Summary

Adsorption of sulfur dioxide by titania gel has been measured at −22.5, 0, 25 and 50°.

The data have been tested by the equations of Patrick and Polanyi and while the data substantiate Patrick's formula at lower relative pressure, over the whole range they can be best represented by the formula of Polanyi.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY AND FROM THE CRUFT LABORATORY OF HARVARD UNIVERSITY]

THE MEASUREMENT OF THE CONDUCTANCE OF ELECTROLYTES. I. AN EXPERIMENTAL AND THEORETICAL STUDY OF PRINCIPLES OF DESIGN OF THE WHEATSTONE BRIDGE FOR USE WITH ALTERNATING CURRENTS AND AN IMPROVED FORM OF DIRECT READING ALTERNATING CURRENT BRIDGE

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Introduction

It would be a pleasure to write an historical review of the previous work on the conductance of electrolytes with appreciative comments on the contributions of many earlier investigators including especially Kohlrausch, Wien, Noyes, Taylor and Acree, Grover and Curtis, Washburn, Kraus, Parker, Miller, Hall and Adams, Morgan and Lammert and many others, but the limitations of space firmly imposed by an Editor who must constantly remember his budget forbid. Moreover, such a review is unessential since the recent paper of Morgan and Lammert[1] contains an excellent summary of the earlier work.

Washburn[2] made substantial improvements in the design of the bridge

[1] (a) J. Livingston R. Morgan and Olive M. Lammert, THIS JOURNAL, **48**, 1220 (1926). In addition to the numerous papers referred to in this article the following will be of interest to students of this subject: (b) Wien, *Wied. Ann.*, **58**, 37 (1896); (c) Miller, *Phys. Rev.*, [2] **22**, 622 (1923); (d) Reichinstein, *Z. Elektrochem.*, **15**, 734, 913 (1909); (e) **16**, 916 (1910); (f) **17**, 85, 699 (1911); (g) **19**, 384, 518 (1913); (h) Hall and Adams, THIS JOURNAL, **41**, 1515 (1919); (i) Randall and Scott, *ibid.*, **49**, 636 (1927).

[2] (a) Washburn, THIS JOURNAL, **38**, 2431 (1916); (b) Washburn and Bell, *ibid.*, **35**, 177 (1913); (c) Washburn and Karr Parker, *ibid.*, **39**, 235 (1917). The senior author of this paper was a colleague of Professor Washburn at the University of Illinois while Washburn was engaged in the earlier part of his researches in this field and thus, although not sharing in these investigations directly, had the opportunity of following their progress in detail and acquired at first hand an appreciation of Washburn's important contributions to the measurement and interpretation of conductance of electrolytes. The researches to be described in this and subsequent papers were begun after

and conductivity cells which have been incorporated in the apparatus built by Leeds and Northrup. This apparatus,[3] which is the best commercially available, is now generally used, at least in the United States, for precision work. Therefore, in the following discussion of bridge design, emphasis will be placed on the defects of this apparatus and upon the changes in design we have found to be desirable.

In this paper is described an experimental and theoretical study of the design of the Wheatstone Bridge for measuring resistances with alternating current of audio frequencies 500 to 3000 cycles per second. Several sources of error, hitherto entirely overlooked or inadequately guarded against, have been found and means for their elimination invented. A new form of bridge which is more precise, sensitive and convenient than any hitherto available has been built, tested in service with satisfaction, and is described in detail. An experimental study of electrode effects and cell design is now in progress and will form the subject of the second paper in this series. A redetermination of the absolute value of the specific conductivity of certain standard solutions by a new method has been planned, and a beginning made in its execution.

In our preliminary study of the behavior of the Wheatstone bridge, we replaced the cell by a metallic resistance in order to avoid complications due to electrode phenomena. We planned to study these phenomena after errors in the bridge itself had been eliminated as much as possible. The apparatus was so constructed that each part could be replaced in turn by others of a different make or design and comparisons made by direct substitution or by interchange of the arms of the bridge. Capacitance could be introduced at will at any point and in any amount by means of variable electrostatic air condensers suitably connected. Various methods of grounding and shielding were tested. We had a double throw switch which permitted either the oscillator (giving controllable frequencies from 500 to 2400 cycles per second) or a direct current battery to be used as the source of the current. There was also a reversing switch in the line supplying power to the bridge. Another double throw switch substituted a direct current galvanometer for the telephone. We could thus detect any difference between the balance of the bridge with direct current and with alternating current of various frequencies, and thus seek out any

Washburn had turned his attention to other subjects and the senior author had left Illinois.

Before the publication by Morgan and Lammert of their second paper which announced their extensive program of investigation on the measurement of the conductance of solutions, we had made substantial progress on a similar program; but our methods were so different from theirs, as disclosed in their first and second papers, that we decided not to abandon our program in spite of the fact that they had an earlier start on the work.

[3] Leeds and Northrup Company, Philadelphia, Catalog No. 48.

abnormal behavior of the bridge or of any of its parts with alternating current due to capacitance, inductance, dielectric losses, improper grounding, shielding or other causes. These effects, although mostly small, were so numerous, subtle and concurrent that we made thousands of measurements in an effort to understand and locate the disturbances and devise remedies. We were endeavoring to avoid any imperfection of design, construction, or operation which might cause an error of 0.001%. This experimental study stimulated theoretical analysis of the sources of error. We have thus reached conclusions as to the correct principles of design which have guided the design and construction of the new bridge to be described below.

A detailed record of these numerous experiments is inadvisable because of their great number, and because the actual numerical data are significant only in regard to particular pieces of apparatus. In many cases, especially in the earlier part of the work, the interpretation of the experiments was greatly complicated by the fact that several sources of error were superimposed on one another. For the sake of brevity and clearness the following discussion is mainly theoretical, with selections from our experimental data used for illustrative purposes, but our method of approach was primarily experimental. Every source of error which is discussed was first found experimentally in apparatus of supposedly good quality and has been shown experimentally to be significant in work of high precision with the forms of apparatus commonly used by investigators who are striving for accuracy.

The Source of Alternating Current

Taylor and Acree[4] have used and recommended the Vreeland Oscillator as a source of alternating current, and have demonstrated that it is superior to other forms of oscillators previously used. Recently Morgan and Lammert have made a careful study of the instrument and have shown that its frequency is not constant when used steadily over long periods but varies by about 1% in the course of several hours' operation. They ascribe this variation to a change in capacitance and inductance due to heating; but as is explained below we do not regard this variation in frequency as a serious fault. This instrument, being supplied as a part of the Leeds and Northrup set, has been most used in precision work in recent years. But the Vreeland Oscillator has many disadvantages. It is expensive in first cost ($225) and in operation. It uses 5 amperes at 110 volts D.C. and therefore requires either a large storage battery or a motor generator to operate it. Its efficiency is very low, as only a small part of this energy is actually supplied to the bridge or needed by the bridge. In the standard form available by purchase it gives an unneces-

[4] Taylor and Acree, This Journal, 38, 2396 (1916).

sarily high voltage which tends to overheat the cell unless the bridge is protected by a high resistance in series or by shunts. This fault is, however, not inherent, as the coils can be wound to give any desired voltage. It has a strong variable magnetic field which produces serious disturbances by inducing currents in the bridge and telephone unless the oscillator is placed at a considerable distance. When operated by a motor generator it often gives erratic rasping noises due to sparks at the commutator of the dynamo. It has a tendency to stop oscillating in the midst of the readings and can then only be started by tipping it by hand, which is a nuisance because the instrument must be located at a considerable distance.

Hall and Adams[5] have suggested the use of the three electrode or triode tube sometimes called an audion tube, suitably connected with inductance and capacitance so that it oscillates. Although the chemical literature gives little indication that such instruments have been used by chemists, audion tube oscillators are now used as a matter of course in radio research laboratories. Splendid instruments of this type may now be purchased.[6]

We give in Fig. 1 a schematic wiring diagram of a simpler and cheaper oscillator which we have used with great satisfaction, although no special merit is claimed for the details of the design. Switches S_1 and S_2 permit four different values of the capacitance and four different values of the inductance to be used in the oscillating circuit so that sixteen different frequencies can be obtained between the limits of 500 and 2400 cycles. We have ordinarily used 1100 and 2400 cycles. It could easily be modified to give frequencies up to 5000 cycles if it were desired. The three coils are mounted on the same axis. By moving the output coil on this axis the voltage supplied to the bridge can be varied in at least a fourfold ratio. The voltage can also be varied in about a 4 to 1 ratio by moving the switch, S_3, which controls the number of turns used in the output coil. By the combination of these two methods the voltage can be varied 16-fold. The maximum voltage of the output coil of this oscillator is about 5 volts. The output coil O, has a grounded electrostatic shield consisting of a wire wound as an open toroid around it in three independent sections, each connected to ground at one end. This shielding of the output coil is the only unusual feature in the design and is of considerable importance for the reason explained below (page 1060).

The audion tube oscillator has several important advantages over the Vreeland Oscillator.

1. It is much cheaper to build and operate. Our instrument was made of standard radio parts and cost only \$60 including all parts and the labor of an experienced builder of radio sets. This cost is, however, not fairly comparable with the prices of purchaseable oscillators mentioned

[5] (a) Hall and Adams, THIS JOURNAL, **41**, 1515 (1919). See also (b) Randall and Vanselow, *ibid.*, **46**, 2424 (1924); (c) Randall and Scott, *ibid.*, **49**, 636 (1927).

[6] Bulletin 803 of the General Radio Company of Cambridge, Mass., describes their type 377 Low Frequency Oscillator having a range from 60 to 75,000 cycles and listed at \$375. The Western Electric Company also makes an instrument having a range from 100 to 50,000 cycles which is sold for \$1750. These instruments have greater power and a greater range of adjustment in voltage and frequency than we have found necessary for our purposes.

above as it does not include any overhead, or selling expenses. It can be operated with a six volt "A" storage battery and a sixty-seven volt "B" dry battery.

2. It is easily adjustable in frequency and voltage within any limits that may be needed and can be designed to give any desired number of steps in frequency.

3. Its outside magnetic field is much less than that of the Vreeland Oscillator.

4. It can be started and stopped conveniently and instantly by a switch in the "A" battery line and never stops of its own accord when in use.

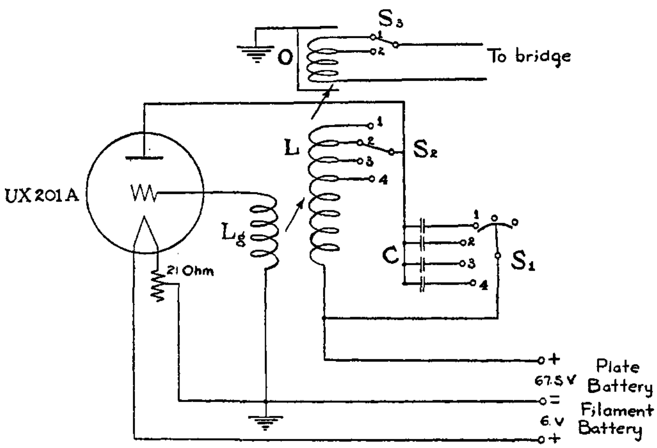

Fig. 1.—L = oscillating coil: 4 in. inside diameter, $6^3/_8$ in. outside diameter, 1 in. length, No. 21 double cotton covered, 760 turns, taps at 650, 520, 475 turns; L_g = grid coil: 5 in. inside diameter, $6^1/_4$ in. outside diameter, $^3/_8$ in. length, No. 30 double cotton covered, 540 turns; O = output coil: $3^3/_4$ in. inside diameter, $4^1/_4$ in. outside diameter, $^1/_4$ in. length, No. 30 double cotton covered, 140 turns, tap at 35 turns, shielded; C = condenser: three, 0.1 μ f. and one, 1.0 μ f. paper condenser, capacitance for successive positions 1–.1 μ f., 2–.2 μ f., 3–.3 μ f., 4–1.2 μ f.

Our instrument has two slight defects which are, however, not serious and can be cured by methods well known to radio engineers but which we have not yet adopted because they did not seem worth the trouble and expense involved. Our instrument has a harmonic of very low intensity barely audible with a two stage amplifier when the primary note is balanced out perfectly. It could be removed by suitable electrical tuning if it were troublesome. The other defect is that the frequency changes slightly with changes in the load, but this has not proved to be of any consequence in any work which we have as yet done with our bridge because our bridge is so designed that the load varies only slightly in use and, as we shall show in the second paper of this series, even relatively great changes in frequency (from 1100 to 2400) have only a very slight effect on the bridge setting, unless the conditions are such that excessive polarization occurs, or unless other sources of error which are functions of the frequency are present. Therefore, a change of frequency of a few per cent. is of no consequence. If it is desired to make the frequency entirely independent of the resistance being measured, this could be done by using two audion tubes, one of which oscillates at a fixed frequency, while the other acts as an amplifier and takes all the variation in the load without influencing the oscillating tube. However, the use of an amplifier in this way may add a weak second harmonic which can be tuned out by the method indicated above.

The Telephone and Amplifier

According to Washburn's analysis of bridge design the controlling factor of many features of the design, especially of the cells, is the sensitiveness of the telephone.[7] Hall and Adams[5a] have suggested the use of an audion tube amplifier with the telephone, which makes it possible to increase the sensitiveness of the detector as much as may be desired. They point out that this device makes it possible to reduce substantially the current in the bridge proper, thus minimizing the heating effect and polarization in the cell, which aids greatly in precision work; at the same time it increases the sensitiveness of the bridge setting and avoids the nervous strain of listening to very weak notes in the telephone. Our experience fully confirms these advantages. We have secured a sensitiveness of one part per million in the bridge setting. On one occasion we have used two stages of amplification with a loud speaker so that the balancing of the bridge could be heard by an audience in a lecture room. Ordinarily we use telephones with one or two stages of amplification. According to Washburn's analysis, which is in accord with our experience with his apparatus, the resistance of the cell should be between 200 and 10,000 ohms for precision measurements. Hall and Adams were successful with the amplifier in extending this limit downward to about 100 ohms but they were not interested in increasing the range in the other direction and record no experiments with cells of high resistance. For our purpose it was desirable to use cells of much higher resistance. By the use of the amplifier and of other improvements to be described below we have obtained sharp settings of the bridge with a cell having a resistance of 60,000 ohms and an approximate setting with a cell having 1,500,000 ohms. The use of high resistances and very small currents minimizes errors due to heating and polarization or other electrode effects and permits the design of a cell as a long narrow tube which gives better thermal contact with the liquid in the thermostat. The latter is of considerable

[7] Washburn, ref. 2 a. See especially p. 2442.

importance since temperature control is expected to be the largest source of error in our final measurements. The amplifier also makes it unnecessary and undesirable to tune the telephone for maximum sensitiveness at some particular frequency with a sacrifice of sensitiveness at other frequencies.

