

essential accessories, the eliminating switch and equipotential shield, (all used, of course, by a person of adequate experience in electrical measurement of great accuracy), the instrument should be one of great usefulness for comparing small differences of temperature, as in careful work on calorimetry. Dr. White's own papers, especially those of 1914, show that the proper installation of the apparatus is not (at least for the average chemist) an altogether easy task—a conclusion which is not altered by our own experience. Of course the reference to the readings of the instruments to the International Temperature Scale depends upon accurate calibration; and we hope that a new investigation upon this question may soon be published by the Bureau of Standards.

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**THE MEASUREMENT OF ELECTROLYTIC CONDUCTIVITY.
II. THE TELEPHONE RECEIVER AS AN INDICATING INSTRUMENT FOR USE WITH THE ALTERNATING CURRENT BRIDGE.¹**

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1. The Suitability of the Telephone Receiver as an Indicating Instrument for Use with the Alternating Current Bridge.—For determining the bridge setting in an alternating current bridge containing an electrolytic cell, a number of indicating instruments have been proposed and used at different times.²

The principal factors which should govern the choice of an indicating instrument for the above purpose are, in the order of their relative importance, (1) sensitivity, (2) ease and convenience in use, and (3) cost.

Now the investigations which have been carried out in this laboratory have demonstrated that a properly constructed telephone receiver is *in every one of the above respects* greatly superior to any of the other instru-

¹ The nomenclature employed in this paper has been given in the preceding paper, *THIS JOURNAL*, 38, 2431 (1916). The following CORRECTION should be made in the preceding paper: p. 2439, line 23, for "Equations 19 and 20" read "Equations 21 and 22."

² Descriptions and discussions of the various types of instruments can be found in Kohlrausch and Holborn's "Leitvermögen der Elektrolyte," page 30, and on page 6 of Catalog 48 of the Leeds & Northrup Company, and in the references there cited.

ments, so superior in fact that all description or discussion of the relative merits of the other instruments may be dispensed with here. The only instance in which this pronounced superiority would not exist would be in the case of an experimenter who is deaf or who is obliged to carry on the measurements amid noisy surroundings, and for these cases the literature cited above will give the required information concerning the types of galvanometers and electro-dynamometers which are available for the purpose in hand.

Not only is the telephone receiver relatively better than any of the other instruments, but it is, as far as its sensitivity is concerned, all that could be desired; that is to say, a greater sensitivity in the telephone would not result in a greater degree of accuracy in the measurements for the following reasons: The degree of precision attainable in the measurement of the conductance of an electrolyte must, aside from all conceivable perfection of measuring instruments, be in most cases finally controlled and limited by the unavoidable fluctuation of the temperature of the bath containing the conductivity cell. If this fluctuation amounts to $\Delta T'$ degrees, then the absolute minimum percentage error in the measurement will be

$$p_{\min.} \leq 100\alpha \cdot \Delta T' \quad (1)$$

where α is the temperature coefficient of the conductivity of the electrolyte.

Now the value of α in the case of aqueous solutions, ranges from 0.05 in the case of water to zero in the case of the so-called Magnanini solution and a few other solutions which at certain concentrations or temperatures exhibit a change in the sign of their temperature coefficient. With very few exceptions, however, all solutions have a value of α which is at all events larger than 10^{-3} , and in the majority of cases is larger than 10^{-2} . Moreover, the lowest value $\Delta T'$ could conceivably have in practice may safely be placed at 10^{-4} degree, and this very small value could probably only be approached in the case of a bath at 0° composed of an intimate mixture of finely chopped ice and water in a vacuum-jacketed vessel.

If, therefore, we write $\Delta T' \leq 10^{-4}$ degree, then, for the extreme case of $\alpha = 10^{-3}$ we would have

$$p_{\min.} = 100\alpha \cdot \Delta T' = 10^{-5}. \quad (2)$$

In the following calculations we shall, therefore, assume that

$$\Delta T' = 10^{-4} \text{ degree,} \quad (3)$$

and that

$$\alpha \leq 10^{-3}. \quad (4)$$

That is, we shall assume that a greater degree of precision than one part in 10 million (which could in any case only be attained with a solution

having a value of α less than 10^{-3}) is not worth while considering. With the above stipulations we are now in a position to compute the maximum sensitivity which could ever conceivably be required in a telephone receiver for use in conductivity measurements. To make this calculation we will first solve Equation 4 of the preceding paper for the audibility current I_T of the telephone and thus obtain the equation

