. The pole on the left was shortened so that the right side made contact first, thus closing the main circuit before the galvanometer circuit was closed. By reversing this switch, the battery circuit is opened and the galvanometer circuit closed through the potentiometer only. The galvanometer scale was set at zero before each reading with this switch in the reverse position. This eliminates errors due to stray electromotive forces which may be in the circuit. The switch is then again changed, and the dials on the box adjusted until the galvanometer is as near zero as is convenient. Care is then taken to get the reading on the scale at the exact end of the interval, and adding (or subtracting) this reading to that indicated on the box. It is readily seen that when using the galvanometer reading in addition to that of the potentiometer, it is more convenient to have a box that may be adjusted by steps, rather than by a continuous contact along the winding.

External Influences.—Great care had to be taken with this arrangement of apparatus to avoid magnetic disturbance and electric leakage from the power circuit. Little trouble was experienced in cold dry weather with electric leakage, but during the warm moist weather of summer, it sometimes seemed almost impossible to avoid leakage.[1]

Formula for Calculating Temperature.—The formula which was used for calculating the temperature is $t = a + be + ce^2$, e representing micro-volts. Substituting the values for t and e obtained from the zinc, silver and copper points, we have three equations as follows:

$$t_1 = a + be_1 + ce_1^2$$

$$t_2 = a + be_2 + ce_2^2$$

$$t_3 = a + be_3 + ce_3^2$$

The values of e_1, e_2 and e_3 obtained for couple F used in the thermal conductivity work (see p. 10), were 3429, 9101 and 10534, respectively. Solving the above equations for a, b, and c, and substituting for t_1, t_2, t_3, e_1, e_2, and e_3,

$$a = 46.41$$

$$b = .11356$$

$$\text{and} \quad c = -1.4300 \times 10^{-6}$$

The temperatures measured by this couple are found by the equation

$$t = 46.41 + .11356\, e - .00000143\, e^2.$$

This parabolic equation is the one generally accepted at the present time for the platinum alloy couples when the cold junction is at 0°, although it will not hold below 250° C., and can be used only approximately below 350° C. If the cold junction is above the ice point, a correction must be added to the observed temperature, equal to 0.5 times the temperature of the cold junction in Centigrade degrees.

$t = t$ (obs) $+ 0.5 \times$ *temperature of cold junction.* The possible accuracy of the above equation is about 0.5° C., between 350° and 1100° C. The probable accuracy of the temperatures as measured

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[1] Discussion by W. P. White, Physical Review, 1907.

above is about 1° over the same range, though the sensibility is 0.1° C.

Other equations have been offered by Regnault, Avenarius and Tait, Stansfield, and others, but are not used at the present time. References [1] on thermal electricity are given below.

Galvanometer Method.—For work which does not require such a high degree of accuracy, it is more convenient to use a galvanometer alone for reading the electromotive force. With a galvanometer of about 400 ohms resistance, by taking proper precautions, the readings are reliable within 5° C. up to 1100° C.

Lower Temperatures.—For temperatures below 400°, a copper-constantan couple will be more satisfactory, as it has about four times the thermo-electric power of the platinum-rhodium couple. It may be used from 0° to 500°.

Contamination.—Great care must be taken to avoid contamination of the platinum couples, as they are very readily attacked by metal vapors at the higher temperatures. The readings of the couple will be lowered by contamination. The couple can be restored only by removing the contaminated portion. With care, however, contamination may be avoided and the readings of the couple kept constant. The two couples used in the conductivity work described on p. 10 did not change within the sensibility of the measurements during four months of almost continuous use.

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[1] A Text-Book of Physics (Watson), p. 714.
High Temperature Measurements (Le Chatelier), p. 120.
A. Stansfield on Some Improvements in the Roberts-Austin Recording Pyrometer, Phil. Mag. July, 1898, p. 73.
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