Mathematical Theory of the Wheatstone Bridge for Alternating Currents

Fig. 2 is a diagrammatic representation of the Wheatstone Bridge for use in measuring the resistance of the cell H with alternating current supplied by the oscillator O. (The oscillator could be replaced by a battery by means of a switch not shown in Fig. 2 but shown in Fig. 8.) The current detector consists of a telephone or an amplifier and a telephone. (When using direct current the telephone could be replaced by a galvanometer by means of a switch not shown in Fig. 2 but shown in Fig. 8.)

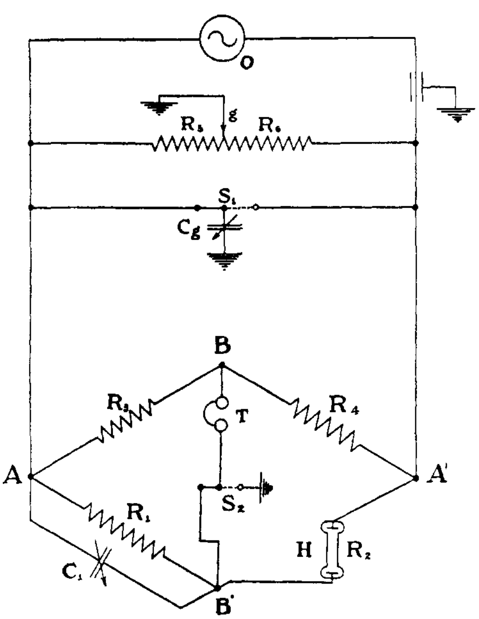

Fig. 2.—Schematic wiring diagram of bridge showing new method of grounding.

The electrolytic cell, H, whose resistance is to be measured is assumed to be in branch 2 of the bridge circuit. The cell unavoidably has some reactance due to its geometrical capacitance or to polarization. Branch 1 consists of a variable resistance box and a variable air condenser in parallel. It will be proved below that this arrangement is the best to compensate for the capacitance of the cell, which is necessary to obtain a precise measurement of the resistance. Branches 3 and 4 are the ratio arms. Subscripts 1, 2, 3, 4, are used to designate the several branches. E_1 is the effective or virtual potential difference across Branch 1 (between A and B′). I_1 is the virtual or effective current in Branch 1.

Both E and I are harmonic functions of the time, but the maximum current and the maximum voltage may not occur at the same instant of time, in which case they are said to be out of phase and are to be treated in the conventional manner as vectors. In a strict sense of the term the voltage and current are not vectors because the difference in phase is not a difference in direction but a difference in time. But in the simplest form of alternating current generator—a single loop of wire revolving at constant angular velocity on an axis at right angles to a uniform and a steady magnetic field—one complete revolution of the loop generates one cycle. Therefore, differences in time are exactly correlated to differences in direction of the loop. This makes it possible to treat the phase relationships by mathematical methods applicable to vectors. One complete cycle corresponds to 2π radians or $360°$ and fractions of a cycle may be expressed in circular degrees.

R_1 is the equivalent series resistance of branch 1. In other words, R_1 is that perfect resistance which when placed in series with a perfect condenser of suitable size would be electrically equivalent to the imperfect resistance actually used when shunted by the imperfect condenser actually used. R_1 is not necessarily the same (unless suitable precautions are taken) as the direct current resistance of the box, since there may be dielectric losses in the resistance box or in the condenser, or other causes for a difference between the direct current resistance and the alternating current resistance.

X_1 is the equivalent series reactance in this branch. It may in theory be due either to inductance or to capacitance or to both. Except in unusual cases, the capacitance predominates. This reactance is due to the condenser and to any capacitance and inductance in the box and connections.

Z_1 is the impedance in the branch AB′, whose magnitude may be computed from the equation $Z_1^2 = R_1^2 + X_1^2$, but this procedure loses sight of the phase relationships. For this purpose it is better to use the conventional symbolism of vectors, $Z_1 = R_1 + jX_1$, where the equality sign signifies geometrical addition of the vectors, R_1 and X_1 and the symbol j means that R_1 and X_1 are to be treated as vectors at right angles to each other. R is commonly plotted horizontally and X vertically so that the resistance is often spoken of as the horizontal component of the impedance and the reactance as the vertical component of the impedance.[8]

[8] Some authors speak of R as the real component and X as the imaginary component of the impedance. This usage is confusing because both R and X are real in the sense that they are definite functions of the dimensions of an electrical circuit (or part of a circuit) and of the frequency and have a definite effect on an electrical current. This use of the term imaginary has its origin in the practice of many mathematicians in calling $\sqrt{-1}$ an imaginary quantity. This is poor pedagogy, which has caused unnecessary confusion in the minds of many defenseless students. Let j be the symbol of the operation of rotating a vector through $90°$ counterclockwise. If a in Fig. 3 represents a vector having magnitude and direction, then ja represents another vector having the same magnitude but a direction at right angles to a, and j^2a would represent the vector obtained by the rotation of a through two right angles, which would

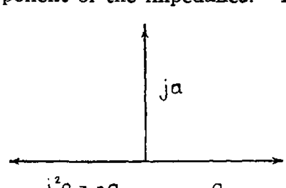

Fig. 3.

According to Ohm's law as applied to alternating current, $E_1 = I_1Z_1 = I_1(R_1 + jX_1)$ (not $E_1 = I_1R_1$ unless $X_1 = 0$ and hence $R_1 = Z_1$ which, in general, is not true).

Branch 2 from B′ to A′ is assumed to contain the cell H which contains the solution whose resistance is to be measured. This cell will act like a resistance R_2 in series with a condenser which gives a reactance X_2 and as before we can write $E_2 = I_2Z_2 = I_2(R_2 + jX_2)$. R_2 is not necessarily the same as the true electrolytic resistance of the solution inside the cell plus the resistance of the electrodes and lead wires, because there may be an irreversible dissipation of energy by other means than the passage of a current through a pure resistance which will influence the measured resistance. These possible sources of error will be studied in detail in the second part of this investigation.

Similarly, X_2 is the reactance which is the combined effect of the inductance and capacitance in this arm together with the reactance due to all other processes which convert electrical energy reversibly, and change the phase relationships of the voltage and current. An example of the latter is reversible polarization. During alternating current electrolysis electrical energy is converted into chemical energy at the electrodes during one half of the cycle and returned to the system as electrical energy during the other half cycle. This process is of the nature of capacitance in that it causes the current to lead the voltage but the reactance due to polarization may not vary with the frequency in the same manner that it does for a geometrical capacity and may be a function of the voltage instead of being independent of the voltage as it is for a geometrical capacity. Therefore, R_2 represents that pure resistance which would dissipate the same amount of electrical energy that is dissipated by all of the other processes in arm 2 under the given conditions of frequency; and X_2 is that pure reactance in series with R_2 which would cause the same phase change. It must be kept in mind, however, that the energy-dissipating and the phase-changing effect of polarization may not be equivalent to any actual combination of pure resistance and pure reactance. $Z_2 = R_2 + jX_2$ and $E_2 = I_2Z_2 = I_2(R_2 + jX_2)$.

Branch 3 (from A to B) and Branch 4 (from B to A′) are the ratio arms of the bridge, which may be either fixed and equal, or variable resistances, R_3 and R_4, but which are variable in the Leeds and Northrup apparatus. In our final apparatus R_3 and R_4 are made fixed and equal, which gives important advantages, as will be pointed out more in detail below. Unless unusual precautions are taken the inductances and capaci-

be represented by $-a$; therefore $j^2 = -1$, or $j = \sqrt{-1}$. But j or $\sqrt{-1}$ is not imaginary, but is a mathematical operator which has a very definite and clear meaning—rotation through a right angle. Steinmetz, "Engineering Mathematics," McGraw-Hill Book Company, New York, 1911, pp. 13–16.

tances in these resistances will not be negligible and therefore we must ascribe reactances, X_3 and X_4, and impedances, Z_3 and Z_4, to these arms also. We may, therefore, write $E_3 = I_3Z_3 = I_3(R_3 + jX_3)$; and $E_4 = I_4Z_4 = I_4(R_4 + jX_4)$.

When the bridge is balanced so that no current flows through the telephone, the potential at B must be equal to the potential at B′ at every instant; or, in other words, the potential must be in phase, as well as have the same numerical value; then $E_1 = E_3$ and $E_2 = E_4$. Therefore we may write

$$\frac{I_1Z_1}{I_2Z_2} = \frac{I_3Z_3}{I_4Z_4} \tag{1}$$

and, moreover, *if there is no escape of current from the bridge network by ground connections or through capacitance to ground or through capacitance to any other conductor and if there is no mutual capacitance or mutual inductance between the arms and if there is no leakage* from any part of the bridge to any other part or to the ground or to any outside conductors, then $I_1 = I_2$ and $I_3 = I_4$ and hence

$$\frac{Z_1}{Z_2} = \frac{Z_3}{Z_4} \tag{2}$$

It is apparent from this analysis that there is a fallacy in the method of grounding incorporated in the Leeds and Northrup apparatus, which consists in making a direct connection to ground from the midpoint of the bridge at B[1]. Such a ground connection makes it easier to secure silence in the telephone, as may easily be verified by trial. But this ground connection can only be effective by leading current to earth and then $I_1 \neq I_2$ and therefore $Z_1/Z_2 \neq Z_3/Z_4$. Therefore, a ground connection at the mid-point of the bridge is inadmissible.

A New Method of Grounding the Bridge

There is, unavoidably, considerable capacitance between the telephone coils and the observer (who may or may not be grounded) or between the primary and secondary coils of the transformer if an amplifier is used. The best way to avoid a charging current into this capacitance, which would upset the proper balance of the bridge and prevent a sharp minimum, is to maintain both the observer and the telephone (when in balance) at earth potential. As a substitute for the method of grounding at the mid-point of the bridge we first tried the method used by Taylor and Acree,[4] which consists of a high resistance shunted across the bridge and grounded at its mid-point. This method is described by Taylor and Acree as a modification of that used by Wagner.[9] But a study of Wagner's article shows that his grounding is essentially different, inasmuch as Wagner was using a capacity bridge and had resistance and capacitance in series in his shunt, with the ground connection between the resistance

[9] Wagner, *Elektrotechnische Zeitschrift*, 32, 1001 (1911).

and capacitance, while Taylor and Acree used no condenser in their ground connection. This method was found to be unsatisfactory, but before explaining our solution of the problem it will be well to discuss another source of error which turned out to be related to the grounding and also curable by proper grounding.

In order to avoid errors due to thermo-electric forces when using direct current in our bridge we had a reversing switch (not shown in Fig. 2, but shown in Fig. 8) in the battery line between the bridge and the switch which controlled the kind of current used. We then noticed that when using alternating current and a Taylor and Acree ground the reading of the bridge when in balance depended upon the position of the reversing switch which was near the bridge. The observation that merely reversing the lead wires which supplied power to the ends of an alternating current bridge could change the reading of the bridge was astonishing in view of the fact that the current was automatically reversing itself one thousand times per second. We have found no record that this phenomenon had been observed before by anyone using an alternating current bridge to measure electrolytic or metallic resistances; but after making this observation we found that Wagner had made a similar observation when using a capacity bridge. After many experiments of a varied character we finally traced the cause to an unbalanced or unsymmetrical capacitance from the oscillator and its lead wires to earth. We connected one side of a variable air condenser to each lead wire from the oscillator at the terminal of the reversing switch nearest the oscillator and connected the other side of each condenser to ground. We then found that by putting the proper amount of capacitance in one or the other of the condensers the reading of the bridge when in balance became independent of the position of the reversing switch. We also found that the definite reading thus obtained was the mean of the two divergent readings previously obtained when the position of the reversing switch was changed, and also the same as the reading with direct current when all other sources of error were eliminated. Then by connecting capacitance to the other lead wire the effect of the reversing switch could be magnified. Errors of one-tenth of one per cent. in the bridge reading can be easily obtained in this way. Apparently an inequality in the capacitance to earth from the two lead wires or an unsymmetrical capacitance between the oscillator and earth causes an error in the setting.

This effect can best be made clear by an example chosen from a great many in our notebooks. In this particular case the bridge was grounded at its midpoint and when balanced with an alternating current gave a result differing by +0.030% from the balance with direct current. Then on reversing the lead wires from the oscillator the new balance was in error by −0.031%. After replacing this ground connection with a ground similar to that used by Taylor and Acree the error was plus or minus 0.025% according to the position of the reversing switch. Then on connecting a condenser of about 1000 micromicrofarads from one lead wire to earth the error was reduced to ±0.006%. By increasing the capacitance between the lead wire and earth to 2000 micromicrofarads the error was reduced to 0.000% as compared with the direct current reading and the position of the reversing switch no longer had any effect on the reading. There was evidently in this case an asymmetry of 2000 micromicrofarads between the ground and the two lead wires, which caused the trouble.

