[CONTRIBUTIONS FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS. PUBLICATION NO. 26.]

THE MEASUREMENT OF ELECTROLYTIC CONDUCTIVITY. I. THE THEORY OF THE DESIGN OF CONDUCTIVITY CELLS.

BY EDWARD W. WASHBURN.

Received September 22, 1916.

TABLE OF CONTENTS.—Nomenclature. 1. Introduction. 2. The Bridge Assembly. 3. The Distribution of the Current in the Bridge Network. 4. The Theory of Cell Design. 5. The Adjustment of the Total Current through the Bridge for a Conductance Measurement. 6. Summary. 7. Numerical Values of the Variables which Control the Cell Design. 8. Types of Conductivity Cells. 9. A Series of Cells Covering the Complete Conductance Range for Aqueous Solutions. 10. A Cell with a Minimum Volume Factor. 11. Connecting the Cell to the Bridge. 12. The Temperature Coefficient of the Cell Constant of a Conductivity Cell. 13. The Choice of the Material for Constructing a Conductivity Cell. 14. The Elimination of Polarization.

NOMENCLATURE.

A	Area of the cross-section between the electrodes.
a	$= p^3 \frac{ds}{\alpha}$
b	$= I_T{}^2 t$
C	Capacity
C_p	Capacity equivalent of polarization.
c	$= R_B + 4R_T$
d	Density of the solution.
f	Frequency of the alternating current.
I	Total current through the Wheatstone bridge network.
I_A	Current through the conductivity cell.
I_T	Audibility current of the telephone.
j	$= \sqrt{-1}$
k	Dielectric constant of the liquid in the cell.
K	Cell constant.
$\overline{L}$	Specific conductance of the solution.
l	Distance between the electrodes of the cell.
p	Percentage error due to the uncertainty in determining the correct bridge setting.
p_L	Percentage error due to lead resistance.
p_K	Percentage error in the cell constant.
p_T	$= p$, Percentage error due to heating of the cell during the measurement.
R	Resistance of the cell = that of the resistance box.
R_B	Resistance of the slide wire with its extension coils.
R_T	Resistance of the telephone.
$R_{\text{min.}}$	Minimum resistance which the cell may have.
$R_{\text{max.}}$	Maximum resistance which the cell may have.
r	Range-ratio for the cell.
s	Specific heat capacity of the liquid in the cell.
ΔT	Rise in temperature of the cell during the passage of the current.
$\Delta T'$	Fluctuation in the temperature of the bath containing the cell.
t	Time required to obtain the bridge setting (sec.).
Z	Impedance of the cell.
α	Temperature coefficient of the conductance of the liquid in the cell.
β	Coefficient of thermal expansion (linear) of the material of which the cell is constructed.
γ	Coefficient of expansion of platinum.
x_C	Condensive reactance.
x_L	Inductive reactance.

1. Introduction.—Since the appearance in 1898 of Kohlrausch and Holborn's "Leitvermögen der Elektrolyte," no comprehensive treatment of the theory and practice of conductance measurements in the case of solutions of electrolytes has appeared. During the period which has elapsed since Kohlrausch's pioneer work in this field the advances in experimental methods and apparatus have made possible a very great improvement in the precision attainable in such measurements and have also led to a more perfect understanding of some of the sources of error and the precautions necessary for their elimination.

Briefly stated the problem of improving the accuracy of the Kohlrausch apparatus for measuring the conductivity of electrolytes is simply a problem of selecting the parts of the apparatus and so disposing them with respect to one another that the whole Wheatstone bridge assembly shall approach as nearly as possible the ideal assembly required by the theory of the alternating current bridge. The principle alterations required in the apparatus itself are (1) the substitution of a high frequency generator giving a pure sure wave of a single frequency, in place of the induction coil; (2) the use of a telephone tuned to the frequency employed; (3) the use of resistance units free from inductance and capacity; and (4) a proper and efficient use of the principle of electromagnetic shielding. A number of other minor improvements have also been made but those just stated are the fundamental changes required by theory.

The writer's first successful experiments with an apparatus incorporating all of the first three changes mentioned above were made in the Fall of 1911, and a preliminary paper describing the advantages of the improved apparatus was published in THIS JOURNAL in February, 1913. Since then a number of other improvements have been made in the details of construction and arrangement of the cells and the bridge and a description of some of these can be found in Cat. 48 of the Leeds & Northrup Company, which was published in May, 1915.

