

# NEW METHOD FOR MEASURING RESISTIVITY OF MOLTEN MATERIALS: RESULTS FOR CERTAIN ALLOYS.\*

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THE first-named writer began an experimental investigation of the electrical conductivity of molten metals and alloys in 1911. The electrical conduction at high temperature of all forms of matter was later considered. The results of these investigations have been described in a series of papers,<sup>1</sup> of which five, relating to metallic conduction, have appeared in the JOURNAL OF THE FRANKLIN INSTITUTE.

To obtain accurate data from which curves may be drawn that give the relation between resistivity and temperature over a wide range of temperatures, it was found necessary to devise entirely new methods of producing the required temperature and, also, entirely new methods for measuring the resistivities of materials when in the molten state. Several different methods were developed and used in measuring the resistivities of metals and alloys.

In the paper by E. F. Northrup on the "Resistivity of Copper in Temperature Range 20° C. to 1450° C." <sup>2</sup> the best method which had been devised prior to the date of its publication was

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\* Communicated by E. F. Northrup.

The method here described is the general method devised by E. F. Northrup, modified in some of its details by R. G. Sherwood, and used by the latter for obtaining the results and all data for curves appearing in this article. E. F. N.

<sup>1</sup> *Trans. of the Amer. Electrochem. Soc.*, vol. xx, 1911; also xxv, 1914. *Metallurgical and Chemical Engineering*, June, 1912; May, 1913; Jan., 1914; Feb., 1914; March, 1914; May, 1914; March, 1915. JOURNAL OF THE FRANKLIN INSTITUTE, Feb., 1913; Jan., 1914; March, 1914; July, 1914; March, 1915; and "High Temperature Investigation and a Study of Metallic Conduction." June, 1915.

<sup>2</sup> *Journal of The Franklin Institute*, Jan., 1914.

fully described. Since that time experiments have been conducted by both writers of the present article with the view of making further improvements in the methods of measurement and of collecting additional data. Thus the method, which we describe here in full, has been reached, as it were, by a process of evolution and is, we believe, sufficiently perfected to meet every requirement of simplicity, speed, and precision. It is entirely a direct-reading and zero-method which yields all results without any calculation whatever. We shall state, therefore, rather categorically, that the details which have been shown by our experience should be observed both in the set-up of the apparatus and in the procedure to follow in taking observations. We do this because nearly every possible modification of apparatus, circuits, and manner of taking readings has been considered, and because we have been led to adopt, for one reason or another, what we here describe as being that which, all things considered, best meets requirements.

#### COOLING CURVES AND RESISTIVITY CURVES.

Importance has long been attached to a study of certain physical characteristics of the metals and alloys by tracing their heating and cooling curves, especially through changes in state. Melting- and freezing-point determinations are made in this way, and data for equilibrium diagrams have been taken largely from such curves. As will appear, however, from what follows, the same and additional information may be obtained, with nearly equal facility and with greater exactness, by tracing, not the progress of cooling of an element, alloy, or compound but the change in resistivity of the material with change in the temperature when this is slowly raised or lowered. The methods which have been perfected for measuring the resistivity of molten materials have enabled us in certain cases to measure simultaneously the resistivities of two metals, under identical temperature conditions, to a temperature as high as  $1680^{\circ}$  C. When, however, the temperature much exceeds  $1000^{\circ}$  C. difficulties are encountered from the formation of new chemical equilibria and the contamination of the sample being measured. Below this temperature difficulties of this character do not arise to any serious extent, and, as will appear later on, it is quite as simple to measure with high precision the resistivity of a molten metal or alloy at a temperature near  $1000^{\circ}$  C. as it is to measure the same property of mercury at room tempera-

tures. Furthermore, below  $1000^{\circ}$  C., resistivity curves can be traced with nearly the same facility as cooling curves, and they may be carried through changes of phase to low temperatures where the materials are solid.

It seems to us quite certain that data on electrical resistance or electrical resistivity of a metal, and more especially of an alloy in the solid, solid-liquid, and liquid phases, will yield new and valuable information which cannot be obtained from cooling curves or from any of the other methods now employed to study the physical characteristics of alloys.

Following the description of methods of measurement are given some results, obtained by the methods described, for alloys of tin and bismuth.

#### REQUIREMENTS TO BE MET.

If measurements of resistivity are to be carried higher than  $1100^{\circ}$  or  $1200^{\circ}$  C., a wire-wound furnace is unsuitable, and it becomes necessary to employ the type of furnace<sup>3</sup> which was developed by the first-named writer for this particular class of work. When, however, a study of the alloys is under consideration it is generally unnecessary and it is often impossible (on account of vaporization of a metal) to take observations above a temperature of  $1000^{\circ}$  C. In this case a vertical-type furnace, made by winding an alundum tube with nichrome wire or ribbon, meets every requirement. In what follows we shall confine ourselves to a consideration of measurements of resistivities which can be made in a furnace of this type.

It is necessary to measure the temperature with precision. This can be done with either a resistance-thermometer or with a thermocouple and, also, by a certain special method which will be briefly considered later. We have found a properly constructed thermocouple (its cold junction being held at  $0^{\circ}$  C. in a Dewar flask filled with cracked ice), which when read with the aid of a Leeds & Northrup potentiometer, fills every requirement of precision. A thermocouple, furthermore, gives the desired temperature-readings in the simplest and most direct manner, and, furthermore, its calibration is effected with greater ease than the calibration of other devices by checking it against the freezing-points of certain metals.

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<sup>3</sup> "A New High Temperature Furnace," by E. F. Northrup, *Metallurgical and Chemical Engineering*, Jan., 1914.

To obtain the value of the resistivity of a molten material, it is very desirable to employ a device which will give this result by direct insertion of the device into a considerable mass of the molten material, contained in a crucible. We have named the instrument devised for this purpose a "resistometer." Its use has many advantages over the earlier devices and methods employed. Previous to the development of the resistometer a small quantity of the molten material was confined in a specially shaped form moulded from refractory material.<sup>4</sup> There are some objections to these earlier methods; for when a small quantity of molten material is confined in a large mass of refractory material the likelihood of contamination of the molten material by contact with its container is considerable, and moulded forms require considerable skill and labor to construct. The resistometer, on the other hand, with its small mass, when inserted in a large mass of molten material, is little to contaminate it.

The desirability of making the readings of resistivity directly in microhms per cm.<sup>3</sup> and by means of a null-method requires the use of a Kelvin double-bridge, which is the best type of low resistance-reading device employed with a null-method.

Alternating current must be used for the measuring current. Our experience has demonstrated that where potential terminals come in contact with a molten metal or alloy a not inconsiderable electromotive force is always developed, and that it rapidly increases in magnitude and irregularity as the temperature increases. Above 500° C. these electromotive forces become so large and erratic that it is exceedingly difficult, and at times impossible, to make accurate measurements, if direct current is used as the measuring current. By substituting alternating current all difficulties arising from parasitic electromotive forces and currents vanish.

An alternating-current galvanometer, or other detector of balance of the bridge, which will be responsive to alternating current only and comparable in sensibility to a good D'Arsonval galvanometer, is required when the measuring current is alternating. An alternating-current galvanometer which possesses new features and fills every requirement was designed especially for this work.

In measuring the resistance of molten materials, connections

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<sup>4</sup>"Resistivity of Copper, etc.," JOURNAL OF THE FRANKLIN INSTITUTE, Jan. 1914, see p. 7.

or electrodes must be used which shall serve both for current and potential terminals. Tungsten wire, and in many cases molybdenum wire, has proved entirely satisfactory for this purpose at the temperatures used, because neither tungsten nor molybdenum fuses or appreciably alloys with any molten metal not belonging to the iron group.