$$I_T = \frac{2 \Delta R_B R I}{(R_B/2 + R)(R_B/2 + R + 2R_T)} \tag{5}$$

We shall now assume that the center of $2\Delta R_B$ can be estimated with an accuracy of one-tenth³ $2\Delta R_B$. We thus have:

$$\frac{\phi}{100} = \frac{0.2 \Delta R_B}{1/2 R_B} = 0.4 \frac{\Delta R_B}{R_B} \tag{6}$$

and hence

$$2 \Delta R_B = \frac{\phi R_B}{20} \tag{7}$$

Combining these equations with Equations 6 and 8 of the preceding paper gives us

$$I_T = \frac{\phi R^{1/2} 0.2 \sqrt{A l d s \Delta T}}{t^{1/2} (R_B/2 + R + 2R_T)} \tag{8}$$

In this equation we shall put as before

$$t = 10 \text{ seconds} \tag{9}$$

$$\Delta T = \Delta T' = 10^{-4} \text{ degree} \tag{10}$$

$$d s = 1 \tag{11}$$

$$\phi = \phi_{\min.} = 100\alpha \cdot \Delta T' = 0.01\alpha \tag{12}$$

$$R = R_{\max.} \tag{13}$$

$$R_B = 250 \tag{14}$$

$$R_T = 200 \tag{15}$$

and $\alpha \ll 10^{-3}$, (16)

giving us

$$I_T = \frac{6.4 \cdot 10^{-6} \alpha R_{\max.}^{1/2} \sqrt{A l}}{(R_{\max.} + 525)} \tag{17}$$

Using this equation with all possible values of α between 0.05 and 10^{-8} we have calculated the minimum value which I_T would ever need to have in the case of all of the cells described in the preceding paper⁴ and we find that in no instance would this value ever need to be less than 10^{-9} ampere. That is, in no instance would the value of $A l$ have to be inconveniently

³ In the previous paper the more conservative value $1/4(2\Delta R_B)$ was used in order to be well within the limit of safety. In the present instance, however, since we are discussing the highest degree of precision attainable in the measurements, we should employ the value $1/10(2\Delta R_B)$ as representing more closely what can actually be attained when conditions of the highest precision are demanded.

⁴ *Loc cit.*, p. 2447.

large or the value of R_{\max} inconveniently small in order to prevent the value of I_T falling below 10^{-9} ampere.

To sum up, therefore, we find from this calculation that in order to attain the maximum degree of precision possible in a conductivity measurement up to and including the extreme case of a precision of one part in 10 million, a telephone receiver with an audibility current no smaller than 10^{-9} ampere will fulfill all possible requirements and in most cases, of course, a less sensitive telephone than this would be quite good enough. Telephones of this sensitivity are now obtainable at a moderate price.

A greater degree of sensitivity than the above could obviously not be used even if it were available, unless the ear of the observer had less than the normal sensitivity; in which case a telephone which had for the normal ear a greater sensitivity than the above value might be desired. Methods for increasing the sensitivity of a telephone are described below.

Since most of the mechanical details of the construction of the telephone will be properly taken care of by the manufacturer, we shall discuss here only the processes involved in tuning a telephone to the frequency of the current employed.

2. Tuning the Telephone.—A telephone employed for conductivity measurements should be tuned to the frequency of the current with which it is to be used. The complete tuning operation consists of three processes which we shall designate as mechanical tuning, electrical tuning, and acoustical tuning, respectively. Any one or all of these tuning processes may be used, but ordinarily only the first or the first and the second would be employed. We shall discuss each of these processes in some detail.

Mechanical Tuning.—This tuning process consists in so restricting the area of the vibrating portion of the diaphragm that its fundamental period of vibration coincides with that of the current. This may be accomplished, for example, by placing on top of the diaphragm a flat brass ring with an opening of the proper size. When the cover is screwed down upon the case, this ring is pressed tightly against the diaphragm, thus limiting the portion of it which is free to vibrate. With the aid of a set of these rings having different sized openings, a single telephone (if provided with adjustable pole pieces) can be successively tuned for a series of different frequencies and while an instrument arranged in this way for variable tuning will perhaps be not quite as sensitive at each frequency as a single instrument constructed especially for that frequency would, it will usually be sufficiently sensitive for all practical purposes. Mechanically tuned telephones⁵ have been successfully constructed for frequencies as high as 6000 cycles.