We then rebuilt our oscillator and leads with a special effort to make the capacity to earth as small, fixed and symmetrical as possible. A grounded electrostatic shield was placed around the output coil of the oscillator. We found that with no ground at all on the bridge the error was ±0.045% according to the position of the reversing switch. With the mid-point grounded or with the Taylor and Acree ground the error was reduced to ±0.002%. This was a substantial improvement over the results obtained before the reconstruction of the oscillator. Moreover, it was now found that only 20 micromicrofarads were needed to bring the effect of reversing the switch to zero. After many experiments we reached the conclusion that the actual amount of the capacitance to earth from the lead wires and oscillator is relatively unimportant provided that this capacitance is made as definite as possible by mounting the lead wires in a fixed position inside a grounded metallic sheath and provided that the capacitance from the two wires to earth is adjusted to equality by means of a condenser until the effect of reversing the switch disappears. Some experiments with a Vreeland Oscillator showed that this effect is also present. The discovery of this source of error throws some suspicion on all previous measurements of the conductance of solutions. This effect is also a function of the frequency and may perhaps account for the apparent change in conductance with frequency which has been reported by several investigators. This is a matter which we expect to investigate carefully with our new and improved bridge.

We have devised a method of grounding which cures the reversing switch effect and also maintains the telephone when in balance at earth potential, which is necessary for the reasons pointed out above, without making a direct connection between the bridge and earth as is customarily done. Our method of grounding is a modification of the method suggested by Wagner.[9] Wagner was working with a capacity bridge, so that his scheme cannot be used for a resistance bridge just as he described it, but the fundamental idea is adaptable to the resistance bridge.

The modified form of the Wagner ground which we have used successfully is shown in Fig. 2. It consists of an auxiliary resistance, AR_5R_6A', in parallel with the bridge proper, provided with a sliding contact, g, which is connected to earth, and a variable air condenser, Cg, one side of which is connected to earth and the other side connected through a switch, S_1, to either A or A′ whichever may prove to be necessary. The sliding contact divides the auxiliary resistance into two parts, R_5 and R_6, and can be adjusted so as to make R_5/R_6 approximately equal to R_3/R_4.

The procedure in adjusting this ground is:

1. Make an approximate adjustment of the bridge proper (R_1 and C_1), leaving the ground as it happens to be from the last use.

2. By means of a suitable switch, S_2, disconnect the telephone from B′ and connect this lead wire to earth instead, while the other side of the telephone remains connected to B.

3. Adjust the sliding contact, g, and the variable condenser, Cg (in magnitude and position across R_5 or R_6), until there is silence in the telephone, thus bringing B to earth potential.

4. Throw the switch, S_2, so that it restores the telephone to its original position from B to B′ and breaks the connection between the telephone and earth.

5. Adjust the bridge (R_1 and C_1) again. If this second adjustment is much different from the original, the adjustment of the ground should be repeated and then the final bridge reading confirmed. In our experience the capacitance adjustment in the grounding device is even more important than the resistance adjustment. With suitable switches built into the apparatus this adjustment of the ground requires only a few seconds for an experienced operator. This arrangement and procedure ensure that B and B′ are at earth potential, accomplishing it in a manner that cannot upset the equality of I_1 and I_2, and of I_3 and I_4.

Wagner had an auxiliary line shunted across the ends of his bridge, consisting of a variable resistance and a variable capacitance in series with the ground connection between the two. In his arrangement the impedance in arm 5 was due wholly to resistance and the impedance in arm 6 was due wholly to capacitance. In a resistance bridge the condenser is most advantageously placed in parallel with either R_5 or R_6 as may be found by trial to be needed so that the impedance in one of these arms is due partly to resistance and partly to capacitance. This is the difference between our arrangement of the ground and Wagner's. The magnitude of R_5 and R_6 should be approximately the same as R_3 and R_4. This method of grounding brings the telephone when in balance to earth potential so that it only remains to ensure that the head of the observer which is near but insulated from the wires in the telephone is also at earth potential. This can be accomplished simply and in a manner which cannot be forgotten by covering the hard rubber of the telephone ear pieces with tin foil which is permanently connected to earth by means of an auxiliary wire mechanically attached to but electrically insulated from the telephone lead wires.

The essential difference between our method and that of Taylor and Acree is that they used no variable condenser, Cg, and their earth connection was fixed rather than sliding so that $R_5 = R_6$ but, since Taylor and Acree were working with an equal arm bridge with R_3 always equal to R_4, an adjustment of R_5 and R_6 was relatively unimportant, although we have found that even with an equal arm bridge some adjustment of R_5 and R_6 is helpful. It is our experience that the proper adjustment of the capacitance is the most important part of the ground connection, although without a test on their apparatus it is impossible to judge how important it may have been in their experiments.

Morgan and Lammert[10] state, "The method of grounding which we have found most effective is the modified form of Wagner described by Taylor and Acree. By this method each end of the bridge is grounded through a 1000-ohm resistance and the lead wires from the oscillator shielded and grounded. We cannot emphasize too much the need for a good ground in order to get a sharp minimum. With the set-up described there is probably nothing which so affects the sharpness of the minimum as the condition of the ground." Evidently Morgan and Lammert, like Taylor and Acree, have no adjustable condenser in their ground connection and therefore no provision for a reactance balance in their modification of the Wagner ground. In Morgan and Lammert's arrangement R_5 and R_6 are maintained constant at 1000 ohms, although in their bridge R_3 and R_4 are variable and therefore for the best results R_5 and R_6 should be capable of corresponding adjustment. In this respect their arrangement is inferior to that of Taylor and Acree, but if in practice R_3 and R_4 are always nearly equal this is less important than the omission of the variable condenser. We agree with Morgan and Lammert as to the importance of a "good ground," but we believe that the resistance in the ground connection is of minor importance compared to having it built in accordance with the principles explained above.

Magnetic Shielding

Care should be taken to make sure that there are no variable magnetic fields in the space occupied by the bridge which might cause an error by inducing a current in the bridge. A sensitive and convenient way to search for variable electromagnetic fields is to take a coil of wire (about 50 turns with a six inch diameter), attach the ends of the coil to a telephone (with or without an amplifier) and hold the coil in various positions near the bridge, taking care to turn it frequently. If a noise is heard in the telephone this proves that there are variable magnetic

[10] Morgan and Lammert, THIS JOURNAL, **48**, 1232 (1926).

fields which may cause error by inducing currents in the bridge circuit. By noticing the pitch of the note heard, the direction of the field and the effect of starting and stopping various electrical machines in the neighborhood the source of the disturbance can be located. The disturbance may come from the oscillator or any near-by electric motor. The bridge itself if properly designed has so little inductance that it is far less sensitive than the testing coil which has been suggested and is not appreciably affected by outside electromagentic fields; but the coils in the telephone itself are sensitive to varying magnetic fields and if an audion tube amplifier is used the trouble is more serious because the coils in the transformers may have alternating currents induced in them which are amplified.

An effective electromagnetic shield requires several concentric enclosures in heavy iron and it is therefore impractical to shield the bridge or telephones, but the amplifier can be shielded. A better remedy is to make the oscillator as nearly as possible astatic (this is not possible with the Vreeland oscillator, which is a particularly bad offender), enclose it in one or more iron shields, such as an iron barrel, and finally and most important and easy, remove it to a considerable distance. We have found it necessary to remove the Vreeland oscillator to a distance of thirty feet, whereas with our form of audion tube oscillator ten feet is ample. If near-by motors are unavoidable they may be stopped momentarily while the final readings are being taken.

Electrostatic Shielding

It is a common practice to place a grounded metallic shield between the parts of the bridge proper[11] or to surround the bridge completely by a grounded shield for the purpose of preventing electrostatic influence on the bridge from the outside. It is our judgment, based on reasoning and experiment, that this practice is apt to cause more error than it cures. In the derivation of the fundamental equation for the bridge it is assumed that there is no escape of current from the bridge to ground and no transfer of electric energy between the four arms through any other means than conduction at the junction points of the arms. Therefore, by reasoning analogous to that used above to prove the fallacy of grounding the midpoint of the bridge, it becomes evident that the bridge must be so constructed and mounted that there is no appreciable capacitance between any of the four arms of the bridge proper to any other conductor, including the other three arms, the line supplying power to the bridge, the telephone leads or any other surrounding object such as the thermostat, the observer, the oscillator, electric light lines or the earth itself. If there is capacitance between arms 1 and 3, for instance, the proper remedy is to spread them

[11] See, for instance, Leeds and Northrup Catalog No. 48, 1924, p. 3, Fig. 1. Numerous investigators have described more or less complete shielding of their bridges.

further apart. To put a grounded metallic plate between these arms does, in a certain sense, prevent direct exchange of energy between these arms, but it introduces a much larger capacitance between each of these arms and the earth, so that the effective indirect exchange of energy is increased and the error magnified. To put a grounded shield around the entire bridge will protect it from outside electrostatic influence but care should be taken that the shield is so far away from the bridge that the capacitance between the bridge and the shield is negligible. Such a shield is a nuisance in operating the bridge. It is better to put the shield around the outside source of disturbance if the disturbance cannot be removed to such a distance as to make it negligible.

The outside electrostatic influence most likely to disturb the bridge is the oscillator itself (this is true particularly of the Vreeland oscillator) because this disturbance is at the frequency used in the bridge and is sure to be operating when readings are to be taken. The best way to avoid this difficulty is to put the oscillator so far away that it is harmless, or to place a shield around the oscillator. A grounded enclosure of thin metal is an effective electrostatic shield. If an amplifier is used a sixty-cycle hum may be heard from electric light lines even at considerable distances. With practice it is possible to ignore this sixty-cycle note and make the balance with the comparatively high note given by the oscillator but it is better to have a double-pole pull switch at considerable distance operated by a cord so that the sixty-cycle line can be entirely disconnected momentarily when readings are to be taken. The lead wires from the oscillator must of course approach the bridge proper but these wires should be themselves shielded to within 15 cm. of the bridge for the reason explained above in the discussion of the grounding. Since these lead wires are at the same potential as the adjacent arms of the bridge they can do no harm provided the resistances through which the fall of potential in the arm occurs are placed far enough away from the junction point. The shield around the lead wires should be removed where it approaches the bridge because this would bring a grounded conductor too near the bridge.

We have tested this question experimentally by using a metallic plate 15 cm. square connected by a flexible wire either to earth, so that it would have zero potential, or to one end of the bridge, so that it would have the maximum potential of any part of the bridge, and then observed the effect on the bridge balance of moving the plate near to the various parts of the bridge. It was definitely proved that errors can be produced in this way although they are small. Even under extremely bad conditions we were only able to produce an error of 5 parts in 100,000 at 1100 cycles. The effect is of course greater at higher frequencies. From numerous experiments with this plate we inferred that 15cm. separation, with air as the medium, for parts having the maximum difference of potential is sufficient to ensure that the error will be less than 0.001% with a frequency not greater than 2400 cycles. The line from bridge to the amplifier should be shielded because this line is at ground potential when the bridge is in balance and very nearly zero when the bridge is slightly out of balance, and therefore capacitance to earth can do no harm and this line is especially sensitive to outside electrostatic influence if an amplifier is used. The net result of these experiments on shielding was the conclusion that this is a comparatively unimportant source of error.

Water vs. Oil in the Thermostats

Most investigators have immersed their cells in thermostats filled with water and many have grounded the thermostat also. It is easier to maintain a constant temperature in a thermostat filled with water than with any other liquid because water has a high specific heat, a low viscosity which facilitates stirring and its slow evaporation dissipates surplus heat. Moreover, water is cheap, clean and odorless. But for electrical purposes water has the great drawback that it is a conductor. From the theory of alternating currents it may be inferred that the presence of a conductor so near the cell may cause an error in the measurement of the resistance due to the following causes.

1. The presence of the grounded conductor near one arm of the bridge causes bridge errors whose existence has been demonstrated by the experiments described above. The capacitance introduced by the grounded conducting liquid in the thermostat would be expected from purely geometrical considerations to be greater than the capacitance introduced by the metal plate in these experiments.

2. The walls of the glass cell may act as a dielectric in a condenser, permitting alternating current to flow in the water outside the cell. This extra parallel path for the current consisting of two condensers and a resistance must decrease the measured resistance of the cell. For convenience this may be referred to as the error due to capacitance by-path.

3. The alternating current in the cell will induce eddy currents in the water outside the cell and thus have the effect of increasing the apparent resistance in accordance with the well-known behavior of a short-circuited transformer. The eddy currents tend to counteract the error due to capacitance by-path.

4. The possibility of error due to skin effect in the relatively wide conductor inside the cell was considered but proved to be negligible by calculation in accordance with the well-known formula.

The above sources of error may be functions of the frequency, the resistance of the solution inside the cell, the specific conductivity of the water outside the cell, the dimensions of the cell and electrodes and proximity of the leads and the thickness and electrical properties of the glass used in making the cells, and the position of the cell with reference to the tub. The theoretical analysis of these three superimposed effects would be a problem of extreme mathematical difficulty which we have not attempted in detail. We have preferred an experimental attack on the problem.

In order to determine whether these errors are large enough to be significant we cleansed our thermostat and filled it with water of specific conductivity of 14×10^{-6}. Six conductivity cells of the pipet type, with cell constants ranging from 0.5 to 145, were filled with potassium chloride solution of a concentration suitable to give a high resistance (21,000–25,700 ohms) and then the resistance of each cell was measured with 1100 cycles and with 2400 cycles, with the metal thermostat tub grounded, and also ungrounded. Then a small amount of potassium chloride was added to the water in the thermostat sufficient to make it about 0.0002 N and to give a specific conductivity of 26 $\times 10^{-6}$ and the measurements were repeated. A further quantity of potassium chloride was then added to give a specific conductivity of 325×10^{-6} and a concentration of about 0.0025 N, and the measurements repeated. Then the water was removed and replaced with a good grade of transformer oil consisting of a refined petroleum distillate of a boiling point high enough to avoid offensive odor (Transil Oil) and the measurements were then repeated. With oil in the thermostat the measured resistances were absolutely independent of whether the tub was grounded or not, as was to be expected since the oil was a very good insulator. The results with oil in the tub were also independent of the frequency within at least 0.01% except in the two cells of the lowest cell constant (G and J) in which the so-called "electrode phenomena" were present.