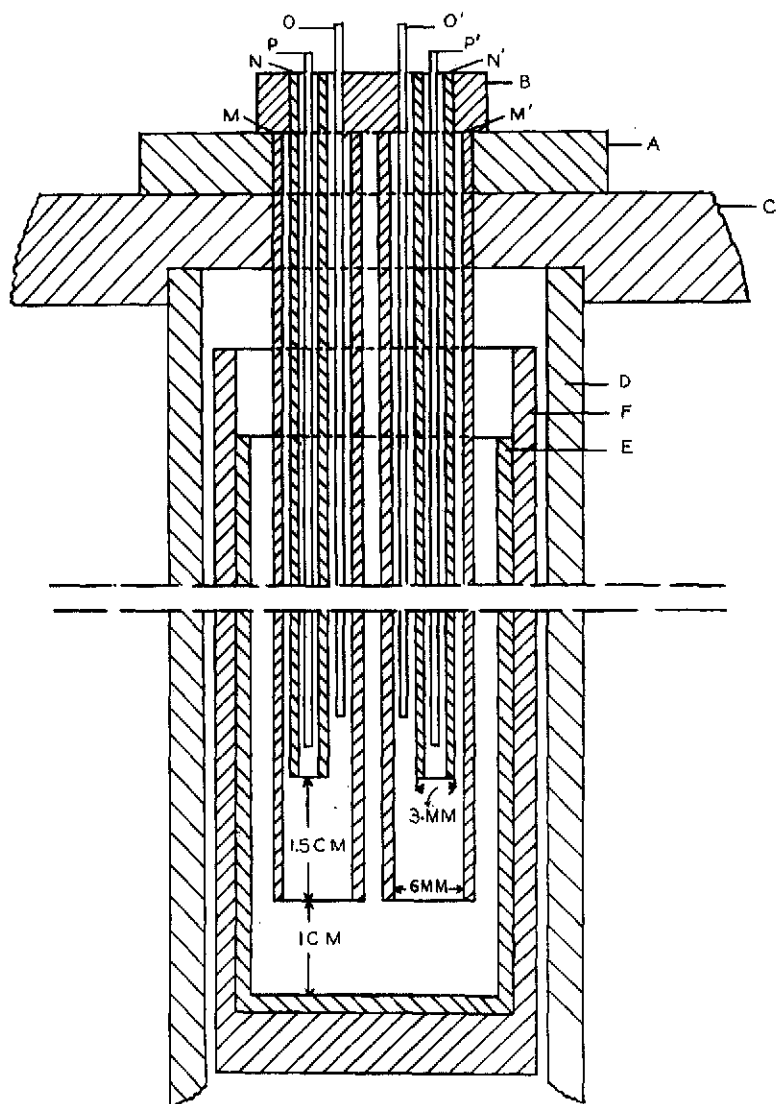
To obtain the results directly in microhms per cm.<sup>3</sup> it is necessary to so design the resistometer that its constant may be obtained readily. This is accomplished by inserting it in pure mercury, which serves as a standard of resistivity. When the constant of the resistometer has been obtained thus, the values of the bridge ratio-coils may be then so chosen that the bridge-readings, when multiplied by a power of ten, are in microhms per cm.<sup>3</sup>. For this reason the ratio-values of two ratio-arms should be adjustable. We proceed to describe in detail the apparatus, and the methods of using it, which have been found to meet the above requirements in all respects.

#### THE RESISTOMETER TYPE 1.

(See Fig. 1.)

Two quartz tubes or Marquardt porcelain tubes  $MM'$ , having about a 6 mm. bore, are firmly cemented into a small square block of Alberene stone  $A$ . A unit is thereby formed which permits the tubes to be lowered into a bath of molten material contained in an alundum crucible  $E$ . A second pair of tubes  $NN'$  of the same material as  $MM'$ , having an outside diameter of about 3 mm., are also firmly cemented in a small square block of Alberene stone  $B$ , thus forming a second unit. When the latter tubes are in position they are concentric with the tubes  $MM'$ , as shown in the figure. We shall call the  $MM'$  *current-tubes* and the tubes  $NN'$  *potential-tubes*. The lower ends of the current-tubes when in position reach to about 1 cm. or more from the bottom of the crucible  $E$ . The potential-tubes are of such length that when in position their lower ends are about 1.5 cm. above the ends of the current-tubes. Two tungsten wires,  $PP'$ , about 1 mm. in diameter, are inserted in the potential-tubes and extend to 1 or 2 mm. from the ends of these tubes. Two other tungsten wires,  $OO'$ , preferably of a little larger diameter, are inserted in the current-tubes and lie alongside the potential-tubes. The lower ends of these wires should be 0.5 cm. or more above the ends of the potential-tubes. These latter

FIG. 1.



wires constitute the current-leads and the former the potential-leads.

The sample contained in the crucible *E* should be sufficient in quantity to reach a little above the lower ends of the current-

terminals. Molybdenum may in many cases be substituted for tungsten for the current- and potential-leads. Tungsten is, however, to be preferred if the temperature is to be carried very high. In one experiment a No. 20 tungsten wire and a No. 20 molybdenum wire were placed in molten tin held at  $1200^{\circ}$  C. for about fourteen hours. The molybdenum wire had dissolved to an extent that reduced it in size to No. 23 B. and S., while the tungsten wire had not perceptibly changed in diameter. Little action is to be expected on either tungsten or molybdenum immersed in any metal or alloy which is molten and under  $1000^{\circ}$  C.

As shown in Fig. 1, the crucible *E* is placed in a container, *F*, made of Acheson graphite. The main object in using the graphite container is to obtain a reducing atmosphere in the furnace, and incidentally, also, to more uniformly distribute the heat about the crucible *E*. When the chamber of the furnace is filled with a reducing atmosphere the surface of metals which readily oxidize in an oxidizing atmosphere is maintained free from oxide and bright. It is specially important to maintain a reducing atmosphere when working with copper, as this metal dissolves the oxide which forms on its surface and so changes in specific resistance.

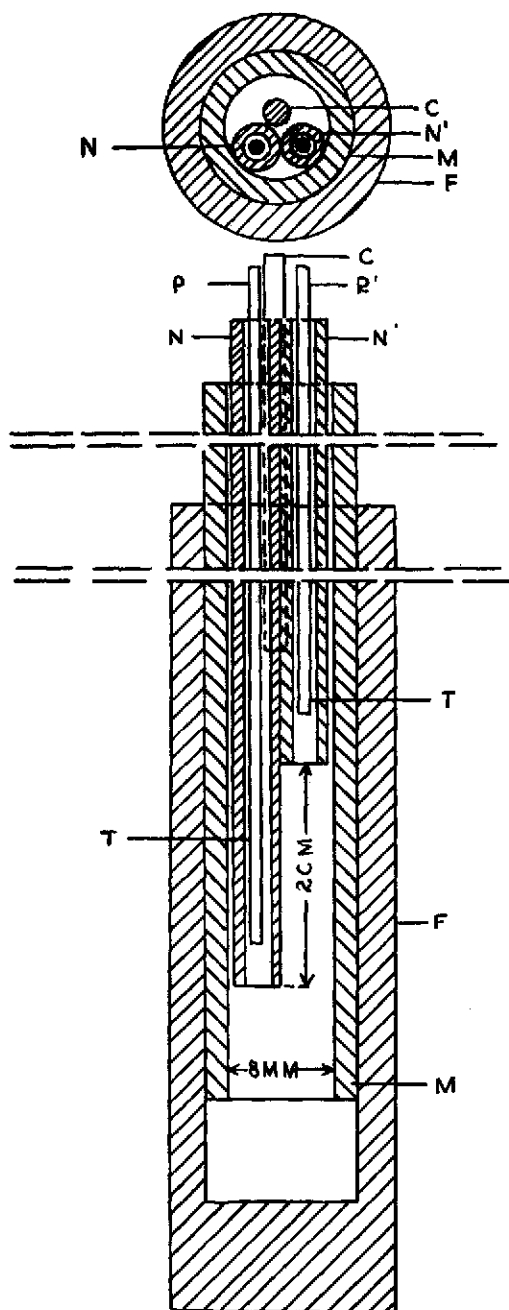
The heater-unit consists of an alundum tube *D* wound with nichrome wire or ribbon. This wire or ribbon winding may with advantage be covered over with alundum cement or "Vulcan paste," which helps to hold the winding securely in position on the alundum cylinder on which it is wound. The alundum cylinder is firmly cemented in a heavy slab, *C*, of Alberene stone. This slab, which may be round or square, also forms the top of any metal or other gas-tight vessel chosen to contain the heater-unit. When working at temperatures under about  $500^{\circ}$  C. it is convenient to have only air insulation around the heater-unit in order to secure rapid cooling when the current is turned off. When slow cooling is desired this is readily secured by maintaining a reduced heating current, adjusted with a control resistance, through the heater-unit.

#### THE RESISTOMETER TYPE 2

(See Fig. 2)

In many cases and for certain kinds of work it is desirable to construct the resistometer in another form, employing, however, the same principle as that used in type 1, and using it in the same circuits and in the same manner when measurements of resistivity

FIG. 2.





are made. In this form a single tube,  $M$ , only is used, which has approximately the same dimensions and is made of the same material as either one of the tubes of type 1.

Two potential-tubes,  $NN'$ , firmly cemented together with Vulcan paste, are arranged so that they will readily enter this outside single tube. One of these potential-tubes is longer than the other by 1.5 cm. to 2 cm. When the potential-tubes are in position the lower end of the longer one may reach within a few millimetres from the bottom of the outside tube,  $M$ , which we designate the *current-tube*. This latter is inserted in a tube,  $F$ , of Acheson graphite closed at the bottom. The current-tube may reach a short distance from, or quite to, the closed bottom of the graphite-tube  $F$ . The sample the resistivity of which is to be measured is poured while molten into the graphite-tube and the current-tube is then inserted, the molten material filling the interior of the current-tube to a level chosen a short distance above the lower end of the shorter potential-tube  $N'$ .

One current-lead  $C$  of tungsten or molybdenum is placed alongside the potential-tubes, its lower end being maintained a little above the lower end of the shorter potential-tube. The graphite-tube or casing forms the second current-lead.