⁵ The principal of mechanical tuning was employed by Wien [*Wied. Ann.*, 42, 596 (1891)] in constructing his so-called "optical" telephone, which had for a frequency

Other things being equal, it is obviously desirable that the frequencies employed in conductivity work should be those to which the human ear is most sensitive. Wien⁶ has investigated the relation between frequency and ear sensitivity and his results are shown in Fig. 1. From this figure

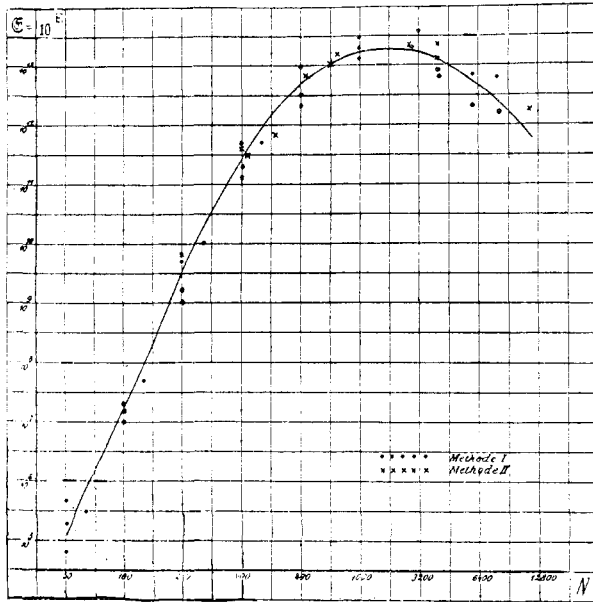


Fig. 1.
 Ordinates = Ear sensitivity. Abscissae = Vibrations per second.

it appears that the sensitivity of the human ear is approximately constant and at its maximum for frequencies between 1000 and 5000 cycles per second, and fortunately this frequency interval harmonizes well with all the other conditions which must be met.

In order to keep the reactance as small as possible, the frequency employed should be kept as low as is compatible with the elimination of polarization influences. For most purposes, therefore, a frequency of 1000 cycles is the most convenient one to employ and a telephone with a diaphragm tuned to this frequency will be the best all around telephone for conductivity work.

Electrical Tuning.—The current which energizes the electromagnet of a telephone receiver will, for a given E. M. F., be inversely proportional of 150 cycles a “visibility current” of 10^{-8} ampere (*loc. cit.*, p. 60). The tuning was accomplished by weighting the vibrating disk. Optical studies of the character of the vibrations of telephone diaphragms have been made by Kempf-Hartmann [*Ann. Phys.*, 313, 489 (1902)] and by Siegbahn [*Ibid.*, 351, 298 (1915)].

⁶ Wien, *Pflüger's Archiv für die Ges. Physiol.*, 97, 28 (1903). See also *Archiv für Anat. u. Physiol. Physiol. Abt.*, 1904, p. 167.

tional to the impedance of the telephone coils. This impedance is given by the equation

$$Z = \sqrt{R_T^2 + (2\pi fL)^2} \quad (18)$$

where R_T is the *effective* resistance of the telephone and L is its effective inductance. The electrical tuning of the telephone consists in compensating the inductive reactance by inserting in series with the telephone coils the proper capacity. To find the value of this capacity we might put

$$\frac{1}{2\pi fC} = 2\pi fL \quad (19)$$

and hence

$$C = \frac{10^{-6}}{4\pi^2 f^2 L} \text{ farads} \quad (20)$$

but owing to the fact that both the effective inductance and the effective resistance vary with the frequency and with the current through the telephone, the proper capacity to use in order to compensate for the inductive reactance is best determined by actual trial.

If the telephone is to be used for one frequency only, this capacity may be built into the instrument and in that case should be arranged so that it can be short circuited if desired. If it is intended to use the telephone for different frequencies, the most convenient arrangement is to connect a duplex variable condenser in series with the telephone coils and adjust it until maximum sensitivity is obtained for the frequency employed.

From Equation 18 it is evident that the electrical tuning is more important the higher the frequency and the lower the resistance of the telephone. If $R_T = 150$ ohms and $L = 0.03-0.04$ henry, then for a frequency of 1000 cycles or less the inductive reactance of the telephone will ordinarily not be much larger than its resistance and hence electrical tuning will not increase the sensitivity of the telephone very much (40 to 50% at most). For a telephone with a low resistance or high inductance, or both, and for higher frequencies, however, the electrical tuning will have an important influence upon the sensitivity of the telephone.