The following table gives the results of these measurements. The figures are the difference between the resistance of the cell when immersed in water and in oil, expressed in per cent. A plus sign means that the resistance in water is the higher. These measurements were made with our new bridge to be described in detail below.

TABLE I

COMPARISON OF OIL AND WATER AS THERMOSTAT LIQUIDS

Cell designation		A	B	C	D	G	J
Approximate cell constant		144.6	51.5	45	9	3.05	0.515
In oil, ohms at 2400 cycles		21,755	21,364	24,118	25,694	24,311	21,071
In oil, ohms at 1100 cycles		21,756	21,363	24,117	25,694	24,314	21,076
Thermostat grounded							
Frequency	Sp. cond. of water	Resistance in water − resistance in oil, %					
2400	0.000014	+0.15	+0.18	+0.23	+0.17		
2400	.000026	.10	.11	.14	.10		
2400	.000325	.03	.02	.03	.02	+0.28	+0.12
1100	.000014	.05	.05	.07	.05		
1100	.000026	.04	.02	.04	.03		
1100	.000325	.01	.01	.01	.01	.24	.10
Thermostat not grounded							
2400	.000014	− .28	− .22	− .51	− .20		
2400	.000026	− .22	− .20	− .47	− .18		
2400	.000325	− .16	− .16	− .28	− .15	− .09	− .34
1100	.000014	− .11	− .09	− .22	− .07		
1100	.000325	− .08	− .07	− .15	− .06	+ .08	− .15

A consideration of these data confirms the theoretical prediction as to the complex character of the phenomena. In view of the almost universal neglect of this source of error by earlier investigators the magnitude of the error is surprising and disconcerting. The errors rise to 0.51% in the extreme case and errors of more than 0.1% are numerous. Other similar experiments which are not published in detail indicate that the errors increase with the increase of resistance being measured. This may be largely responsible for the difficulty found by many experimenters in the past in obtaining concordant results with high resistances, which has forced most experimenters to design their cells so as to give moderate resistances. These errors are appreciable in most cases even with the resistance in the cell as low as 300 ohms.

The error due to grounding the thermostat seems to be the most important. The effect of grounding was increased by moving the cell near the walls of the tub. In all of our measurements the effect of grounding the thermostat was to increase the apparent resistance. The error due to the capacitance by-path seems to take second rank in most cases. The error also varies from cell to cell but the correlation of these variations with the geometry of the cell is not clear. The large errors with cell C which is intermediate in its design are puzzling.

A quantitative interpretation of these data is beyond our powers at present and there are many anomalies for which a clear explanation is lacking. Interchanging the lead wires to the cell in some cases had a marked influence on the error. The grounding of the tub also had a marked influence upon the necessary adjustment in the grounding of the bridge and upon the reactance balance in the bridge proper.

But since we have a single remedy for all three errors which is theoretically sound and which is shown above to give results independent of the frequency and of grounding on all cells except those with very low cell constants, we have thought it unnecessary for our present purposes to analyze further the relative importance of each of these errors. We have decided, therefore, that for precision measurements of the conductivity of solutions, oil must be used instead of water in the thermostat and the drawbacks of oil must be tolerated or remedied as much as possible by a reconstruction of the stirring mechanism and regulators and heaters and by adding cooling coils to take the place of the cooling effect of evaporation in a water thermostat.

Conditions of Balance of the Bridge Analyzed

We will now substitute $Z = R + jX$ in the general condition of balance of the bridge, $Z_1/Z_2 = Z_3/Z_4$, giving

$$\frac{R_1 + jX_1}{R_2 + jX_2} = \frac{R_3 + jX_3}{R_4 + jX_4} \tag{3}$$

Clearing of fractions, remembering that $j^2 = -1$, and separating the horizontal and vertical components gives

$$R_1R_4 - X_1X_4 = R_2R_3 - X_2X_3, \text{ and} \quad (4)$$

$$R_1X_4 + R_4X_1 = R_2X_3 + R_3X_2 \quad (5)$$

which are conditions that must be satisfied to obtain a sharp balance of the bridge. It is generally assumed that at balance

$$R_1R_4 = R_2R_3 \quad (6)$$

but this in general is not true, and will only be true if the precautions which are shown below to be necessary are observed. It will be proved below that the apparatus commonly used is imperfect in this respect.

In the light of these equations there are three possible plans of bridge design and operation.

1. Construct the bridge so that both the resistance and reactance are known in three of the arms, that is, in the two ratio arms and in the arm containing the resistance box, and then both the resistance and reactance of the cell can be computed from the two equations of balance. Or, expressed mathematically, if R_1, R_3, R_4, X_1, X_3 and X_4 are known, R_2 and X_2 can be computed from the two conditions of balance [Equations (4) and (5)]. This is the method suggested by Taylor and Acree. Although this method is theoretically sound there are serious experimental difficulties in carrying it out. The reactance is a function of inductance, capacitance and frequency. If the resistance, inductance and capacitance are all in series, then $X = L\omega - 1/C\omega$, where X is the reactance in ohms, L the inductance in henrys, C the capacitance in farads, $\omega = 2\pi f$, and f is the number of cycles per second. If the capacitance is in parallel with the resistance, a more complicated relationship holds which will be explained below.

There may be both inductance and capacitance in each arm and it is difficult to measure these quantities with precision, especially in the presence of each other and of a high resistance. Moreover, the frequency would have to be measured or otherwise known accurately whenever the bridge is used, which would add undesirable complications to the experiments. Furthermore, if R_2 must be computed from Equations (4) and (5), the bridge cannot be made direct reading.

2. Equation (4) can be transformed into

$$R_2 = \frac{R_1R_4}{R_3}\left(1 - \frac{X_1X_4 - X_2X_3}{R_1R_4}\right) \quad (7)$$

where the expression inside the parentheses may be regarded as a correcting factor. It is obvious that this correcting factor should be avoided if possible but it should be avoided by designing the bridge so as to make the correction negligible, not merely by ignoring it as is the common practice.

It is evident from Equation (7) that if the bridge can be designed and built so that the reactances of any two adjacent arms (for instance, the two ratio arms 3 and 4) are negligible so that we can write $X_3 = X_4 = 0$, then the correcting factor becomes 1 and drops out. This means that the two ratio arms should be pure resistances free from inductance and capacitance; but it would be very difficult to carry out this ideal in practice, especially if it is desired to make the ratio arms variable in resistance.

However, it would be a mistake to assume from Equation (7) that if $X_3 = X_4 = 0$, then the reactance in arms 1 and 2 is a matter of indifference because Equation (5) must also be satisfied at balance. If we substitute $X_3 = X_4 = 0$ in Equation (5), we obtain $R_4X_1 = R_3X_2$. Then if we have an equal arm bridge $R_3 = R_4$ and therefore $X_1 = X_2$ is a condition of balance; but X_2 is the equivalent series reactance in the cell which is due to capacitance and which cannot be made equal to zero rigidly (although we have found means to reduce X_2 substantially below the usual previous practice as will be explained in the second paper of this series), therefore a variable condenser must be placed in arm 1 in order to bring $X_1 = X_2$.

3. Even if the ratio arms cannot be constructed so that they have no reactance, there is an advantage in making them as nearly as possible identical in resistance and reactance. Equations (4) and (5) can readily be transformed algebraically into the following forms

$$R_1R_4\left(1 - \frac{X_1X_4}{R_1R_4}\right) = R_2R_3\left(1 - \frac{X_2X_3}{R_2R_3}\right) \tag{8}$$

$$R_1R_4\left(\frac{X_1}{R_1} + \frac{X_4}{R_4}\right) = R_2R_3\left(\frac{X_2}{R_2} + \frac{X_3}{R_3}\right) \tag{9}$$

but a balance may be obtained without satisfying the relationship $R_1R_4 = R_2R_3$, as may be shown in the following manner. Even if $R_1R_4 \neq R_2R_3$, dividing (9) by (8) gives

$$\frac{\dfrac{X_1}{R_1} + \dfrac{X_4}{R_4}}{1 - \dfrac{X_1X_4}{R_1R_4}} = \frac{\dfrac{X_2}{R_2} + \dfrac{X_3}{R_3}}{1 - \dfrac{X_2X_3}{R_2R_3}} \tag{10}$$

which is a condition which must be met to secure a balance. But X_1/R_1 is the tangent of the angle of phase displacement in arm 1, or the tangent of the angle by which the voltage leads the current in arm 1, or

$$\tan\theta_1 = X_1/R_1 \tag{11}$$

Therefore the above condition of balance may be written

$$\frac{\tan\theta_1 + \tan\theta_4}{1 - \tan\theta_1\cdot\tan\theta_4} = \frac{\tan\theta_2 + \tan\theta_3}{1 - \tan\theta_2\cdot\tan\theta_3} \tag{12}$$

and hence by a general rule of trigonometry

$$\tan(\theta_1 + \theta_4) = \tan(\theta_2 + \theta_3) \tag{13}$$

or

$$\theta_1 + \theta_4 = \theta_2 + \theta_3 \tag{14}$$

is a condition which must be met to secure a balance. This condition may be realized experimentally even if R_1R_4 is not equal to R_2R_3.

From an inspection of equations (8) and (9) it will be evident that the relationship $R_1R_4 = R_2R_3$ (which is commonly but erroneously assumed to be true at balance in any bridge) cannot be true unless both of the following relationships hold:

$$\frac{X_1X_4}{R_1R_4} = \frac{X_2X_3}{R_2R_3} \text{ and } \frac{X_1}{R_1} + \frac{X_4}{R_4} = \frac{X_2}{R_2} + \frac{X_3}{R_3} \tag{15}$$

and it is easy to show by algebraic analysis that both of these relationships cannot be true unless either

$$\text{(a)} \quad \frac{X_1}{R_1} = \frac{X_2}{R_2} \text{ and } \frac{X_3}{R_3} = \frac{X_4}{R_4}, \text{ or} \tag{16}$$

$$\text{(b)} \quad \frac{X_1}{R_1} = \frac{X_3}{R_3} \text{ and } \frac{X_2}{R_2} = \frac{X_4}{R_4} \tag{17}$$

An equivalent way of stating the conditions that must be met to make the simple relationship $R_1R_4 = R_2R_3$ valid is

$$\text{(a)} \quad \theta_1 = \theta_2 \text{ and } \theta_3 = \theta_4, \text{ or} \tag{18}$$

$$\text{(b)} \quad \theta_1 = \theta_3 \text{ and } \theta_2 = \theta_4 \tag{19}$$

It will readily be seen that this is a special case of the general condition of balance deduced above. Therefore, the conclusion of this analysis may be stated as follows. The simple relationship $R_1R_4 = R_2R_3$ is valid only if the bridge has been so constructed and balanced that the phase angle between the voltage and the current is the same in two pairs of adjacent arms of the bridge. (If this condition is not met then the sum of the phase angles in the two pairs of opposite arms must be equal and Equations (4) and (5) must be used to compute R_2.) One-half of this requirement to make $R_1R_4 = R_2R_3$ can be met by making the two ratio arms as nearly as possible pure resistances and as nearly as possible identical in resistance and construction so that any unavoidable reactance will be the same (that is, $X_3/R_3 = X_4/R_4 =$ very nearly zero). The reactance in the cell (X_2) should be made as small as possible but in general cannot be reduced to zero, and therefore provision must be made to introduce a controllable reactance (X_1) into the arm containing the variable resistance R_1. Then at balance $X_1/R_1 = X_2/R_2$ and $R_1R_4 = R_2R_3$ and, since $R_3 = R_4$, therefore $R_1 = R_2$.[12]

A bridge built in this way can be made direct reading since the unknown resistance of the cell, R_2, will be the same as the reading of the box, R_1. This is a very great advantage in the practical use of the bridge as it avoids the calculations necessary with bridges using variable ratio arms.

The foregoing theoretical analysis was stimulated by some experiments on the slide wire which is made by Leeds and Northrup for use as the variable ratio arms of a bridge (No. 4258 of their catalog No. 48, 1924)

[12] It should be clear that R_1 and X_1 (R_2 and X_2) are that pure resistance and that pure reactance which when placed in series are electrically equivalent (that is, give the same impedance and phase angle) to the impure resistance and the impure capacitance actually used even if connected in parallel. (See page 1075.)

and which has been much used in precision work, although it has also been criticized by others.[13] This bridge has a wire wound in a helix with ten turns each 15 cm. in diameter and with extension coils at each end and a sliding contact attached to the cover which moves up and down with the slider. The helix is the geometrical form most favorable for creating inductance and there is a heavy mass of metal in the center of the helix in which weak eddy currents will be generated, thus dissipating electrical energy as heat outside the bridge circuit proper and influencing the effective alternating current resistance of the helix. This inductance, although equally divided between the ratio arms when the slider is at the mid-point, is unequally divided with any other setting and the asymmetry is a function of the setting of the slider. Moreover, in this instrument there is mutual inductance between the two ratio arms. It becomes of interest, therefore, to determine whether or not this unbalanced inductance is great enough to cause an error in the measurement of the resistance and whether or not it can be compensated by capacitance without introducing an error in the resistance balance.

In the older form of this instrument the drum is of marble and the cover is of metal electrically connected with the sliding contact, thus introducing some capacity as well as a path for induced currents. The end coils are wound in four sections apparently according to the specifications of Curtis and Grover.[14] In the newer and supposedly improved form of the instrument the drum and cover are of Bakelite and the extension coils are apparently bifilar wound in two layers on thin wooden spools (see the section below on resistances). As compared with the older form the capacitance in the coils is presumably greater and the capacitance in the cover less; but any attempt to compensate inductance by a capacitance in the instrument has the drawback that inductance and capacitance are different functions of the frequency.