When current is passed through the resistometer there is a drop in potential between the lower end of the shorter and the lower end of the longer potential-tube. There is inserted in each of the potential-tubes a tungsten wire,  $T$ , which reaches to within a millimetre or two from the lower end of each of these tubes. These potential-leads serve as a means for measuring this potential drop. If the two potential-tubes are firmly cemented together, then the distance between their ends,—that is, the distance between potential-points,—is fixed, and if the two potential-tubes occupy the same position in the current-tube at the time the constant of the resistometer is obtained by measuring its resistance when filled with pure mercury as when measuring its resistance when filled with the molten metal, the resistivity of this latter is to the resistivity of pure mercury as the measured resistance of the latter is to the measured resistance of the mercury. In other words, the cross-section and length of the fluid-column of which the resistance is measured is invariant, because the very slight expansion with temperature of the Marquardt porcelain or quartz of which the current- and potential-tubes are made is quite negligible.

If the lower potential-terminal ends 3 or 4 mm. above the end of the current-tube it is immaterial whether the current-tube reaches to the bottom of the graphite casing or not. All parts of this type of resistometer, current-tube, potential-tubes, tungsten wire potential-leads, and current-lead should be arranged so as to be readily assembled and taken apart because, after the resistometer has been filled with pure mercury for obtaining its constant, it must be freed from the last traces of mercury, which tend to cling to the potential-tubes, before filling it with molten metal or alloy.

The advantages of this single-tube type of resistometer consist largely in its simplicity and compactness and in the fact that it is better adapted than the former type to the measurement of the resistivity of a precious metal or an alloy of precious metals, where, for reason of cost, it is desirable to use small quantities of metal. Again, this type of resistometer when filled with pure molten tin can be used as a pyrometer which will measure temperatures up to  $1600^{\circ}$  or  $1700^{\circ}$  C. As has already been shown by the first writer in a previous paper,<sup>5</sup> tin increases linearly in resistance from its melting-point ( $232^{\circ}$  C.) to at least  $1680^{\circ}$  C., and hence can be used in a resistometer as a pyrometric substance. A measurement of the resistance of the tin contained in the resistometer need only be made at two known temperatures to obtain the calibration of the resistometer, used as a pyrometer up to a temperature of at least  $1680^{\circ}$  C.

On the other hand, this second type of resistometer is less desirable than the first when one has in view the tracing of the resistivity curves of base metals or their alloys. The first type can be made more robust and is more easily cleaned, as it must be when used with different samples, and the vertical distance of the liquid column the resistance of which is measured can be made less than in the second type, a circumstance which insures greater uniformity of temperature in the mass of metal being measured.

In either type of resistometer it is important that the thermocouple should have its hot junction in as close proximity as possible to the column or columns of molten metal contained between the potential-points when the resistance is being measured. In using resistometer type 1, the thermocouple can be immersed with

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<sup>5</sup> JOURNAL OF THE FRANKLIN INSTITUTE, June, 1915, p. 625.

the resistometer in the same bath of molten material, and by placing it alongside of and between the two current-tubes the temperature of the columns of material being measured is given with great exactness. When resistometer type 2 is used, it is desirable to submerge the graphite-casing of this, and the thermocouple in close contact with it, in a bath of molten tin. By so doing the temperature will be sensibly the same at the end of the thermocouple and in the interior of the resistometer. We recommend for most classes of work type 1 in preference to type 2.

#### ALTERNATING-CURRENT GALVANOMETER.

As previously stated the large electromotive forces of a parasitic character which are developed in the resistometer, when this is immersed in a molten metal or alloy, preclude the use of direct current for the measuring current and, therefore, a direct-current galvanometer. We have worked with both 60-cycle and 25-cycle alternating current. The latter is to be preferred, as it is then of less importance, when high precision is required, that the ratio-coils in the Kelvin double-bridge should be free from capacity or inductance. The alternating-current galvanometer which has been designed, two of which were constructed for this work in the shop of the Palmer Physical Laboratory, has proved a very great success and completely fulfils the following requirements for a satisfactory instrument:

The sensibility of the instrument should be fully equal to the sensibility of a good D'Arsonval galvanometer of the type of a Leeds & Northrup "High Sensibility Narrow-coil Galvanometer," known as catalogue No. 2294 and described in the Leeds & Northrup catalogue No. 20. In fact, it was aimed to give the alternating-current galvanometer the same characteristics in performance as this direct-current instrument. The sensibility, however, of the alternating-current galvanometer is not a constant quantity as with a direct-current instrument, but may be varied to any degree within wide limits by simply changing the value of the alternating-current passed through its magnetizing coils. As the damping of the system varies with the square of the field-strength, this latter is chosen of such value, by adjusting the current through the magnetizing coils, that the system after deflection returns aperiodically to zero with the particular resistance in circuit with the swinging coil which is in use. With an adjustment of field-

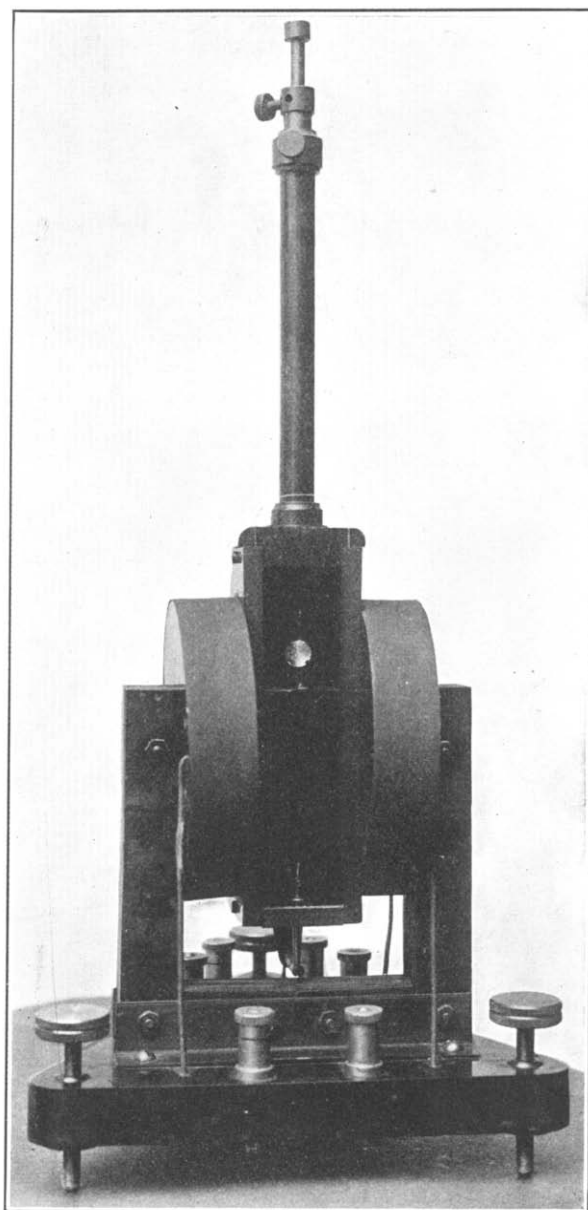
strength made thus, the sensibility of the galvanometer should equal that of the direct-current instrument referred to. The aperiodic time of swing of the galvanometer should not exceed two or three seconds, and this requirement makes it necessary to use a narrow, light coil for the swinging system. In fact, the swinging system used was identical with that used in the Leeds & Northrup galvanometer just referred to.

When the alternating-current galvanometer is in use the swinging system is necessarily on closed circuit, and, as this latter hangs in a field in which the magnetic flux is alternating, currents are induced in the swinging-coil circuit. It is essential that these induced currents should not cause the system to seek a position of stable equilibrium other than that at which it comes to rest when no currents are flowing. This requirement has been fully met by the special shape which has been given the pole-pieces of the laminated galvanometer-magnet. It has never been found necessary to make any phase adjustments of any of the currents.

The magnetizing coils, two in number, may be joined in series or parallel combination. They are always connected *in series* with the main circuit of the Kelvin double-bridge, and hence must be able to carry without heating and without too strongly magnetizing the magnet, a current which is at least as large as the current passed through the bridge. It is inadvisable to cut down the current through the magnetizing coils, which are highly inductive, by means of a shunt. The bridge, however, being non-inductive, may be shunted to any extent. Hence it follows that the current through the magnetizing coils required to energize the field-magnet may be chosen much larger than, but never less than, the current which is passed through the bridge.

The general appearance of the galvanometer is given in Fig. 3, reproduced from a photograph, while Fig. 4 shows a few details of construction. In referring to Fig. 4 it will be noted that the fixed iron core-piece between the pole-faces, which is generally used with direct-current instruments, is omitted. The pole-faces are hollowed out so that the coil swings in a hollow cylinder. This construction is used for the reason that when the coil is on short circuit it will tend to set itself in the weakest part of the field. The shape which has been given the pole-pieces makes the position of stable equilibrium for the system that which corresponds to zero reading on the scale.