In addition, however, to the effect which the electrical tuning has in increasing the sensitivity of the telephone, it may be advantageously employed for damping out any residual harmonics⁷ which may be present in the current employed. Thus, for example, one of the telephones which has been used in this laboratory has at 1000 cycles an effective resistance of 220 ohms and an inductance of 0.04 henry. For the fundamental, the impedance of the telephone will be 330 ohms according to Equation 18. To the third harmonic, however, the telephone would offer an impedance of considerably more than double this value, and

⁷ For this purpose the principle of electrical tuning was employed by Wien in his studies of ear sensitivity (*loc. cit.*).

this, together with the mechanical tuning of the diaphragm, would be very efficient in damping out harmonics. As a matter of fact, however, with a proper source of power there would never be any trouble from harmonics anyway.

Acoustical Tuning.—A properly constructed telephone which has been mechanically tuned or, at the most, both mechanically and electrically tuned, is sufficiently sensitive for practically all the demands of conductivity work, and in fact a more completely tuned telephone might be actually less sensitive than an untuned one unless the frequency of the current could be very perfectly and closely controlled. If, however, the observer has at his disposal a source of alternating current of practically unvarying frequency, acoustical tuning could be employed to advantage in case the observer was hard of hearing or was obliged to work amid noisy surroundings. It may, therefore, be briefly described.

The use of the principle of acoustical tuning in order to increase the sensitivity of a telephone receiver has been recently suggested by Max Wien⁸ and under his direction an investigation of its practicability is now being conducted.⁹ The method consists in interposing a Helmholtz resonator between the telephone case and the observer's ear, the connection to the ear being made with the ordinary stethoscopic tubes of the physician. For the frequencies which would be employed in conductivity measurements, it was found most desirable to place the telephone at the center of the resonating hemisphere as shown in Fig. 2. For the lower frequencies the complete sphere was employed and was connected to the telephone case by a rubber tube. Further details concerning acoustically tuned telephones will doubtless appear in subsequent papers describing the results of these investigations.

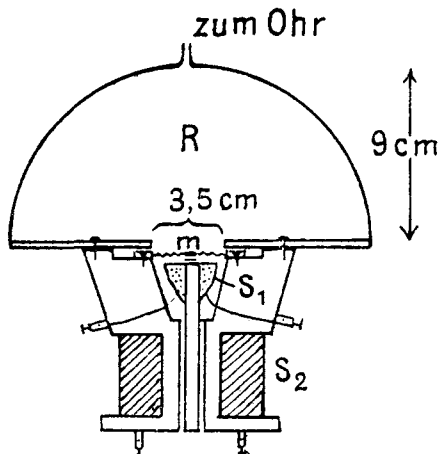


Fig. 2.—Telephone with attached resonator [Birnbäum, *Ann. Phys.*, 49, 219 (1916)].

3. The Variation of Sensitivity with Frequency. The Volt Sensitivity Curve.—The volt sensitivity of a telephone is usually determined¹⁰ with the aid of a slide-wire connected in shunt across a noninductive branch

⁸ Wien, *Phys. Z.*, 13, 1034 (1912). As a source of current of unvarying frequency, he suggested using the damped vibrations of a discharging condenser.

⁹ See Birnbäum, *Ann. Phys.*, 49, 219 (1916).

¹⁰ Cf. Wien, *Ibid.*, 63, 390 (1897) and 4, 456 (1901).

of an alternating current circuit provided with a hot wire ammeter. Such an apparatus is shown in Fig. 3, which is self-explanatory. Knowing the resistance of the slide-wire, the resistance of the noninductive shunt and the current in the main circuit, the voltage drop across the telephone when it produces a barely audible sound can evidently be calculated.