In the experiments recorded below the newer type of slide wire with the extension coils in the circuits was used as the ratio arms. The wire had a resistance of 6.60 ohms and each extension coil 30.1 ohms. Arm 2 consisted throughout of 30,000 ohms in a good resistance box shunted by an air condenser set so that there was approximately 55$\mu\mu$f. capacitance in the condenser. Arm 1 consisted of a variable resistance box of the same type shunted by a similar calibrated condenser. In the successive experiments this box was adjusted so as to give readings at various points on the slide wire. The exact balance was next found using direct current and a galvanometer. Then without changing either resistance, alternating current of 2400 cycles was substituted, the galvanometer was

[13] See especially Morgan and Lammert, THIS JOURNAL, **48,** 1231 (1926), and other references given there.

[14] Curtis and Grover, *Bull. Bur. Standards,* **8,** 495 (1912).

replaced by a telephone and a new balance obtained by a slight movement of the slide wire and adjustment of the condenser in arm 1. The following table shows difference between the alternating current and direct current reading in per cent. and the approximate capacitance in arm 1 at balance. A. C. error is error in measuring R_2 (assuming R_1 to be known) by the use of A. C. (2400 cycles) as compared with direct current. R_2 is computed as usual by the simple formula $R_1R_4 = R_2R_3$.

TABLE II

TEST ON LEEDS AND NORTHRUP SLIDE WIRE WITH 2400 CYCLES

Slide wire reading with D. C.	Slide wire reading with A. C.	Capacitance in arm 1 in $\mu\mu$f.	A. C. error, %
0.387	0.367	104	−0.082
2.757	2.748	75	− .036
4.082	4.079	59	− .012
4.804	4.805	...	+ .005
4.930	4.930	49	.000
5.174	5.175	45	+ .004
5.753	5.757	40	+ .016
7.313	7.324	29	+ .044
9.477	9.500	24	+ .092

These experiments show that with alternating current there is a systematic variation in the capacitance required in arm 1 and also show that there is an error in the bridge setting which is a function of the position of the sliding contact; it amounts to 0.1% at the ends of the bridge and cannot be compensated by the condenser without an error in the resistance balance.

We have made many similar experiments with variations but it does not seem worth while to publish these data in detail because the final outcome was a decision to reject this type of instrument entirely in favor of a better form which we have devised. These results will, therefore, be given only in the form of curves in Figs. 4 and 5. Curve A is the plot of the data given above. Curve C shows the results with 1000$\mu\mu$f. in arm 2 instead of 55$\mu\mu$f. The results of using the metal cover from the older instrument with the helix and extension coils of the newer instrument, with 55$\mu\mu$f. in arm 2 are shown in Curve B and with 1000$\mu\mu$f. in Curve D. This is an improvement. Fig. 5 gives similar data with the older form of instrument, with low capacitance in arm 1 (Curve H) and high capacitance (Curve F); and with the Bakelite cover belonging to the newer instrument on the old base with low capacitance (Curve G) and high capacitance (Curve E).

That this effect was due to the helix and not due solely to differences in behavior of the resistances used in arms 1 and 2 was proved by a similar experiment with a long straight slide wire which gave no such systematic variation. In the experiments with the straight wire slight variations between the direct and alternating resistance were found which depended upon the kind of box used but were not greater than 0.005% with the particular boxes used in the experiments recorded above and did not show the same systematic variation with the setting. The greater errors with the helical slide wire evidently show that this form of ratio arm is defective.[15] Evidently in this instrument in which a helically wound slide wire is used as a part of the ratio arms the phase angles in two ratio arms are not equal and independent of the setting, and the necessary conditions to permit the computation of the resistance by the simple formula, $R_1R_4 = R_2R_3$, are not satisfied with this apparatus. Moreover, the errors introduced by this defect are a function of the frequency, and therefore any apparent changes of resistance with frequency found by the use of this bridge are of questionable validity.

The presence of appreciable and variable reactance in the ratio arms obscures the interpretation of the reactance balance so that it has been ignored by most chemists.[1b,c] With our new form of bridge in which this disturbance of the reactance is eliminated the amount of capacitance required in arm 1 (C_1) becomes a measure of the reactance in the cell which is a function of cell design, method and extent of platinization

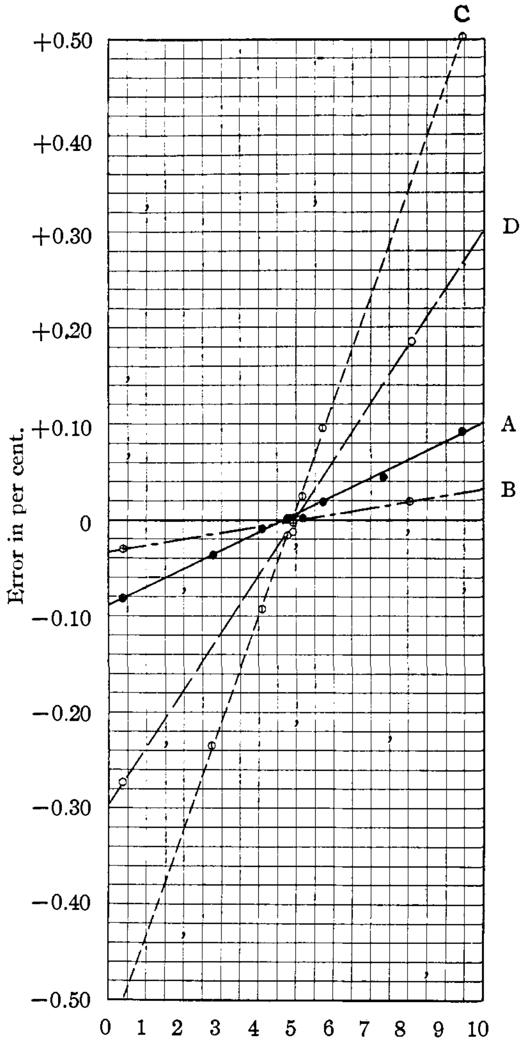

Fig. 4.—Errors caused by helical slide wire—Bakelite drum.

[15] Of course this criticism does not apply at all to the use of a helix of similar construction in the Type K Potentiometer which is intended for use with direct current.

and the frequency. As will be explained in detail in the second paper in this series, the reactance balance has given us a measure of the quality of the platinization and has enabled us to devise a procedure for platinizing which gives an improvement in the results.

The Reactance Balance

In general there is some unavoidable capacity in the cell causing reactance (X_2), and, therefore, even with identical ratio arms some reactance must be introduced into arm 1 (X_1) so that $X_1/R_1 = X_2/R_2$ in order to obtain a sharp balance. This can be accomplished theoretically in three different ways.

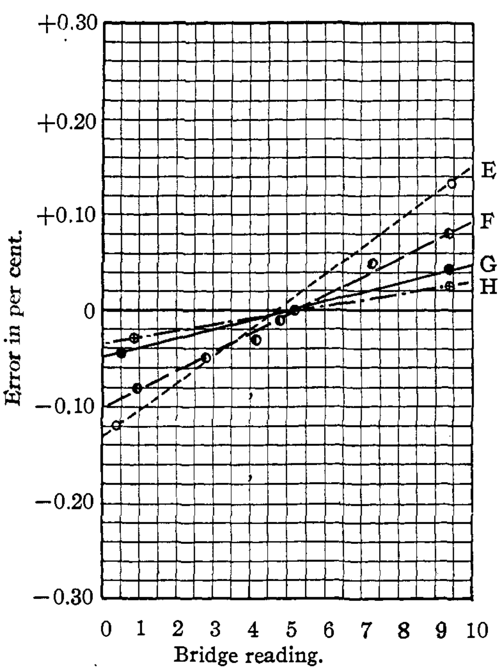

Fig. 5.—Errors caused by helical slide wire—marble drum.

1. Introduce inductance into the same arm of the bridge as the cell to compensate for the capacitance and thus make the reactance zero, as was done by Taylor and Acree. This method has the drawbacks that (a) it is difficult to construct a variable inductance whose resistance does not change appreciably with the frequency and the setting (so far as we know no such instruments are on the market); (b) a correction must be applied for the resistance of the variable inductance, and it is difficult to determine this A. C. resistance accurately in the presence of the inductance; (c) such variable inductances have a variable magnetic field which may influence the rest of the bridge and introduce errors.

2. Put a variable capacitance in series with the resistance box. This method is in practice not useful because the capacity required is enormous.

3. Put a variable capacitance in parallel with the resistance box. This is the method which was suggested by Kohlrausch and is generally used. In our judgment it is better than either of the alternative methods; but the theory of condensers indicates that there may be sources of error in this arrangement, and therefore it is important to determine whether with the available condensers at the working frequencies and resistances

the errors introduced thereby are great enough to require a correction to the box reading.

When a condenser is connected in parallel with a resistor, the resistance of the combination for alternating current is less than the direct current resistance or, in other words, even a perfect condenser has a shunting effect which diminishes the effective resistance. Furthermore, the condenser may not be perfect but may dissipate a significant amount of energy as heat in the dielectric. There may also be leakage along the surface of the insulator, which acts as an additional shunt. This will commonly be negligible except in very humid weather.

Such a real condenser may be considered as an ideal perfect condenser with a high resistance, R_P, in parallel. In a well-designed air condenser this parallel resistance depends primarily on the design and materials of the insulators used and not on the setting of the plates, and is therefore essentially a constant for any given instrument, independent of the setting; but the parallel resistance is inversely proportional to the frequency.

We may consider the arm 1 as being composed of three branches in parallel: the resistance box, R_R, an ideal perfect variable condenser, C_1, and a constant high resistance, R_P. The parallel resistance of the condenser, R_P, can be measured easily with a capacity bridge. In a good low loss condenser such as may be purchased it should be at least 10^9 ohms at 1000 cycles. The influence of the condenser resistance may be computed by the formula

$$R = R_R\left(1 - \frac{R_R}{R_P} + \dots\right) \tag{20}$$

Therefore, if R_P is 10^9 it may be neglected without producing an error greater than 0.001% if R_R is not greater than 10,000 ohms. In the condenser which we used R_P was found by measurement to be 3×10^9 ohms and therefore the effect of its parallel resistance was negligible in all measurements up to 30,000 ohms at 1000 cycles and up to 10,000 ohms at 3000 cycles.

It now remains to consider the shunting effect of a perfect condenser whose capacitance is C and reactance $X_c = 1/\omega C$. According to the law of parallel branches

$$\frac{1}{Z} = \frac{1}{R_R} + \frac{1}{jX_c} \tag{21}$$

This may be transformed algebraically into

$$Z = R_R\left(\frac{X_c^2}{R_R^2 + X_c^2}\right) + jX_c\left(\frac{R_R^2}{R_R^2 + X_c^2}\right) \tag{22}$$

where the first term is the equivalent series resistance of the combination and the second term gives the equivalent series reactance of the combination. Therefore, unless R_R^2 is negligible in comparison with X_c^2, a correction must be applied to the reading of the resistance box, R_R, on account of the shunting effect of the parallel condenser. But we may write $X_c^2 = 1/C^2\omega^2$ and therefore the correcting factor becomes $1/(1 + R_R^2C^2\omega^2)$. Therefore with sufficient accuracy

$$R = R_R(1 - R_R^2C^2\omega^2 + \dots) \tag{23}$$

We have found that with our improved bridge the neglect of this correcting factor will not make an error of as much as 0.001% except under extreme conditions, but it may become appreciable at high resistances, high frequencies or with unplatinized electrodes which require a high parallel capacitance in another arm to balance their reactance. Thus if the condenser reading is 100$\mu\mu$f. and the resistance 30,000 ohms and the frequency 2500 cycles, this factor becomes 1/1.0022, so that an error of 0.22% would be made by ignoring this correction. But if 50 $\mu\mu$f. were required while measuring 10,000 ohms with 1000 cycles, the factor would be 1/1.00001, or an error of only 0.001%. The following table shows the capacitance which may be present as a shunt across the resistance box without causing an error of more than 0.001% from this cause at the resistances and frequencies indicated.

Table III

Capacitances in Shunt which Require a Correction of 0.001%

Resistance	Capacitance in micromicrofarads at 1000 cycles	at 2500 cycles
100	5000	2000
500	1000	400
1000	500	200
5000	100	40
10,000	50	20
30,000	17	7

Very few of the previous workers on conductivity record the capacitance required to adjust their bridges to balance and therefore it is impossible to determine whether or not this error was significant, but it is a function of the resistance, of the frequency and of the capacitance, and the latter is a function of the cell design and of the grounding of the thermostat. Therefore, any conclusions drawn by earlier workers as to an apparent change of cell constant with frequency or with change of concentration of the solution contained therein cannot be accepted without reserve pending further examination with the improved bridge and with an allowance if necessary for this source of error. Such an experimental study is now in progress in this Laboratory.

The cell itself contains a reactance and therefore it might be argued that the effective resistance of the cell is changed in the same way as the resistance shunted by a condenser in arm 1, so that these effects would compensate each other and make a correction unnecessary. Whether this is true or not depends on the mechanism which produces the reactance in the cell. If the capacitance of the cell is due to a gas film on the electrodes then this is in series and requires no correction. Reversible polarization is also probably equivalent in electrical effect to a series capacitance although it may not be the same function of the frequency as a condenser and it may not be harmonic. True geometrical capacitance between large electrodes close together is presumably in parallel with the resistance. This matter will be discussed more in detail in the second paper of this series. It is generally considered that in a cell the capacitance and resistance are in series and the fact that variations in frequency require variations in capacitance in arm 1 to secure a balance indicates that the mechanism of the capacitance in the cell is different in the cell than in arm 1. Whatever decision is finally made about the capacitance in the cell, it seems best to apply the correction in arm 1 if it is significant..

Resistance Boxes

Much to our astonishment and dismay none of the resistance boxes which were available to us proved to be entirely suitable for work of the precision for which we were aiming. The study of the cause of the defects and the design and construction of an improved box caused a considerable and unexpected delay in our program. The resistance box is probably the most important part of the bridge because it is the working standard on which all of the measurements depend.