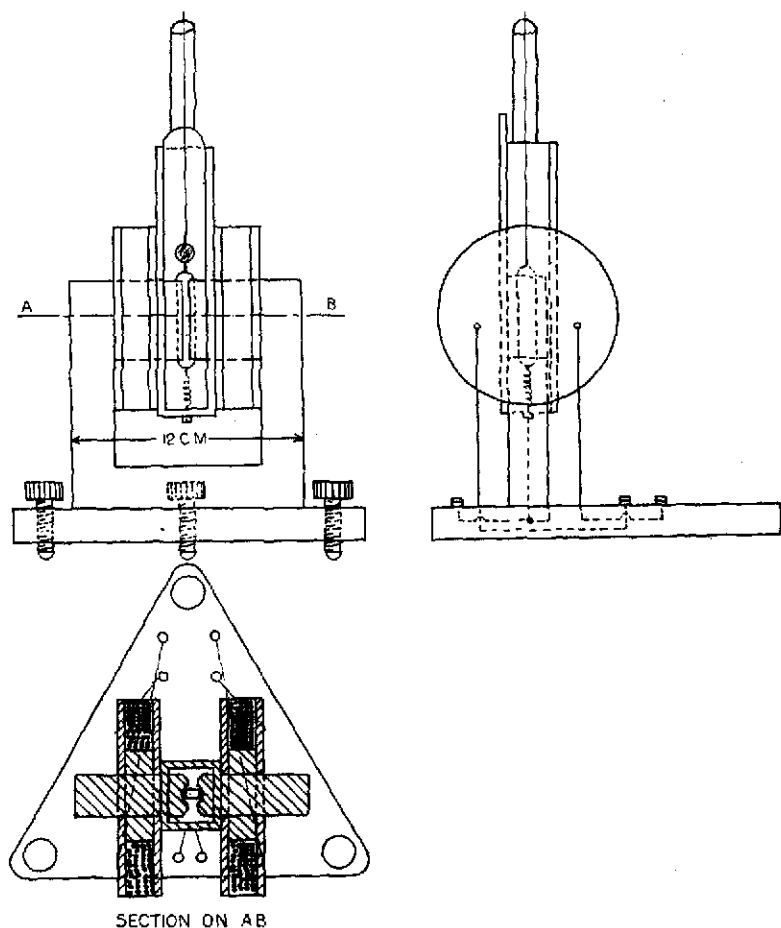
FIG. 3.



Alternating Current Galvanometer

The system hangs in a box of hard rubber with a glass front which exposes it to view. All metal parts in the neighborhood of the system are avoided to prevent the formation of eddy currents.

FIG. 4.



When adjustments are properly made the performance of this instrument with current of 25 cycles or 60 cycles is in all respects like that of a quick-acting, aperiodic, highly-sensitive direct-current instrument.

## THE KELVIN DOUBLE-BRIDGE.

It is very much more convenient for work of this class to employ a type of Kelvin double-bridge in which a balance is obtained by varying the position of the potential-points on a low-resistance standard than one in which a balance is obtained by varying the ratio-coils and using a fixed low-resistance standard. The type of variable low-resistance standard used in all our work is the one made by Leeds & Northrup known as catalogue No. 4300 and described in catalogue No. 40, p. 7 *et seq.*\* The variable ratios were obtained with an Otto Wolff box, designed for use with low-resistance fixed standards for measuring low resistances. The fixed ratio-coils were obtained with single-resistance units.

## CIRCUIT-CONNECTIONS, USING RESISTOMETER TYPE 1 AND A THERMOCOUPLE.

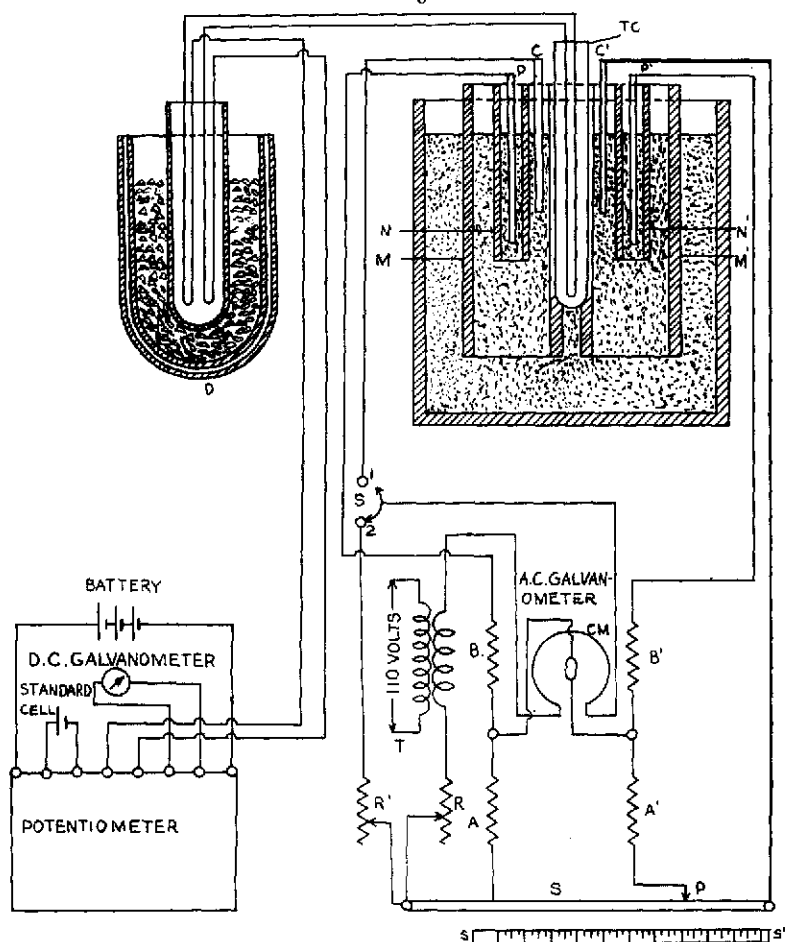
(See Fig. 5.)

The electrical circuits employed and the manner of including the resistometer type 1 in these circuits are shown diagrammatically in Fig. 5. The resistometer itself is shown with its lateral dimensions greatly exaggerated for the sake of clearness. The source of current is the secondary of a step-down transformer  $T$ .  $S$  is a switch which when in position 2 cuts the resistometer and Kelvin double-bridge out of circuit and puts the magnetizing coils,  $CM$ , of the galvanometer in circuit with the transformer-secondary and the two resistances,  $R'$  and  $R$ . When the switch  $S$  is in position 1 the resistance  $R'$  is cut out of circuit and the resistometer and Kelvin double-bridge are thrown into circuit with the source of current. The switch  $S$  is so constructed that neither contact 1 or 2 is broken before the other is made. This is necessary to prevent a sudden small deflection of the galvanometer which would result if the current through its magnetizing coils were momentarily stopped. The resistance  $R'$  is given such a value that the total resistance in circuit with the secondary of the transformer is the same whether the switch  $S$  is in position 1 or in position 2. The object in being able by means of the switch  $S$  to throw the bridge and resistometer out of circuit is, that by so doing the zero position of the galvanometer may be located. Re-

\* For full treatment of the theory and use of the Kelvin double-bridge, see Northrup, "Methods of Measuring Electrical Resistance," McGraw-Hill Book Co., 1912. *Arts.*, 609-612.

distances  $A$  and  $A'$  are fixed ratio-coils, generally chosen 1000 ohms each. Resistances  $B$  and  $B'$  are ratio-coils which can be varied. They are chosen of such a value that the settings of the slider  $P$ , as read on the scales  $S, S'$  shall indicate the resistivity of

FIG. 5.



the sample, when multiplied by some power of ten, in microhms per  $\text{cm}^{-3}$ . In our work we used the set of Otto Wolff ratio-coils above referred to for obtaining the required resistance values of  $B$  and  $B'$ . The method of finding the proper values for  $B$  and  $B'$ , to make the bridge read directly resistivity in microhms will be explained later.



The thermocouple,  $TC$ , is located in the bath of molten material so that its hot junction is midway between the bottom ends of the two potential-tubes,  $N N'$  and the two current-tubes  $M M'$ . Its cold junction is located in the Dewar flask  $D$ , filled with cracked ice, and the terminals of copper wire which lead from the cold junction are joined to the potentiometer as shown in Fig. 5. Our work was all done with a Leeds & Northrup potentiometer, catalogue No. 7551, described in catalogue No. 70.