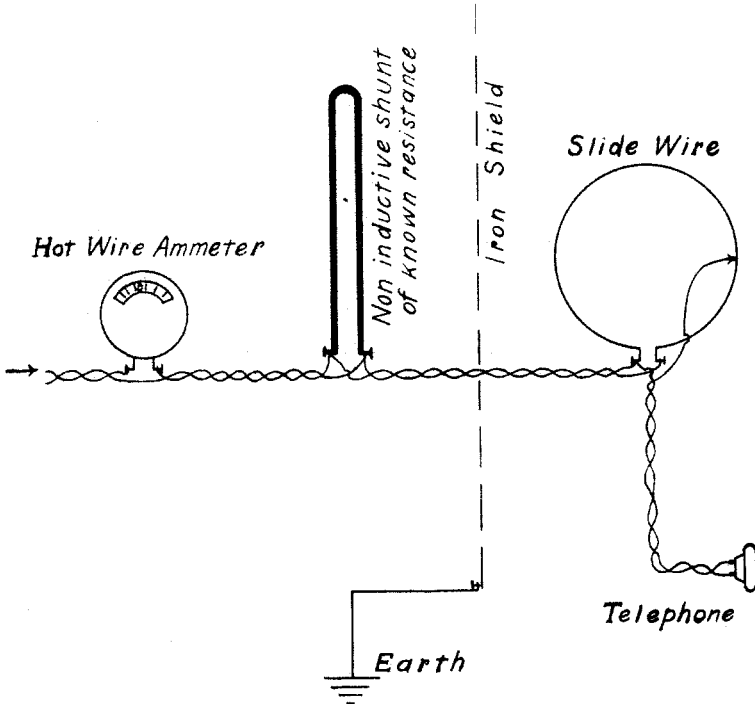


Fig. 3.

With the apparatus shown in the figure, we have determined the volt sensitivity curve for three telephone receivers which had been employed for conductivity measurements.

The results of these determinations are shown in Fig. 4.

The curve marked A is the curve of a mechanically tuned telephone of English manufacture. Its effective resistance at 1000 cycles was found to be 220 ohms, its D. C. resistance being 170 ohms. Its inductance at 1000 cycles was 0.04 henry.

The curve marked C is the curve for a telephone of German manufacture which is advertised as being especially adapted for conductivity measurements. Its D. C. resistance was 105 ohms and its inductance at 1000 cycles was 0.05 henry.

The curve marked D is the curve for a unipolar telephone of unknown

make which was sold by an American firm for use in conductivity measurements.

The curve marked B is based upon Austin's measurements of a Schmidt-Wilkes' 900 ohm telephone receiver employed in wireless telegraphy. The figures on the left-hand margin represent the reciprocals ($\times 10^{-4}$) of the number of microvolts necessary to produce an audible sound in

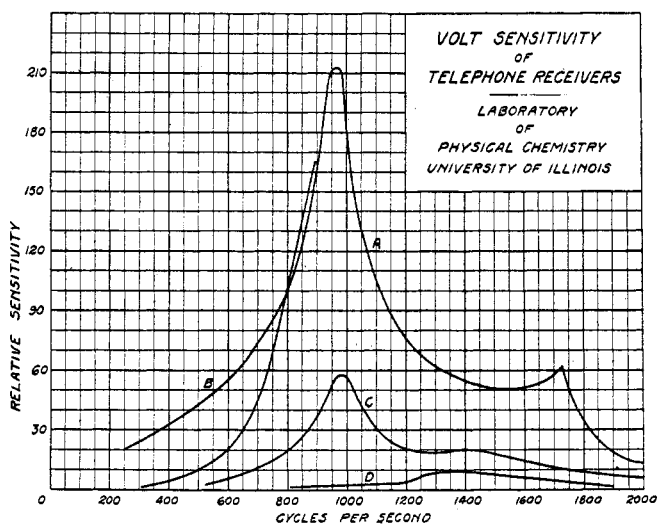


Fig. 4.

the telephone. These figures, of course, are as much dependent upon the ear of the observer as they are upon the characteristics of the telephone.¹¹

4. Determination of the Audibility Current of a Telephone Receiver.—

As explained in the first paper of this series, every observer should determine for himself the audibility current of his telephone for the frequency at which he expects to employ it; in fact it is well to know the complete curve connecting the audibility current with the frequency for the range between, say 500 and 3000 cycles. The usual method of determining such a curve is to divide the volt sensitivity of the telephone (obtained as described above) for each frequency, by the impedance for that frequency. Since, however, both the effective resistance and the inductance of the telephone depend upon the frequency,¹² it is necessary in this method to determine the value of each of these quantities for each frequency, and for these measurements a standard variable inductance should be available. Moreover it is doubtful¹³ if the values thus obtained are strictly

¹¹ The values given are for the left ear of the senior author.

¹² Cf. Wien, *Ann. Phys.*, 4, 456 (1901).

¹³ Austin, *Bur. Standards. Bull.* 5, 155 (1908).

applicable for the purpose in hand since they are determined with the use of currents much greater than the audibility current.

A much simpler method¹⁴ of measuring the audibility current of a telephone and one which does not require a knowledge either of the impedance of the telephone or of its volt sensitivity, may be based upon the equation of the Wheatstone bridge; that is, upon Equation 5 of this paper.