In our preliminary experiments, after every part of the earlier bridge except the resistance boxes had been investigated and perfected, it was found that the A. C. balance was different from the D. C. balance. This difference was found in all cases in which two boxes of different make or type were compared with 10,000 ohms or more in use and in a few cases with resistances as low as 1000 ohms. We did not detect the effect with the 100 ohm coils except in one box of poor quality. By interchanging the two resistance boxes it was proved conclusively that the trouble was in the boxes rather than in the bridge. Since the balance with direct current doubtless gave the true relative resistances, the deviation when using alternating current must have been due to some error which we call the alternating current error. For example, in one series of experiments we compared a box made by Leeds and Northrup containing Curtis coils, Type 4238 (hereafter called Box C), with a five dial box made by the General Radio Company, Type 102 (Bulletin 2050), which was supposed to be suitable for this work (called by us Box D). At this stage of our work we assumed that the Curtis coil box was free from A. C. errors. (This assumption was later proved to be very nearly although not rigidly true. See Table IV.) The resistance of the 10,000-ohm coil in box D was 2.5 ohms less when measured with 2400 cycles than when measured with direct current, or its A. C. error was -25 parts per 100,000. In this box there was a wire leading from one binding post to the other end of the box which passed very close to the coils and other wiring. After this wire had been removed and replaced by another at as great a distance from the other wires and coils as the space inside the box permitted, but without changing anything else, the error was -1.1 ohms. After removing the varnished cotton insulation from the wiring inside the box the error was -0.5 ohms. The leads from the 10,000-ohm coil to the contact studs in the box were entirely disconnected and the leads connected directly to the bridge. The error was then +0.2 ohms (+2 parts per 100,000) compared with the 10,000-ohm Curtis coil as mounted in its box. This reversal of the sign was of great interest as it suggested that the Curtis box which we had been using as a standard of reference may have an error. Then the 10,000-ohm G. R. coil was removed and mounted by itself on a hard rubber panel in the same manner as in the box. This coil and the Curtis coil in its box were now identical. Since the mounting could not have improved the coil this indicates that the Curtis box must have a small negative error. Furthermore, this G. R. coil had been previously measured in its box in a mounting similar in all respects except that other coils were appended thereto and then gave an error of −0.5 ohms. This indicated that appended coils which were connected at one end to the coil measured but which were not in the circuit proper were nevertheless capable of causing an alternating current error.

In order to determine the magnitude of these errors and to locate them definitely and in order to determine their cause, it was necessary to have some standard of reference so designed as to be as free as possible from these errors.

The most nearly pure resistance is a short, straight, thin wire of high specific resistance. We realized this in the form of a thread of mercury in an extremely fine capillary tube of Pyrex glass. A piece of small bore, thick walled Pyrex tubing about 2.5 cm. long was sealed at each end to a tube of some 5 mm. internal diameter, the central portion was heated until it was about to collapse and then quickly drawn out to about 40 cm., thus giving a very fine capillary tube. The end tubes were then bent at right angles to the capillary for convenience in filling. Mercury was then put in one end tube and attached to a source of compressed air at a pressure of 90 pounds per square inch. About half of the tubes proved to be completely closed, whereas others had too coarse a capillary to be useful. The best of many required several hours before the mercury appeared at the other end of the tube and when measured was found to have a little more than seven thousand ohms' resistance. Several others having smaller resistance were also made. These tubes were then mounted on a suitable frame for mechanical support and immersed in oil in order to control the temperature without introducing the undesirable secondary effects which would have been caused by mounting in water. These mercury threads have a high temperature coefficient, a low heat capacity, and poor heat conductivity through the relatively thick glass walls; they do not remain constant over long periods and cannot be adjusted to convenient round values of resistance; but in spite of these drawbacks there is a strong theoretical presumption that they have the same resistance with direct current as with alternating current up to at least 3000 cycles and, therefore, they have proved to be very useful in testing the behavior of resistance boxes with alternating current.

Then with the aid of these mercury threads and of our new bridge, which was built after the preliminary experiments described above, we were able to determine the difference between the A. C. and D. C. resistances of the various boxes available to us. Some of the results are shown in Table IV.

Box A. A Leeds and Northrup plug-box type, which is not designed for use with alternating current and is not even listed in their Catalog No. 48, "Apparatus for Measuring Conductivity of Electrolytes." These boxes have been used for the purpose and it was therefore of interest to determine the error in this type when used with alternating current.

Box B. A new type of box made by Leeds and Northrup, Type No. 4784, for use with alternating current. It is a six decade dial box with all switches enclosed inside the box. It is well designed mechanically.

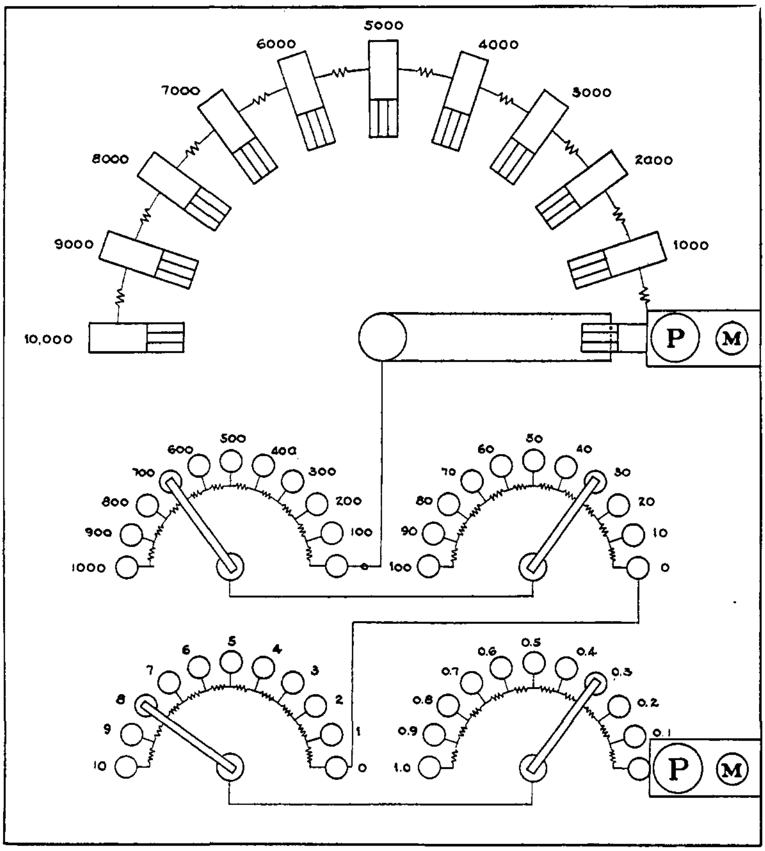

Fig. 6.—Resistance Box E.

Box C. A resistance box built by Leeds and Northrup, Type No. 4238, containing Curtis coils of manganin and recommended by them for use in measuring the conductivity of electrolytes. It is not a dial box and the leads from each coil are brought to separate binding posts so that any coil not in use is disconnected from all others. It covers the range 1000–40,000 ohms in steps of 1000 ohms. It is an inconvenient box to use, especially in a direct reading bridge. It is the box which served as our provisional standard referred to above.

Box D. A box built by the General Radio Company, which has been used in the preliminary experiments and improved by modification. In addition to removing the varnished cotton insulation and rearranging the internal wiring as described above, half of the 10,000-ohm coils had been removed and the remainder attached to the terminals in such a way that the 10,000-ohm coils which were not in use were not appended to the coils which were being used. It had in addition four lower decades with dial switches connected as usual, so that the coils not selected for use by the switches are appended. The 100-ohm and 1000-ohm coils were wound by the method suggested in principle by Ayrton and Mather[16] and perfected by the General Radio Co. To make a 1000-ohm coil by this method an insulated manganin wire having 2000 ohms resistance is wound on a thin Bakelite card with spaces left between turns equal to the diameter of the wire.

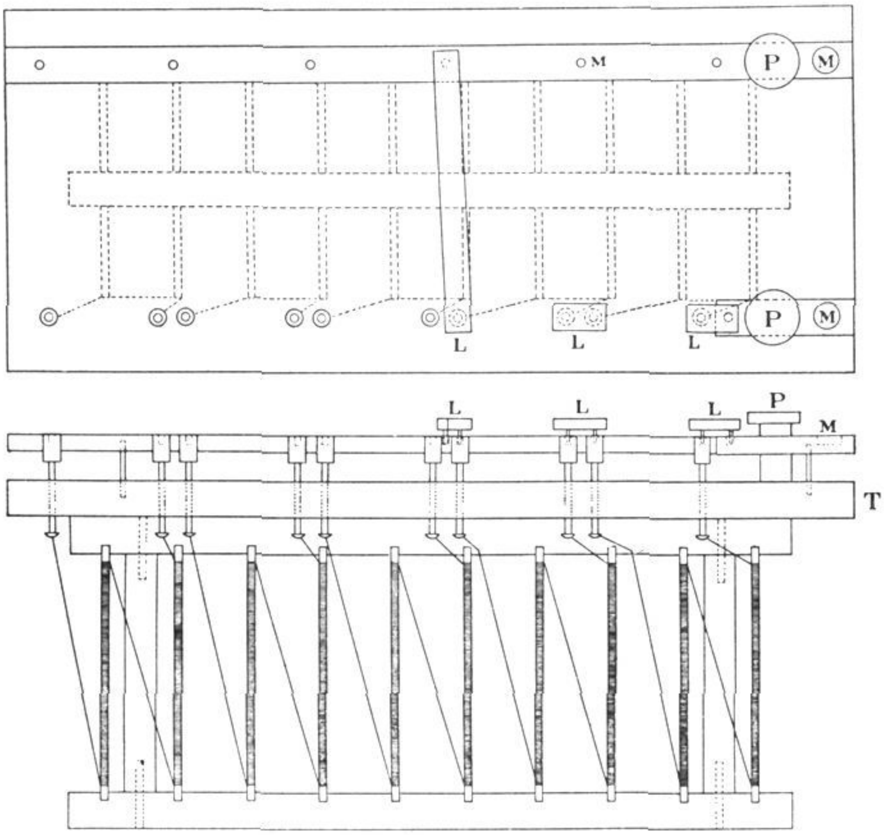

Fig. 7.—Resistance Box F.

Then another similar wire is wound on the same card starting at the same end as the first wire but rotated in the opposite direction so that on the edge of the card the second wire fills the spaces left between the turns of the first wire. These two wires of course cross each other twice in every turn. These two wires are then connected at the ends so that they are electrically in parallel. The inductance of the coil is low because the two portions oppose each other inductively and because the area enclosed by the coil is small. The distributed capacity is low because the adjacent turns are at nearly the same potential during use. The 10,000 units were each made up of two 5000-ohm coils in series, wound inductively on thin Bakelite cards. All these coils were made of manganin.

Boxes E and F. Two new boxes built in our shop which are described in detail below and shown in Figs. 6 and 7. The coils were similar to those in box D, the only difference in the boxes being in the mounting and switches.

[16] Ayrton and Mather, *Proc. Phys. Soc.*, **11**, 269 (1892).

TABLE IV

ALTERNATING CURRENT ERRORS IN CERTAIN RESISTANCE BOXES

A. C. RESISTANCE—D. C. RESISTANCE IN PER CENT.

Box	Resistance measured	Error at 1100 cycles	Error at 2400 cycles
A (L & N plug type)	5000	−0.012%	−0.032%
B (L & N dial new type)	5000	− .002	− .003
	9000	− .005	− .007
	10,000	− .006	− .011
	20,000	− .009	− .016
	30,000	− .013	− .019
Unmounted 10,000-ohm coil of this type		− .004	− .008
C (L & N Curtis box type 4238)	10,000	− .002	− .003
	20,000	− .003	− .004
	30,000	− .005	− .007
D (G. R. dial modified)	ten 1000 coils	− .002	− .004
	10,000	− .002	− .003
	20,000	− .006	− .008
E (Our new box) Fig. 6	ten 1000 coils	.000	.000
F (Our new box) Fig. 7	10,000	.000	.000
	20,000	.000	− .001
	30,000	− .002	− .003

These experiments showed that none of the makes of resistance box which were available to us is free from alternating current error. The best of the boxes available by purchase which was tested was the box containing Curtis coils, C, and the second best was the modified General Radio box, D. In all of the boxes the percentage error increases with the resistance. In all of these boxes (except A which was not designed for A. C.) this effect is negligible at 1000 ohms and below. The fact that these errors finally turned out to be all negative and to increase with frequency is extremely significant because it shows that the cause is dielectric loss in the insulator. Skin effects and eddy currents would make the alternating current resistance greater than the direct current resistance. A capacitance if pure would cause no error in the resistance except for the shunting effect which is probably negligible in this case (see Equation 23 and Table III); but an alternating electric field across any dielectric except air is always accompanied by an irreversible dissipation of energy as heat within the dielectric medium, commonly called the dielectric loss, which has the effect of an increase of conductance or a decrease in resistance. The error due to this dielectric loss is approximately proportional to the resistance across which it is shunted, the capacitance, the frequency and the power factor of the particular kind of substance within the electric field; or, expressed mathematically

$$R = R_R\,(1 - R_R\,C\omega\eta + \ldots) \qquad (24)$$

The resistance and frequency are not controllable factors in the design of boxes, but it should be noted that greater care must be taken with the high resistance coils.

Air has a power factor essentially zero and therefore the box should be constructed so as to bring the strong dielectric fields in air as much as possible. Some solid dielectric is, however, essential for mechanical support but care should be taken to use no more than is required to produce sufficient mechanical rigidity, to have the supports where the electric fields are weak, if possible, and to use only the better dielectrics. Conductance along the surface of the solid dielectric in condensers or resistance boxes may also cause an error but is not likely to be troublesome except on occasions when the weather is abnormally humid. Bakelite is superior to hard rubber in this respect. Coating the surface with a thin layer of paraffin helps to avoid error from this cause.