#### CIRCUIT-CONNECTIONS, USING RESISTOMETER TYPE 2 AND A TIN-PYROMETER.

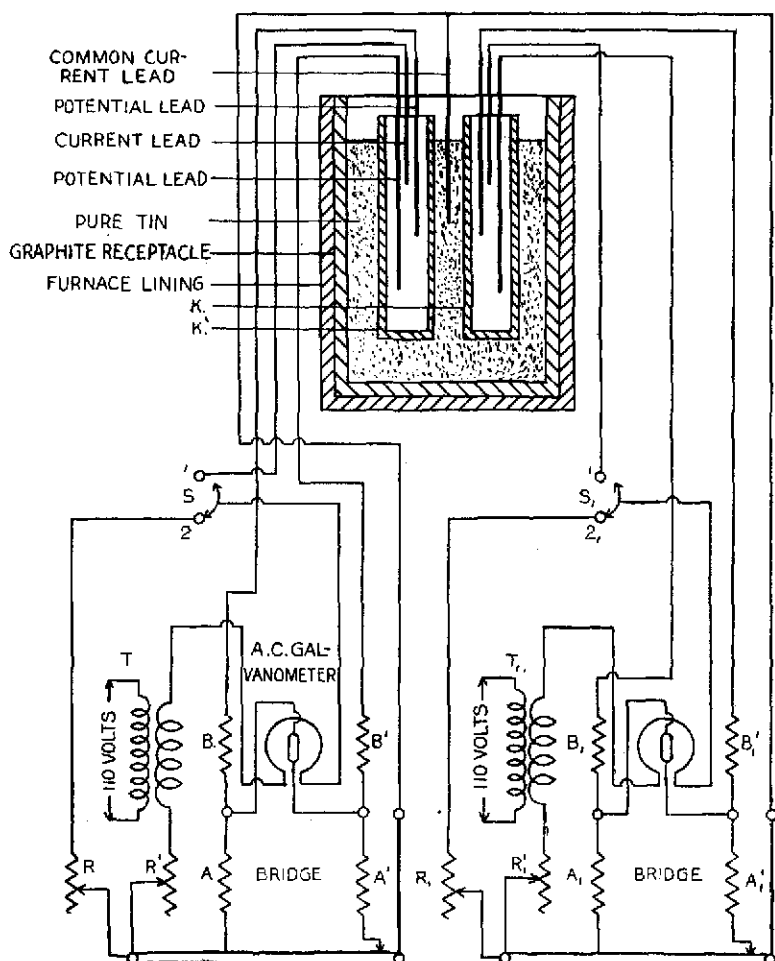
When using resistometer, type 2, it is convenient, if one is supplied with two alternating-current galvanometers and two Kelvin double-bridges, to also measure the temperature with a resistometer, type 2, filled with pure tin. In this case the two resistometers, one of which becomes a pyrometer, are both inserted in a bath of molten tin, as indicated at  $K$  and  $K'$ , Fig. 6. It is possible to so choose the resistances of the Kelvin double-bridge, used with the resistometer filled with pure tin and now called a pyrometer, that the bridge-readings are directly in degrees C., and also to so choose the values of the ratio-coils connected to the resistometer used for determining resistivity that bridge-readings in this case are in microhms per cm.<sup>3</sup> We shall omit explaining these adjustments in detail, but give the circuit connections in Fig. 6.

An extremely important line of high-temperature investigation is an inquiry into the linear increase in resistance of pure metals when carried to a very high temperature. By simultaneously tracing the increase in resistance of two different metals when subjected to identical temperature-conditions, it is possible to ascertain, by studying different pairs of metals taken in different combinations, whether or not they all increase in resistance linearly. The method and connections shown in Fig. 6 are well adapted to this study. By a somewhat similar arrangement the first-named writer has investigated the pair of metals tin and copper<sup>6</sup> and has found that both these metals when in the molten state increase linearly in resistance to at least 1680° C. The second-named writer made this comparison also between the metals lead and tin by using the apparatus and method shown in Fig. 6 and found,

<sup>6</sup> JOURNAL OF THE FRANKLIN INSTITUTE, JUNE, 1915, p. 635.

likewise, that both tin and lead increased linearly in resistance when molten up to about  $1575^{\circ}\text{C}$ . We believe that the method devised, as shown in Fig. 6, is most convenient for direct comparison to a very high temperature of the rate of increase in resistance

FIG. 6.

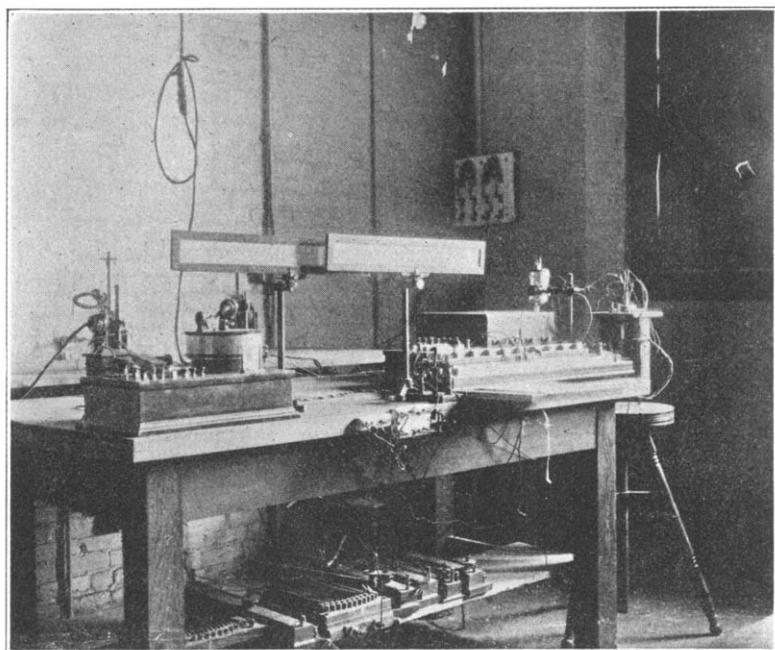


of two molten metals or alloys. If this comparison were to be made of various pairs of metals chosen in different combinations it would firmly establish an extension, to a high temperature, of the temperature-scale on a basis new and quite as reproducible as the gas-scale.

## CALIBRATION OF RESISTOMETER; ADJUSTMENT OF RATIOS.

The theory of the method of adjusting the ratio-coils in a Kelvin double-bridge so that the readings on the variable low-resistance standard when multiplied by a power of ten will be in microhms per cm.<sup>3</sup> has been given by the first-named writer in a former paper.<sup>7</sup> The calibration of the resistometer and the adjustment of the ratio-coils, however, may be determined experi-

FIG. 7.



Assembled apparatus used in measurements

mentally and simultaneously without any calculation, in the simplest manner possible, as follows:

A container of the same dimensions as the one destined to contain the sample is filled with pure mercury. The resistometer is placed in this mercury, the temperature of which is accurately taken with a mercury thermometer. The two ratio-coils  $A$   $A'$  (Fig. 5) are given some arbitrary value, say 1000 ohms. A set-

<sup>7</sup> "Resistivity of Copper in Temperature Range 20° C. to 1450°," JOURNAL OF THE FRANKLIN INSTITUTE, Jan., 1914, pp. 9-11.

ting is then made on the variable low-resistance standard which when multiplied by some power of ten is equal to the specific resistance of the mercury in ohms when at the temperature recorded. A balance of the bridge is then effected by the simultaneous adjustment of the ratio-coils  $B B'$ . The readings of the bridge when multiplied by the proper power of ten will now give the resistivity of the mercury in microhms per cm.<sup>3</sup>. Likewise, if a molten metal of unknown resistivity be substituted for the mercury and the bridge be again balanced by changing the setting on the variable low-resistance standard the new setting, when multiplied by the same proper power of ten, is the resistivity of the molten metal. For example: if the mercury has the temperature of 25° C. its resistivity is 96.268 microhms per cm.<sup>8</sup> Choosing the ratio-coils  $A A'$ , 1000 ohms, and setting the variable resistance at 0.009628 ohm, the bridge is balanced by adjusting the ratio-coils  $B B'$ . It is evident that the bridge-reading when multiplied by  $10^4$  is the resistivity in microhms of mercury at 25° C., and it is obvious that, the ratio-coils being left unchanged, all bridge-readings henceforth, whatever sample is chosen, will give the resistivity of this in microhms per cm.<sup>3</sup>.

By making these adjustments the resistivities of the samples studied are determined without any calculation whatever, and the result is that it is actually simpler to measure the resistivity of molten brass, for example, at 800° C. than to determine the resistivity of a rod of metal at room temperature. When the resistometer-tubes are made of Marquardt porcelain the temperature, given a suitable furnace, can be carried to 1600° or 1700° C., and it follows that, when one is supplied with the equipment which has been described, the resistivities of molten metals can be determined with the greatest ease, simplicity, and accuracy to even this high temperature.

#### MANIPULATION.

Before beginning a series of observations a test should be made of the measuring apparatus to ascertain if any defects exist in the circuits, such as incorrect connections, bad contacts, poor insulation, etc. For making this test the ratio-values of the bridge are set close to the values which are to be used in the measurements, and the same current- and potential-leads, which attach to the resistometer, are connected to a low-resistance standard of

manganin. A standard should be selected which has a resistance not far from the average resistance of the resistometer. The resistance of this manganin standard is then measured, a balance being obtained by varying the setting on the low-resistance standard. If a correct resistance value is now obtained for the manganin standard-resistance, one is assured that the bridge and measuring circuits will yield correct results when used to measure the unknown resistance of the resistometer. In fact, by this procedure the determination of the unknown resistance is reduced, almost, to a substitution method of measurement, and the chance of introducing a systematic error into the resistance-measurements becomes practically nil.

There is one important precaution which requires consideration, if high precision is desired. This consists in so selecting the values of the ratio-coils  $A A'$  that when the resistance values of the ratio-coils  $B B'$  are correctly chosen in the manner previously described, these latter values will be very large in comparison with the resistance of the tungsten or molybdenum potential-leads. The reason for this depends upon the fact that, so much of these leads as are in the lower end of the resistometer, change in resistance when the temperature of the resistometer is changed. By making the resistances of  $B B'$  very large in comparison with this variable resistance of the potential-leads, the per cent. variation in the ratios  $B/A$  and  $B'/A'$  may be made quite negligible under all variations in temperature.