The quantities appearing in the equation have the significance shown in Fig. 5 [Fig. 1 of the preceding paper, *THIS JOURNAL*, 38, 2434 (1916)], except that the cell in one of the bridge arms is replaced by a pure metallic resistance.

The procedure for determining the value of I_T for an electrically tuned telephone by this method is as follows:

1. Place in series with the bridge and the high frequency generator a vacuum thermocouple connected to a suitable millivoltmeter.

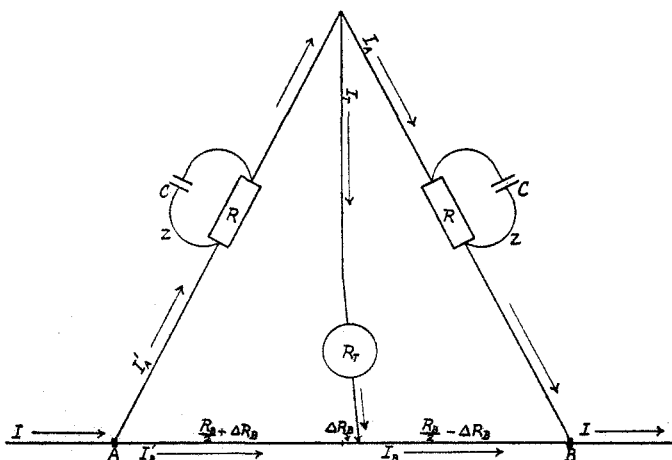


Fig. 5.—Bridge arrangement for determining the audibility current of a telephone.

2. Make the values of R in the two arms of the bridge (Fig. 5) of such magnitude that $2R_T$ may be neglected in comparison with $R + R_B/2$, or at least so that an estimated value for R_T may be used without appreciable error.

3. Adjust the current I until the value of $2\Delta R_B$, the range of silence on the bridge wire, is of such a magnitude as to permit an easy estimation of its value.

4. Determine carefully the value of $2\Delta R_B$ and then read the millivoltmeter from which the value of I is readily obtained.

¹⁴ Washburn, see *Phys. Rev.* (1917), Reports of the December (1916) meeting of the American Physical Society; and *Proc. Inst. Radio-Eng.*, March or April, 1917.

5. Finally, substitute the data thus obtained in Equation 5 and calculate the value of I_T .

This method has the obvious advantage not only of simplicity but also of closely reproducing the conditions under which the telephone is actually used in conductivity work, and the observer may take for $2\Delta R_B$ the value which he finds to be the most convenient one for him to use; that is, instead of making $2\Delta R_B$ the actual range of silence, he may, if he wishes, make it equal to the range between the two *tone limits* which he desires to employ. The determination can of course be repeated using different values of I and R . The conversion factor for the vacuum thermoelement may be checked by means of a D. C. current, although the value given on the instrument as purchased may usually be safely taken as the correct one, since an accuracy of 10% or so is all that is required in the value of I .

As an example of the determination of the audibility current of a telephone by this method, the data obtained with one of the instruments employed in this laboratory will be given here. The high frequency generator was operated at a frequency of 990 cycles per second. No exciting current was used in its electromagnets. A resistance box of Curtis coils was employed in each arm of the bridge, each box being set at $R = 5000$ ohms. The range of silence on the bridge wire was found to be one scale division, that is, $0.0001 \times 250 = 0.025$ ohm. The millivoltmeter read 0.35 millivolt and the conversion factor for the thermojunction being $10/9$, the value of I was, therefore, practically 0.4 milliamperes. The value of R_T for 1000 cycles was known to be 220 ohms, the direct-current value being 170 ohms. For $R_B/2 + R$ we have $125 + 5000 = 5125$ ohms. The value of $2R_T$ would thus be 440 ohms, and this could evidently be neglected in comparison with 5125 ohms since the error involved would be less than 10%. Or, knowing the D. C. resistance of the telephone to be 170 ohms, we could employ this value for R_T or could estimate that the effective resistance at 1000 cycles would be about 200 ohms. In either case on substituting the above values in Equation 5 we find $I_T = 2.10^{-6}$ milliamperes.

5. Connecting the Telephone to the Bridge.—In using the telephone in conductivity measurements, a pair of non-inductive telephone leads should be employed, and these should be inclosed in a flexible metal sheath which should be grounded. This is for the purpose of protecting the telephone from any stray alternating electromagnetic field in the surroundings. Care should also be taken to see that the telephone is completely insulated from the observer. If a head piece is employed, the insulation can be conveniently effected by slipping a piece of rubber-band tubing over the steel head clamp.