We are indebted to Professor R. F. Field of the Cruft Laboratory for making available to us the results of an investigation, as yet unpublished, on the power factors and dielectric constants of many insulators at both audio and radio frequencies. Professor Field has kindly consented to the publication of selections from his data which are especially pertinent in designing resistance boxes and condensers. These values vary only slightly with the frequency within the audio range.

TABLE V

POWER FACTORS AND DIELECTRIC CONSTANTS OF INSULATORS AT 1000 CYCLES FROM HITHERTO UNPUBLISHED MEASUREMENTS BY PROFESSOR FIELD

Material	Power factor	Dielectric constant
Sulfur	0.0001	2.7
Paraffin	.0001	2.3
Mica	.0008–0.0015	5.9–6.8
Hard rubber	.004	3.5
Pyrex glass	.0055	6.3
Transparent Bakelite	.0063	5.6
Transparent Bakelite, another specimen	.0073	5.2
Transparent Bakelite, another specimen	.026	6.2
Common sheet Bakelite	.1	8
Silk cloth	.06	2.2
Cotton cloth	.16	2.1

Hard rubber and selected specimens of transparent Bakelite are the best available materials with suitable mechanical properties for panels to support coils, terminals, switch contacts and switches.

The factor of the error due to dielectric loss which can be most readily reduced in the design is the capacitance. The capacitance is proportional to the dielectric constant of the insulator and therefore a material with low dielectric constant should be used. Hard rubber is the best of the available materials in this respect. By spreading apart the switch contacts and all connections which pass through the solid dielectric the capacitance can be reduced. The capacity between two points is inversely proportional to the square of the distance and between plates inversely proportional to the distance apart. In designing our boxes we have used a purely empirical rule that the distance between contacts, binding posts or the shafts of switches should be at least 0.04 $\sqrt{R}$ cm., where R is the resistance mounted between these same contacts. This rule applies where the areas of the conductors are small (as for example a No. 4 screw) and where there are not many of these capacitances.

The quality of the coils to be used must be considered, as well as the mounting. A capacitance inside the coil, even if compensated by inductance, may cause a dielectric loss. For the 10-ohm or lower decades any moderately good coil, such as the common bifilar winding on a wooden spool, is good enough. But the common bifilar winding is not satisfactory in the 100-ohm and 1000-ohm decades because dielectric losses become significant and because the capacitance in the box may exceed the capacitance in the cell, necessitating a condenser across the cell, which is undesirable. Fortunately, there are available by purchase two kinds of coils which are entirely satisfactory in the 100-, 1000- and 5000-ohm units. Both the Curtis coils such as are used in the Leeds and Northrup box (Type 4238 or 4656) and the coils made by the General Radio Company were found to have essentially the same resistance with direct current as with alternating current up to 2400 cycles when tested with our mercury thread resistances. The General Radio 100-ohm and 1000-ohm coils are wound according to the Ayrton principle. The 5000-ohm coils are wound inductively on flat cards of Bakelite. Two of these in series make each 10,000-ohm unit. The Curtis coils which we tested were adjusted more closely to their nominal values than others but this is a matter of convenience rather than precision; the greater care in adjustment and the more complicated method of winding make the Curtis coils much more expensive. In all of these coils the wires are so thin that skin effects are negligible at the frequencies of interest to us.

Akin to the error caused by dielectric loss in the insulation is the error caused by appended coils. In the usual form of switch or plug box the coils which are not in use, although not in the circuit, are nevertheless attached at one end to the coils which are in use. This arrangement is unobjectionable with direct current but with alternating current it permits current to flow into the appended coils sufficient to charge the capacitance between the appended coils and the rest of the circuit, and this current reverses itself twice in every cycle. This charging current passes through the resistance of the coils themselves and therefore dissipates energy as heat and thus influences the apparent resistance. It is in effect an additional branch consisting of a small capacitance and a high resistance in parallel with the coils in use and therefore acting like a shunt diminishes the effective resistance of the combination. In Table VI are shown the results of some experiments demonstrating the existence of this source of error. Coils totaling 30,000 ohms in the General Radio box D were measured with A. C. and with D. C. with various coils appended.

Table VI

Alternating Current Errors Due to Coils Appended to 30,000 Ohms, in Per Cent.

Appended coils	Error at 1100 cycles	Error at 2400 cycles
Ten 1000-ohm Ayrtons	−0.002	−0.003
Ten 1000-ohm Ayrtons plus one 10,000 G. R.	− .003	− .006
Ten 1000-ohm Ayrtons plus two 10,000 G. R.	− .004	− .008

We were unable to detect the effect in a box containing a decade of 1000-ohm coils and three smaller decades. As the result of these experiments (only reported in part above) we decided that the coils in the 10,000-ohm decade should be completely disconnected at both ends when not in use, but that in the lower decade it was permissible to have the coils appended when not in use provided they were not mounted too close together. The possibility of errors due to dielectric loss and to appended coils is mentioned briefly by Curtis and Grover.

As a result of these experiments and theoretical analysis we concluded that the box for use in arm 1 of the bridge should meet the following specifications if possible.

1. The resistance of each coil and of any combination as mounted in the box and selected by the switches should be the same (within 0.001%) with direct current as with alternating current of any frequency up to the maximum to be used (say 3000 cycles per second) and the reactance should be as low as possible. In order to meet this specification the following conditions are necessary or desirable.

(a) The mutual capacitance between parts of the box should be low. This can be accomplished by using coils of suitable quality, mounted so as to avoid undue proximity of coils, lead wires and switch terminals, and by using insulators of low dielectric constant.

(b) Dielectric losses associated with the capacitance should be made negligible by designing the box so that strong electric fields do not occur in a dielectric other than air, by using the minimum amounts of solid dielectrics, and by using only dielectrics of low power factor.

(c) The inductance should be low, which is easily attainable by using good coils.

(d) Hysteresis and eddy current losses associated with the inductance should be made negligible by avoiding entirely the use of iron and by avoiding the presence of masses of metals of any kind within the magnetic field.

(e) The wire used in coils and lead wires must be fine enough so that skin effects are negligible; this presents no difficulty.

(f) Coils of 10,000 ohms or more must be entirely disconnected from the circuit when not in use.

Losses associated with the inductance are more easily avoidable than the dielectric losses associated with the capacitance. Therefore, in designing coils and boxes, special emphasis should be placed on keeping capacitance low and dielectric losses negligible. It should also be emphasized that the mere compensation of capacitance by inductance so that the coil has a small net reactance does not solve the problem, because such a coil or box may have an appreciable dielectric loss and therefore its effective resistance with alternating current will be different from its true direct current resistance and will be a function of the frequency.

2. The temperature coefficient of the box should be low, constant and known. Manganin and Advance wire are satisfactory in this respect.

3. For convenience the box should be of the decade type with dial switches in order that the bridge may be made direct reading by the use of equal ratio arms. In order to have the desirable range and precision it should have six decades, reading in tenths, units, tens, hundreds, thousands and ten thousands of ohms. To determine the hundredths and thousandths of an ohm we have devised a special sliding contact in the bridge which will be described below. We have found it desirable to mount the highest decade (tens of thousands of ohms) in a separate box with connections made by links dipping into mercury cups instead of dial switches in this box and have not yet found it necessary to have more than 50,000 ohms in this box, giving a total of 61,111 ohms in the two boxes. Each decade should have ten coils instead of nine as usual in order that the sum of all ten may be compared with the next higher coil during calibration.

4. The contact resistance in the switches and the resistance of the lead wires should be made as small as possible and should not vary more than 0.001 ohm during use.

5. The coils should be accurately adjusted to their nominal values. This is of relatively minor importance, however, as it is purely a matter of convenience, because any box will have calibration corrections which must be applied in precision work and it makes comparatively little difference whether these corrections are large or small. Insistence on close adjustment adds greatly to the cost of the box.

6. The coils should be so constructed, aged and protected against moisture and the fumes of a chemical laboratory that their resistance remains constant over long periods.

7. The thermo-electromotive force should be small. This is of no importance when using alternating currents but it is necessary to cali-

brate the box with direct current because the standard coils for which a Bureau of Standards certificate can be obtained are not designed for use with alternating current. Moreover, it is desirable to be able to compare alternating and direct current readings (with a metallic resistance in place of the cell as a means of proving the absence of error in the bridge). This is an argument in favor of using manganin; but if thermoelectric forces are unavoidable, error from this source can be avoided by the use of a reversing switch.

8. The switch terminals and lead wires connecting the coils and terminals must be so designed that the lead wires are included in the value of each coil in exactly the same manner for all settings of the switch and also permit each coil to be calibrated independently with the resistance of the lead wires included in exactly the same manner as in the actual use of the box.

We built two new boxes designed in accordance with these principles. One covering the range 0.1 to 11,111 ohms in steps of 0.1 ohms is shown in Fig. 6 which is a top view with the wiring shown diagrammatically. The top was made of hard rubber. The coils were made by the General Radio Company, wound on the Ayrton principle, of manganin wire. Standard General Radio dial switches were used for the 0.1-ohm, 1-ohm, 10-ohm and 100-ohm decades. The controlling factor which determines the radius of the switch for the 1000-ohm decade is the capacitance between the shaft of the switch and the contacts. This radius was 9 cm., which required a special switch. Ten coils were used in each decade instead of the usual nine. Care was taken in the arrangement of coils and lead wires inside the box to avoid dangerous proximity of wires differing greatly in potential. The terminals are provided with mercury cups, M, and binding posts, P.

The 10,000-ohm units were placed in an entirely different box (Fig. 7). The panel, T, and supports for the coils were of transparent Bakelite, which was selected because it is less hydroscopic than rubber. The panel was supported by a tight wooden box (not shown in the figure) enclosing the coils. Each 10,000-ohm unit consisted of two 5000-ohm coils wound inductively on cards of Bakelite. They were made of manganin wire by the General Radio Company. The lead wires from each end of each 10,000-ohm unit were 4 cm. apart where they passed through the panel and terminated in mercury cups. It was necessary to design the box so that any coil not in use was entirely disconnected from the circuit to avoid the effect of appended coils. Since a switch which would meet these specifications would be cumbersome and complicated we adopted a simple system of links, L, dipping into mercury cups, M, for this box. The coils in use were connected by short links and the last coil in use was connected by a long link to a bus bar across the box. With the links in the position shown in the diagram the resistance between the binding posts, P, would be 20,000 ohms. Only five 10,000-ohm units were assembled in this box as this seemed to be ample for any requirements that we could foresee. The terminals were provided with both binding posts and mercury cups for convenience and nickel plated to avoid spreading amalgam over the surface. The box when assembled and tested was found to be superior to any on the market, as is shown by the data in Table IV.

Description of the New Bridge

We have built a new bridge which is designed in conformity with the principles explained above and is also convenient and rapid in operation.

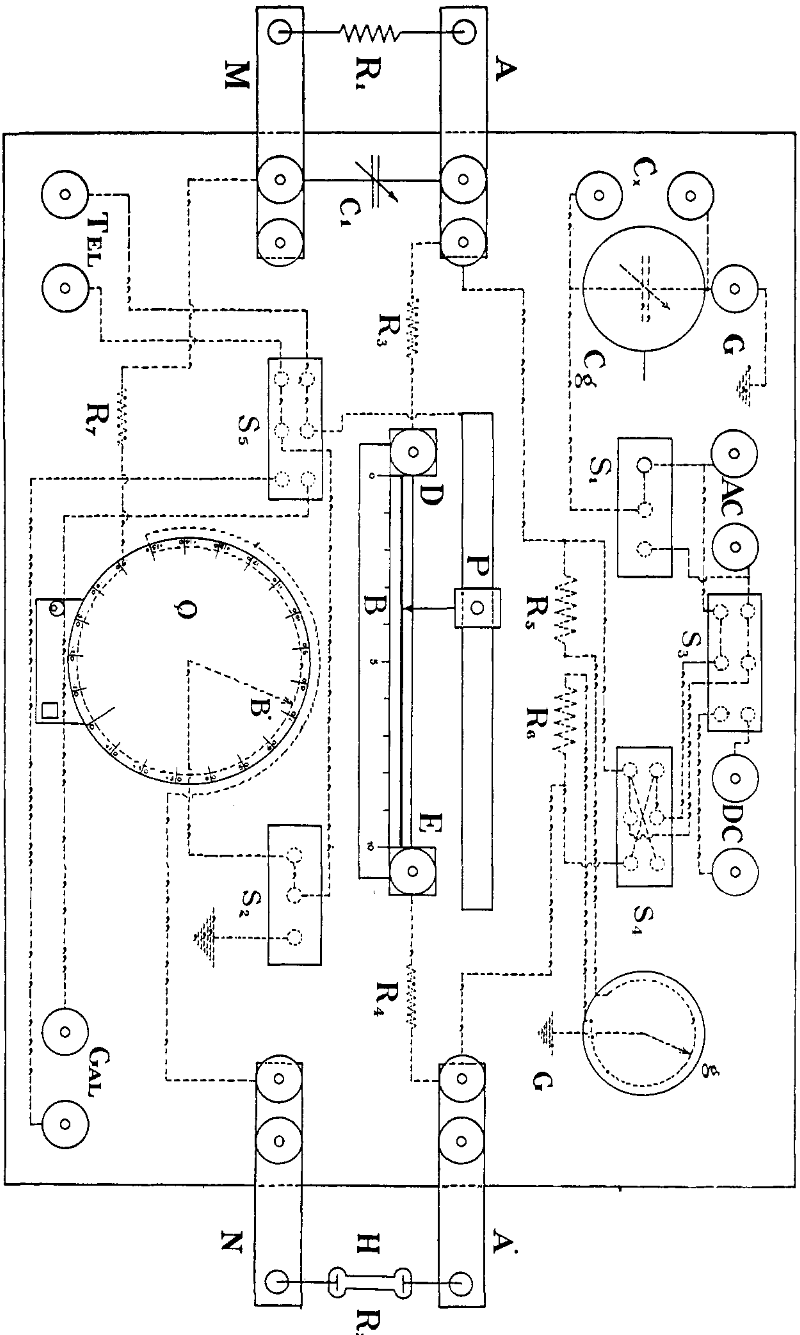
M
A
R_1
C_1
TEL
C_x
C_g
G
R_3
R_7
S_5
S_1
AC
D
P
Q
B
R_5
S_3
B'
R_6
DC
E
S_4
S_2
R_4
G
g
GAL
N
H
A'
R_2

Fig. 8.—Bridge.