It is not improbable that on first heating a sample in a crucible some contaminating material may be dissolved out of the substance of the crucible and so affect the resistivity of the sample. To guard against this possibility it is well to first heat in the crucible to be used some of the sample material, carrying the temperature higher than one intends to carry it in making measurements. This first lot of sample material is then replaced by a fresh lot, when it may be safely assumed that the first lot of material has taken up all contamination from the crucible and that the second lot will not take up any contamination, and hence may be used for the sample to be measured. After a test on a sample has been completed it becomes necessary to thoroughly free the resistometer from all traces of the material tested before it can be used for testing another sample of a different kind. If the sample tested has a melting-point lower than the boiling-point of mercury

and is soluble in mercury, the resistometer may be easily cleaned by immersing it in hot mercury until all traces of the sample tested are dissolved off the tubes and metal terminals. Any mercury which clings to the parts of the apparatus is easily wiped off with a cloth. If the material to be removed has a higher melting-point than boiling mercury or does not readily dissolve in mercury, it may still be removed by first immersing the resistometer in molten tin, carried to the necessary temperature to dissolve the material to be removed, and then later remove with hot mercury the tin which remains.

Either type of resistometer may be used as a pyrometer for temperatures up to 1600 to 1700° C. Type 2, however, is better adapted to this service. It is very advantageous to so calibrate and employ it that the readings on the variable low-resistance standard of the Kelvin double-bridge will be (with the subtraction of a single constant) in degrees of temperature.

The following affords a simple and wholly satisfactory method of calibrating the resistometer and evaluating the constants:

Assume that a metal is selected for the pyrometric substance which is molten over the range of temperature to be measured, and that the resistance of this metal, when molten, is a linear function of the temperature. Then calling  $R_t$  the resistance at temperature  $t$  and  $R_0$  the resistance at 0° C. of this metal between potential-points of the resistometer, we can write,

$$R_t = mt + R_0 \dots \dots \dots (1)$$

where  $m$  is a constant and  $t$  is the temperature.

By the law of the Kelvin double-bridge,

$$R_t = \frac{b}{a} S \dots \dots \dots (2)$$

where  $S$  is the reading of the bridge on the variable low-resistance standard and  $b/a$  is the ratio-setting used. Then from Equations (1) and (2)

$$\frac{b}{a} S = mt + R_0$$

from which

$$t = \frac{b}{ma} S - \frac{R_0}{m} \dots \dots \dots (3)$$

The value of the resistance  $a$  may be chosen arbitrarily and the

values of  $m$  and  $R_0$  may be obtained by experiment, in the manner presently to be described, and  $\frac{R_0}{m}$  will equal some constant  $K$ . When, therefore,  $m$ ,  $a$ , and  $K$  are known, the resistance  $b$  can be given a value such that  $\frac{b}{ma} = 10^x$ , where  $10^x$  is any desired power of 10. When this particular value is assigned to  $b$ , Equation (3) becomes

$$t = S 10^x - K \dots \dots \dots (4)$$

Equation (4) states that the temperature will be given directly in degrees when the reading of the variable low-resistance standard is multiplied by some power of 10 and a constant quantity subtracted from the result. The power of 10 to use will depend upon the resistance-range of the variable low-resistance standard employed. The multiplier of  $S$  is  $10^5$  if the resistance-range of the standard is from 0 to 0.01 ohm. To evaluate the constants  $m$  and  $R_0$  in Equation (1) it is, of course, only necessary to obtain experimentally the resistance of the resistometer at any two known temperatures where the metal, used as a pyrometric substance, is molten. Thus according to Equation (1) we have for a temperature  $t$

$$R = mt + R_0 \dots \dots \dots (5)$$

and for temperature  $t_1$

$$R_1 = mt_1 + R_0 \dots \dots \dots (6)$$

From Equations (5) and (6) we easily derive

$$m = \frac{R - R_1}{t - t_1},$$

$$R_0 = \frac{R_1 t - R t_1}{t - t_1} \text{ and}$$

$$\frac{R_0}{m} = \frac{R_1 t - R t_1}{R - R_1} = K, \text{ a constant.}$$

The best method of obtaining the two resistance-values of the pyrometer  $R$  and  $R_1$  at the two temperatures  $t$  and  $t_1$  may be applied as follows:

Select generous quantities of two metals, as lead and copper, the freezing-points of which are accurately known. Then place the pyrometer in a bath of one of these metals and record its

resistance as the metal slowly cools. When the metal begins to freeze its temperature holds constant at the freezing-point temperature of the metal for an appreciable time, and likewise the resistance of the pyrometer holds constant over this same period. This resistance is then the resistance of the pyrometer at the known freezing temperature of the metal used, and the quantities  $R$  and  $t$  become known. Repeat with the other metal, and then the quantities  $R_1$  and  $t_1$  become known. Curve 3, Plate IV, shows a resistance cooling curve taken in the above manner with the pyrometer placed in a lead-bath. It should be noticed how marked is the freezing-point.

The freezing-points on similar curves for Sb, Cd, Zn, and Cu, all of which may be used to give fixed points of temperature, are even more sharply defined, and hence it is easily seen how very accurately the necessary data may be obtained for determining the constants  $m$  and  $R_0$ . In making these determinations it is advisable to use crucibles made out of Acheson graphite. They are easily constructed by drilling out, with about a one-inch drill, a rod of graphite. The walls of the crucible should not be over one or two millimetres thick, because the heat capacity of the container should be kept as small as possible. If the heat capacity of the container and pyrometer are large in comparison with the heat capacity of the metal that constitutes the bath, then if the metal is one which on starting to freeze, undercools, the temperature will not ascend again to the normal temperature of solidification. The reason for this is that heat will be taken from the bath by the container and the pyrometer while the metal is rising from its undercooled temperature to its normal freezing-point temperature. The use of a thick-walled crucible, rapid cooling of the furnace, and insufficient quantity of metal in the bath, all contribute especially in the case of antimony, which greatly undercools, toward an inaccurate determination; the temperature given to the pyrometer, at the time its resistance is recorded as momentarily constant, being lower than the true freezing-point temperature.

As an illustration of the above method of calibrating a pyrometer we record the data obtained in a particular case. The pyrometric substance employed was pure tin. This metal was chosen because it is inexpensive, its melting-point is low ( $232^\circ \text{C.}$ ) and its boiling-point very high (over  $2000^\circ \text{C.}$ ), and because its



increase in resistance with temperature, when in the molten state, is strictly linear to at least  $1680^{\circ}$  C. and probably higher. From data taken we have:

$$R \text{ (resistance of pyrometer at freezing-point of copper, } 1082.8^{\circ} \text{ C.)} \\ = 0.0021544 \text{ ohm.}$$

$$R_1 \text{ (resistance of pyrometer at freezing-point of antimony, } 630^{\circ} \text{ C.)} \\ = 0.0018252 \text{ ohm.}$$

Substituting these values in the expression for the value of  $m$  gives,

$$m = \frac{0.0021544 - 0.0018252}{1082.8 - 630} = 7.268 \times 10^{-7}$$

and in the expression for  $R_0$  gives,

$$R_0 = \frac{0.0018252 \times 1082.8 - 0.0021544 \times 630}{1082.8 - 630} = 1.367 \times 10^{-4}$$

and

$$\frac{R_0}{m} = 1880 = K.$$

From the expression  $\frac{b}{ma} = 10^x$  we obtain, by giving to  $x$

the value 5 and to  $a$  the value  $2 \times 10^3$  ohms,

$$b = ma 10^5 = 7.268 \times 10^{-7} \times 2 \times 10^3 \times 10^5 = 145.36 \text{ ohms.}$$

Hence, using this pyrometer with the above constants and a variable low-resistance standard, which has an upper limit for the value  $S$  of 0.1 ohm, we obtain, according to Equation (4),

$$t = S 10^5 - 1880, \text{ degrees Centigrade.}$$

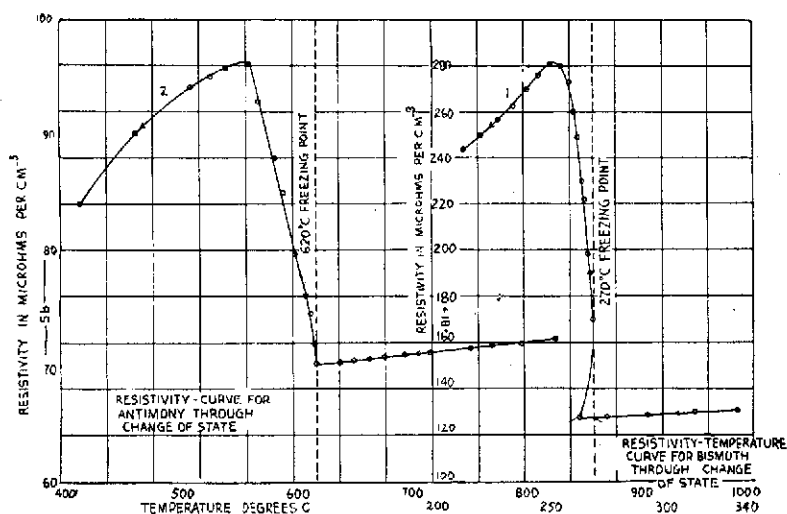
If the upper limit of  $S$  had been 0.01 ohm it would have been necessary to use the factor  $10^6$  instead of  $10^5$ , and then  $b$  would have been 1453.6 ohms instead of 145.36.

When employing the resistance as a pyrometer we used the variable low-resistance standard belonging to a Leeds & Northrup Kelvin double-bridge, catalogue No. 4307, the upper limit of which is 0.1 ohm, and when using the resistometer for resistivity measurements we used a Leeds & Northrup variable low-resistance standard, catalogue No. 4300, which has an upper limit of 0.01 ohm.

## OBSERVATIONS AND RESULTS.

The second-named writer, in the course of an investigation undertaken for the purpose of studying the electrical resistivity of some pure metals and also of some alloys, as these slowly changed from the liquid phase to the solid phase, and *vice versa*, has obtained some results which will serve to illustrate the usefulness and precision of the methods of measurement which have been described. It is hoped that these results, furthermore, will prove to have an interest of their own, although what is here

PLATE I.



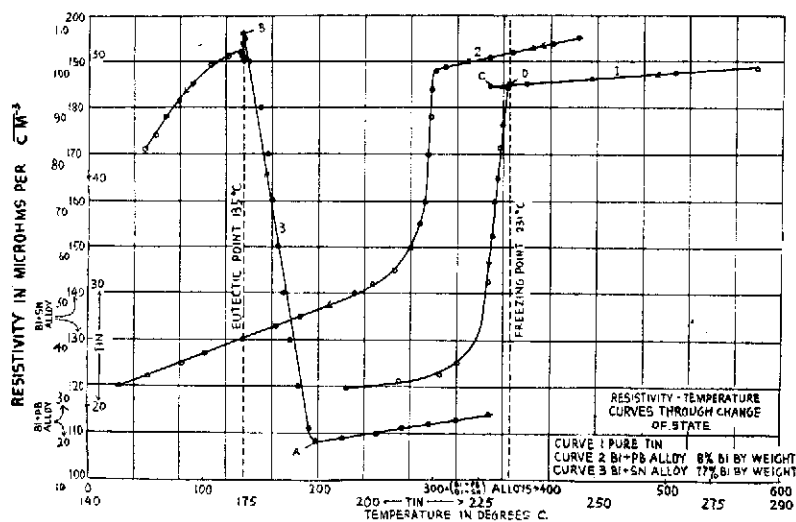
given is more or less limited in character and scope, because the research is necessarily an extended one and was only well begun at the time this article was prepared.

Curve 1, Plate IV, is a resistivity-temperature curve drawn from data obtained for pure Kahlbaum lead. The resistivity measurements were made with a type 2 resistometer, while another resistometer of the same type was used for the temperature-measuring device. This latter was filled with pure tin, which served as the pyrometric substance. The arrangement of apparatus used is shown diagrammatically in Fig. 6.

Curve 2, Plate IV, is a curve of the same character for the alloy bismuth-tin in atomic proportions. Attention is called to

the upper portion of this curve, where it will be noticed there is a sharp change, beginning at about  $1140^{\circ}$  C., from its otherwise linear character. This, very probably, is to be interpreted as the temperature at which the bismuth starts to vaporize and pass off, thus modifying the composition of the alloy. In this connection attention is directed to a phenomenon of the same character observed by the first-named writer in brass, an alloy of zinc and copper.<sup>8</sup> The resistivity curve of brass shows a marked inflection at about  $1090^{\circ}$  C., at which temperature the zinc began to

PLATE II.

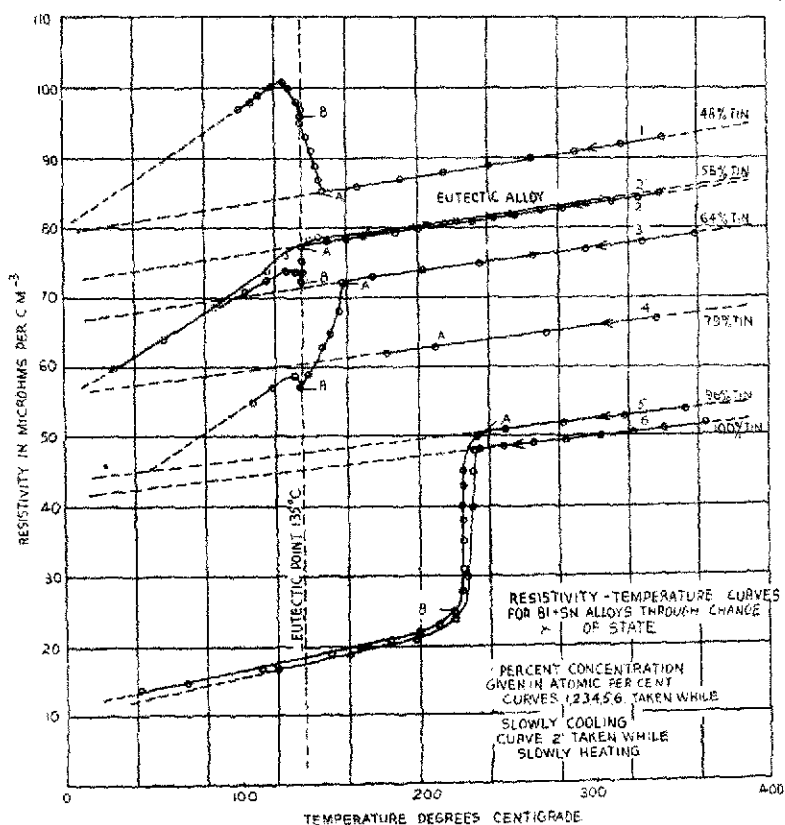


vaporize out. Curves 1 and 2, Plate I, are resistivity-temperature curves for pure bismuth and pure antimony respectively, taken as the metal cooled. Curve 1, Plate II, is a similar curve for pure tin, also taken as the metal cooled. Curves 1, 2, 3, 4, 5, 6, Plate III, and Curve 3, Plate II, are resistivity-temperature curves for various alloys of bismuth and tin. The per cent. of each component, in each of the different alloys used, is designated in connection with each of the curves. Curve 2, Plate II, is a resistivity-temperature curve of a Bi-Pb alloy containing 8 per cent. by weight of Bi.

<sup>8</sup> *Metallurgical and Chemical Engineering*, March, 1914, p. 161.

In all the above cases the resistivity measurements were made using a type I resistometer. The temperature measurements were all made with a copper *versus* constantan thermocouple, except with antimony, in which case a platinum-rhodium couple was employed. The hot junction of the copper-constantan couple

PLATE III.



was encased in a thin-walled quartz-tube and immersed in the sample and laid close alongside the resistometer-tubes, as previously described. The calibration of this thermocouple was carefully checked at frequent intervals during the investigation and no change in its calibration was observed. Before taking any observations on an alloy care was used to thoroughly mix the sample when at a temperature of 600-700° C. This precaution

was taken to give assurance that perfect homogeneity was secured throughout the entire mass of the sample contained in the crucible E.

#### DISCUSSION AND DEDUCTIONS.\*

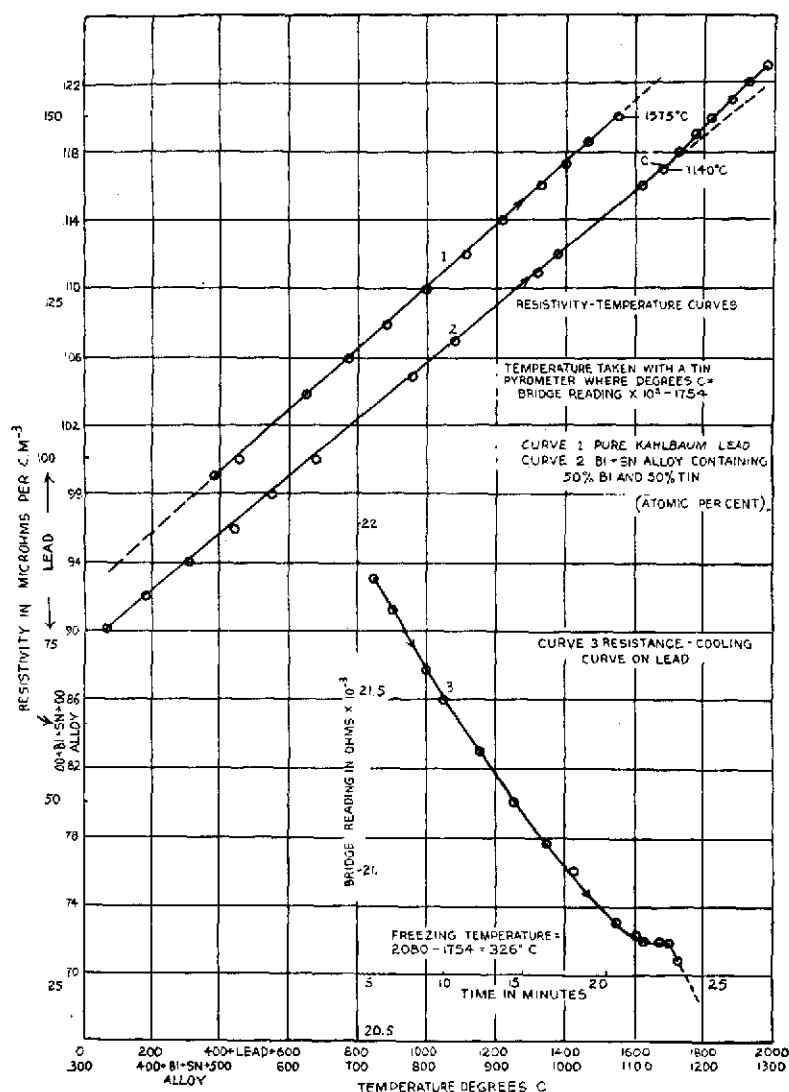
A common characteristic shown by all these resistivity-curves, both for the pure metals and the alloys, is their linear character in the molten state. Moreover, it is interesting to note that the slope  $\frac{dR}{dT}$  for all the curves of the Bi-Sn alloys in the molten state is approximately constant. The phenomenon of undercooling, indicated on the curves by *CD*, is clearly shown in the case of bismuth and tin (see Plates I and II). This phenomenon should also have appeared, presumably, in the case of antimony, since this metal exhibits undercooling in a marked degree. That the phenomenon did not appear on the temperature-resistivity curve is to be explained, probably, by failure to use a sufficient quantity of the metal when taking the measurements. So far as we are informed, this is the first time that the phenomenon of undercooling has been made to reveal itself on a temperature-resistivity curve when tracing this for a metal or alloy passing from the molten to the solid state.