The bridge consists of a flat wooden box five inches deep and 13 × 17 inches in length and breadth, with a hard rubber top which supports all of the electrical parts. The co ls, switch contacts, sliding contacts (with one exception) and ground condenser, Cg, are inside the box, protected from fumes and mechanical injury. The resistance box, R_1, is a separate unit and is connected to the bridge by heavy links dipping in mercury cups and the variable condenser, C_1, is also a separate unit and is shunted across the box. The oscillator, amplifier and telephone (or battery and galvanometer) are separate units which are connected at suitable binding posts. Everything else is built into the bridge. Fig. 8 gives the actual layout of the top of the box, showing the actual position of all binding posts, dials, scales and switches, with the wiring, where it is under the top, shown in dotted lines. Along the northern edge[17] are located the binding posts for the ground connection and for the A. C. and D. C. power lines, and a switch, S_3, to select one or the other; near at hand is the reversing switch, S_4. The double throw, double pole switches used were made by the Federal Telegraph and Telephone Company of Buffalo, N. Y., and are their Type No. 1425W. The grounding device, which is one of the novel features of the new bridge, is also placed in the northern part of the box. A variable air condenser, C_g, of $500\mu\mu$f. capacitance is mounted in the northwest corner, with dial and scale on top and plates inside. One side of the condenser is permanently connected to the post, which in turn is grounded. The other side of the condenser may be connected to either of the two alternating current power lines as may be desired by means of the switch, S_1. For ordinary use with our oscillator the capacity provided is large enough but in some abnormal cases, or when using other oscillators, we have found more capacity to be needed and we have, therefore, added two more binding posts, C_x, which make it possible to attach a larger condenser if needed. From the reversing switch, S_4, the current passes to the resistance part of the grounding device which is shunted across the line as shown. R_5 and R_6 are each a 1000-ohm coil of the Ayrton winding made by the General Radio Company. Between R_5 and R_6 electrically (and a part thereof in electric function) but placed in the northeast corner for convenience, is a manganin wire of about 0.75-ohm resistance wound in a single turn around a hard rubber cylinder with a sliding contact, g, which is always connected to ground. This slider is mounted inside the box but is controlled by a dial on the top. With this arrangement the possible variation in the ratio of R_5 to R_6 is 0.15%. This ratio must be approximately unity because $R_3 \doteq R_4$, but the ratio is also influenced by losses and leakage to ground in the lead wires from the oscillator. For most cases, including all normal uses of the bridge, this possible variation of 0.15% is ample; but in a few unusual and abnormal cases the available variation was insufficient. It would therefore be better to make the resistance in this slide wire somewhat larger. This comparatively minor defect in our final bridge is the greatest which we have yet discovered in it. The remedy is easy if we ever have occasion to use the bridge under such conditions that this fault becomes troublesome.

The adjustment of the ground balance should be made with every measurement, otherwise erroneous results may easily be obtained, especially when measuring high resistances. This is well illustrated by some experiments which will be described in more detail in the second paper of this series. These experiments were planned to determine whether or not the resistance of a solution is a function of the voltage applied or of the current density. The resistance was measured with the new bridge and then an adjustment made in the oscillator to give a higher voltage and therefore greater current density in the cell. There was an apparent change of resistance of a few thousandths

[17] The points of the compass are used for clearness and convenience in referring to the diagram, which may be regarded as a map. The actual orientation of the bridge is of no consequence.

of one per cent. but it was then found that the ground balance had changed greatly. On adjusting the ground balance correctly the bridge setting returned to its former value. Therefore without our improved method of grounding the bridge, we should have been in danger of drawing erroneous conclusions on this point. The inside of the northern third of the box was lined with sheet copper and grounded to serve as a shield for the electrical parts heretofore described. The bridge proper was not shielded.

From the ends of the shunt, R_5 and R_6, the power lines pass through a hole in the shield to the ends of the bridge proper, A and A′, which consist of heavy nickel-plated brass bars, mounted on top of the box and provided with a mercury cup and two binding posts each.

Between A and A′ are mounted the ratio arms, AB and BA′, consisting of two coils, R_3 and R_4, each a General Radio Ayrton coil of 1000 ohms mounted under the cover. These coils cannot be adjusted to exact equality and, moreover, they will change slightly with age. In order that the ratio arms may be adjusted to exact equality 15 cm. of a heavy (2 ohms per meter) manganin wire, DBE, with a sliding contact, B, is mounted between them. With this arrangement a movement of the slider of 1 mm. changes the ratio of the arms by four parts in a million. This wire is soldered to a heavy brass plate which is fastened to binding posts. Several interchangeable wires of different diameters and resistance are provided which increase the range of adjustment with this slider and adapt the bridge for special uses as a percentage differential bridge. A scale, also interchangeable, is indicated just south of the wire. This scale may be calibrated to read in percentage change in resistance or, if desired, as a differential thermometer. A sliding contact, B, makes connection with the heavy bus bar, P, and has a screw clamp which holds it in place after adjustment. The method of adjustment to make B the exact electrical center of the bridge will be described later. The resistance in the sliding contact is not in the bridge circuit proper, but only in the line to the detector.

To the south of A and A′ are two similar bars, M and N. The cell, H, is mounted in its thermostat and connected by suitable lead wires across A′ and N, as indicated in the figure. The variable resistance box, R_1, is connected across A and M by means of heavy links dipping into mercury cups. A variable air condenser, C_1, of suitable capacitance for the measurements being made is also connected across A and M. Ordinarily we use two condensers in parallel—one having a total capacitance of about $1000\mu\mu$f. made by the General Radio Company, Type 239E, and the other a small condenser made in our shop with one stationary and one movable plate capable of very fine adjustment; but some of our cells are so good that the large condenser may be removed as the small condenser is ample.

The resistance box, R_1, can be adjusted to tenths of an ohm. As a rule we prefer to use cells of high cell constant and make measurements with 10,000 ohms or more in the cell and in such case a box adjustable to tenths of an ohm gives adequate precision. It may be necessary or desirable to measure resistance as low as 100 ohms, which requires a means of adjusting the resistance continuously with a means for measuring in thousandths of an ohm. For this purpose we mount a single turn of manganin wire on a cylinder, Q, with a sliding contact, B′, which is the mid-point of the bridge. An auxiliary resistance, R_7, of the proper magnitude to bring the mid point of the resistance between M and N at the point marked 0 on the dial, is inserted between M and the slide wire. Then if the slider, B′, is at 0 the resistance between M and B′ is equal to the resistance between N and B′ and if this is the position of balance the resistance of the cell can be read off directly from the box (assuming of course that $R_3 = R_4$). But if B′ must be moved along the scale to obtain a balance then resistance is being added to R_1 and subtracted from R_2 and by proper calibration the reading of B′ on the scale can be added to the reading of the box R_1 to give the actual resistance of the cell. This makes the bridge direct reading even down to the thousandths of an ohm. Of course in actual use an additive calibration correction for imperfect adjustment of the coils in the resistance box to their nominal values will be necessary, but no cumbersome calculations by ratios are required as in the common type of slide wire bridge. The resistance in the sliding contact at B′ is not in the bridge circuit but only in the telephone circuit where it does no harm. In our instrument each division of the scale representing 0.001 ohm had a length of a little more than 1 mm. The scale is extended below the zero to −0.050 ohm and beyond the 100 to +0.150 ohm for convenience. The resistance wire and sliding contact are mounted under the cover but the dial and scale are on top. This device has given entire satisfaction in use. The very slight inductance of this single turn of wire can do no harm because, unlike the bridge criticized above, it is in the reactive arms of the bridge where it partly compensates the unavoidable capacitance in the cell.

It is difficult to exaggerate the advantage of having the bridge direct reading. The actual saving in time required by the calculations is important but by no means the chief advantage. Of greater importance is the fact that the significance of measurements can be appreciated at the time the measurements are being made instead of an hour or a month afterward, when the calculations are completed and the results tabulated. This helps tremendously in gaining an insight into a complexity of several subtle and superimposed effects.

The sliding contact B between the ratio arms is connected to switch S_5, which can be thrown so as to connect B either to the amplifier and telephone or to a galvanometer. After passing through the telephone (or galvanometer) the current returns to the other pole of S_5 and hence to the middle of switch S_2 which can be thrown during measurements so as to connect with the sliding contact, B′, or during adjustment of ground so as to connect B with ground through the telephone (with B′ entirely disconnected from anything). The amplifier is connected to the instrument by shielded lead wires which are attached to binding posts in the southwest corner. The galvanometer is connected to suitable binding posts in the southeast corner.

The adjustment of the sliding contact B so as to make R_3 equal to R_4 is accomplished as follows. Two extra coils of 1000 ohms each, which have been adjusted so as to make them very nearly equal, are connected across the gaps AM and A′N, respectively, and the slider, B′, is set at zero. Then the bridge is balanced by moving the slider, B, and the position of B on the scale noted. Next the two 1000-ohm coils are interchanged and the slider, B, moved to a new balance and this position noted. The mid-point between these two readings of B will be the true mid-point of the ratio arms. The slider, B, is then moved to the proper point and firmly clamped in place, thus making the ratio arms exactly equal. This adjustment requires only a few minutes and may be checked at frequent intervals to make sure that the coils R_3 and R_4 are not changing.

Then with B at its proper place heavy links having equal and negligible resistance are placed across AM and A′N. B′ is now moved until the bridge is in balance, which gives the true mid-point between M and N. If the scale does not read zero the scale is loosened on its shaft by turning its set screw and moved to the proper point without moving the slider and then tightened again.

The scale was then marked at intervals of 0.01 ohm experimentally without assuming that the wire was uniform. A standard 10-ohm coil was placed across the gap AM and another 10-ohm coil and an adjustable shunt placed across the gap A′N and the shunt adjusted to give a balance with the slider B′ set at zero. Then by placing a shunt of suitable magnitude (9990 ohms) across the standard 10-ohm coil the resistance of the combination was reduced by 0.01 ohm and the slider B′ moved until the balance was restored, which made it possible to mark this point on the scale. In like manner by changing the shunt the successive increments of 0.01 ohm were marked on the scale. These graduations were then subdivided into 0.001-ohm divisions.

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Summary

This paper, the first of a series on the measurement of the conductance of solutions, discusses the design of alternating current bridges and accessories, for this purpose.

1. The best source of the current is an audion tube oscillator adjustable to several frequencies, and adjustable in voltage.

2. A one- or two-stage audion tube amplifier should be used with the telephone, as the detector. The amplifier, supplemented by the other improvements, gives a sensitiveness of one part in a million.

3. The use of cells of high cell constant (length divided by cross section) is recommended so that the resistance to be measured will be high (10,000–30,000 ohms), thereby reducing polarization and heating effects in the cell.

4. All methods of grounding hitherto used are erroneous, as was proved by the fact that the position of balance may be changed by reversing the lead wires from the oscillator to the ends of the bridge. A new method of grounding which avoids this source of error has been invented and is described in detail.

5. Electromagnetic and electrostatic shielding of the bridge proper are not recommended, but shielding of the source of outside disturbances is preferable.

6. It is proved experimentally that the use of water in the thermostat and the grounding of the thermostat may result in serious errors due to three causes. The use of oil as a thermostat liquid is recommended instead.

7. The conditions of balance of the bridge are analyzed mathematically. The equation, $R_1R_4 = R_2R_3$, which is commonly but erroneously assumed to be valid in any balanced bridge, is valid only if the phase angles between the voltage and current are equal in two pairs of adjacent arms. Special care in design and construction is necessary to ensure that these conditions are satisfied.

8. It is demonstrated that with the usual type of helical slide wire

bridge serious errors may be made if the results are computed in accordance with the formula $R_1R_4 = R_2R_3$, owing to the inductance in the helix.

9. It is recommended that the ratio arms R_3 and R_4 be constructed so as to be as nearly as possible free from reactance and identical in resistance and construction. Means of accomplishing this are discussed.

10. Means of providing reactance in one arm of the bridge to balance the unavoidable reactance of the cell are discussed. Kohlrausch's device of using a condenser in parallel with the resistance box is recommended. The error due to the shunting effect of such a condenser is discussed and a formula for its calculation given. This error is negligible except under abnormal conditions.

11. The reactance balance is made significant for the study of cell design.

12. It is demonstrated experimentally that the resistance boxes available by purchase have alternating current errors in the upper ranges, that is, their effective resistance with alternating current of audio frequency is a function of the frequency and different from the direct current resistance. It is shown that coils are available in which these errors are negligible. The errors in the best of the available boxes are traced to two causes: (a) dielectric losses in the insulators, chiefly between the switch contacts but also in some cases in unnecessary insulation on the lead wires, and (b) dissipation of energy in appended coils not in use. Means for avoiding these errors have been devised.

13. The specifications of an ideal box are described in detail.

14. Two new resistance boxes superior to any on the market for this purpose were built and are described.

15. A new form of bridge designed in accordance with the above principles has been built and is described in detail. It has the following improvements over those commonly used:

(a) A new and correct method of grounding.

(b) Non-reactive ratio arms easily adjustable to exact equality of resistance.

(c) Fine adjustment of the resistance down to 0.001 ohm in the resistance arm instead of the ratio arms.

(d) The reactance balance is significant.

(e) The bridge is sensitive to one part in a million.

(f) It can be used with either direct current or alternating current and changed by merely throwing two switches.

(g) The bridge is direct reading.

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