The chief interest in the results obtained, however, is connected with the curves obtained for the alloys of bismuth and tin given in Plate III. Attention is directed to the following features:

1. The linear portion of the curves gives the resistivity-temperature relation of the alloy when this exists as a homogeneous liquid-solution. When cooling has reached the point designated by the letter *A* on all the curves, there suddenly takes place a separating out of a mixed crystal. Between the points *A* and *B* on the curves the alloy consists of this mixed-crystal and a liquid solution, the latter, however, gradually disappearing while the mixed-crystal increases in amount until the point *B* on the curves is reached. Here the last trace of liquid solution disappears and at the same instant the single mixed-crystal immediately begins to separate into two conjugate mixed-crystals. This is shown sharply on the curves. The remaining portion of the curve gives the resistivity of the alloy while the two mixed-crystals

\* All that follows is contributed by and is entirely based on the work done by R. G. Sherwood.

PLATE IV.



gradually change their relative composition, as the cooling progresses. The temperature at which the last trace of the liquid solution disappears and the two mixed-crystal formation begins is, for this class of alloys, always at the definite

fixed-temperature called the "Eutectic Point." The reason why Curve 5, Plate III, does not exhibit this common characteristic is to be explained by the fact that the proportion of the constituents is such that, after the point *B* is reached, the single mixed-crystal remains as an unsaturated solid-solution of bismuth in tin, for the lowest temperature recorded. Hence there is no breaking up of the alloy into the two conjugate solid-solutions or mixed-crystals above referred to. In the case of the curve for the eutectic alloy the points *A* and *B* are at the same temperature, since, by definition of the eutectic, the homogeneous liquid solution at its freezing-point does not pass into a single mixed-crystal, as do the other alloys, but passes immediately into two conjugate mixed-crystals. The character of the curve for the eutectic brings out this point well.

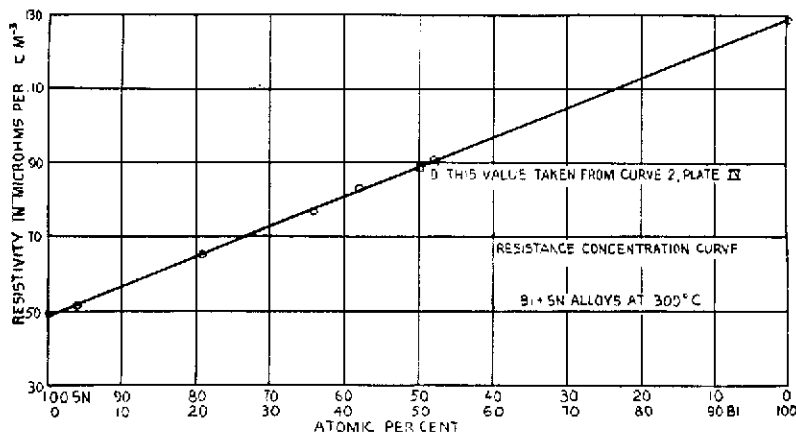
2. The heating curve for the eutectic alloy, curve 2, is interesting, since it apparently shows that the mixture represented by the proportions of this alloy are the proper proportions to "wipe out," so to speak, the abrupt break exhibited by all the other curves, as well as by the pure metals themselves. Heating-curves for these latter have been taken, but, since they differ only slightly from the cooling-curves given and seem to be of no special interest, they have not been included. The phenomenon above mentioned, associated as it is with the alloy having the lowest freezing-temperature, rather suggests some sort of a definite relation existing between the molecular condition or arrangement which causes a lowering of the freezing-point of the alloy and the molecular condition or arrangement functioning to change the resistance of the alloy.

3. When consideration is taken of the fact that the liquid phase of a metal or alloy possesses no crystalline structure, at least in the case here referred to, and is homogeneous throughout, it is logical to conclude that a systematic study of the electrical resistivity of various metals and alloys in their liquid phases might yield some very interesting and important information and furnish thereby a new basis for the comparison of this property with other properties of the metals or alloys. In this connection the curve, Plate V, is of unusual interest. This curve shows that a linear relation exists between the resistivity of the various alloys of bismuth and tin and the percentage of gramme-atoms of each constituent forming the alloy. Whether such a relation or some

other simple relation holds true for alloys of other metals is, of course, a matter of more or less speculation.

To obtain a more specific relation between the resistivity, concentration, and temperature of the alloy Bi-Sn, we can proceed as follows: Let  $R$  = resistivity of an alloy of Bi and Sn at concentration  $c$  and temperature  $t$ , where  $c$  is a quantity varying from zero to unity, being unity when the alloy consists of, say, 100 per

PLATE V.



cent. tin and zero per cent. bismuth—per cent. to be reckoned as above described. The temperature will be reckoned in degrees Centigrade. Then assuming  $R = f(ct)$ ,

$$dR = \frac{\partial R}{\partial c} dc + \frac{\partial R}{\partial t} dt \dots \dots \dots (7)$$

But on the assumption that all the resistivity-temperature curves have approximately the same slope, we may write

$$\frac{\partial R}{\partial t} = m.$$

Again, considering Equation (7) as a total differential,

$$\frac{\partial}{\partial t} \left( \frac{\partial R}{\partial c} \right)_t = \frac{\partial}{\partial c} \left( \frac{\partial R}{\partial t} \right)_c \text{ or } \frac{\partial}{\partial t} \left( \frac{\partial R}{\partial c} \right)_t = \frac{\partial}{\partial c} \left( \frac{\partial R}{\partial t} \right)_c = \frac{\partial}{\partial c} (m) = 0.$$

Here  $\frac{\partial R}{\partial c} = K$  where  $K$  is a constant (see curve, Plate V), Equation (7) now can be written  $dR = Kdc + mdt$ , which upon



integration gives,  $R = Kc + mt + p$ , where  $p$  is the constant of integration.

To evaluate  $p$ , let  $t = 0$  and  $c = 0$ , then  $p = R_0^{Bi}$  where  $R_0^{Bi}$  is defined as the intercept of the linear portion of the resistivity-temperature curve for pure bismuth projected back to cut the  $R$  axis.

Finally then,

$$R = Kc + mt + R_0^{Bi} \dots \dots \dots (8)$$

The constant  $K$  and  $m$  in Equation (8) must, of course, be obtained from the slopes of the resistivity-concentration curve and the resistivity-temperature curves, respectively.

The resistance-temperature coefficients of the alloys in the liquid phase can, of course, also be expressed in terms of the concentration  $c$  and the temperature  $t$ . While this gives no new information, it is interesting to find an expression for it. Calling this coefficient  $\alpha$  defined as  $\frac{1}{R} \frac{dR}{dt}$ , we obtain from Equation (8)

$$\alpha = \frac{1}{R} \frac{dR}{dt} = \frac{K \frac{dc}{dt} + m}{Kc + R_0^{Bi}}.$$

Since  $c$  and  $t$  are independent variables,  $\frac{dc}{dt} = 0$ , whence

$$\alpha = \frac{m}{Kc + R_0^{Bi}} \quad \text{or}$$

$$K\alpha c + \alpha R_0^{Bi} = m \dots \dots \dots (9)$$

Equation (9) is obviously the equation of an hyperbola.

Referring again to Curve 2, Plate IV, it will be noticed that the resistivity of this alloy of Bi and Sn (50 per cent. Bi and 50 per cent. Sn, each being in per cent. of gramme-atoms of each constituent) at 300° C. checks exactly with the value taken from the curve, Plate V. When it is considered that the data for the former were taken with apparatus differing quite essentially from that used in the case of the latter, the agreement is indeed gratifying and illustrates fully the practical value of the methods herein described.

PALMER PHYSICAL LABORATORY,  
Princeton, N. J.,  
May, 1916.