In developing the improved apparatus the writer has been ably assisted by his students, especially by Dr. J. E. Bell and Mr. Karr Parker with whose assistance most of the experimental work has been carried out. It had been the writer's intention to incorporate the results of the investigations in this laboratory in a monograph which would deal rather exhaustively with the whole subject of the electrical conductivity of solutions, but owing to the transfer of the writer's activities to a new field the project will have to be abandoned. The present series of papers will, therefore, deal only with the theory of the construction, assembly and use of the apparatus as finally perfected.

As an apparatus for accomplishing its purpose it is now perfect, in the respect that the degree of precision attainable in the measurements is governed and limited solely by the accuracy with which the temperature of the constant temperature bath containing the cell can be controlled. All other sources of error which affect the precision of the measurement are negligible in comparison with this one.

The present paper deals only with the design, construction and use of the conductivity cells. The two following papers will be devoted to a discussion of the telephone as an indicating instrument and to the make-up and arrangement of the bridge assembly, respectively.

2. The Bridge Assembly.—With regard to its behavior towards an alternating current, an electrolytic cell together with its lead wires may be considered as a resistance and a capacity in series, shunted by a condenser.[1] In practice, however, the influence of polarization, which has the effect of a capacity in series with the cell, is usually eliminated by employing platinized electrodes or by using a sufficiently high frequency, or both, and hence in nearly all cases this factor may be neglected. Under these circumstances the cell and its connecting wires may be regarded as a resistance shunted by a condenser.[2]

In measuring the conductance of such a cell with the aid of a Kohlrausch slide-wire bridge, one of the arms of the bridge contains a variable

---

[1] Or according to Wien (*Ann. Phys.*, 58, 67 (1906)) as a resistance in parallel with a condenser and in series with a capacity. For the cases considered in this paper the two arrangements become identical.

[2] Assuming that its specific inductive reactance is negligible in comparison with its specific condensive reactance (the value of x_L for a water cell—Type A—exclusive of the platinum leads, is only about 0.0002 microhenry), the specific admittance of an aqueous solution for a frequency of 1000 cycles is practically equal to $\sqrt{0.197 . 10^{-14} + \bar{L}^2}$ reciprocal ohm. Evidently the admittance does not differ appreciably from the conductance until the latter falls to a very low value. Thus for $L = 10^{-6}$ (ordinary conductivity water) the admittance differs from the conductance only by 0.1%. The dielectric condensive reactance of the conductivity cell itself is thus ordinarily a *very small* quantity. Practically all of the reactance usually ascribed to the cell is due to the leads which connect it to the bridge. The general expression for the impedance of a non-polarizable cell and its leads is

$$Z = \sqrt{\frac{(R^2 + x_L^2)x_C^2}{(x_C - x_L)^2 + R^2}}.$$

Evidently, therefore, the residual reactance may be either inductive or condensive according to the arrangement of the leads. The best arrangement is twisted or twin wire leads and under these circumstances the residual reactance is condensive and the above expression reduces to

$$Z = \frac{Rx_C}{\sqrt{R^2 + x_C^2}}$$

which is an expression of the same form as that for the cell alone. In other words the condensive reactance of the twisted leads can be treated practically as though it were part of the dielectric condensive reactance of the cell. By using leads of the same length and form on both sides of the bridge the residual condensive reactance will ordinarily be on the side of the cell and the variable air condenser will then be connected across the terminals of the variable pure resistance as shown in Fig. 1.

known resistance. We shall assume that this resistance is free from both inductance and capacity and that a variable capacity is employed in parallel with it. These are the ideal conditions and are the ones which should be approximated at least, in practice.

With this understanding the ideal Wheatstone-bridge network may be represented diagrammatically by Fig. 1. A slide-wire having the resistance R_B is stretched between the points A and B. The sine-wave alternating current I of a single frequency f will be considered as entering at A and dividing as indicated by the arrows. The left arm of the bridge contains the variable resistance R shunted by the variable capacity C (an air condenser), the impedence of this arm of the bridge being Z. The current through this arm of the bridge is I_A'. The other arm of the bridge contains the cell, of resistance R and having a condensive reactance[2] equivalent to that which would result from a capacity C in parallel with the resistance R. The impedance of this arm of the bridge will be Z and the current through it will be I_A. It will be noticed that this arrangement brings the bridge setting *in the center of the wire*, where it should be in all accurate work in which a slide-wire bridge of the type indicated is employed.

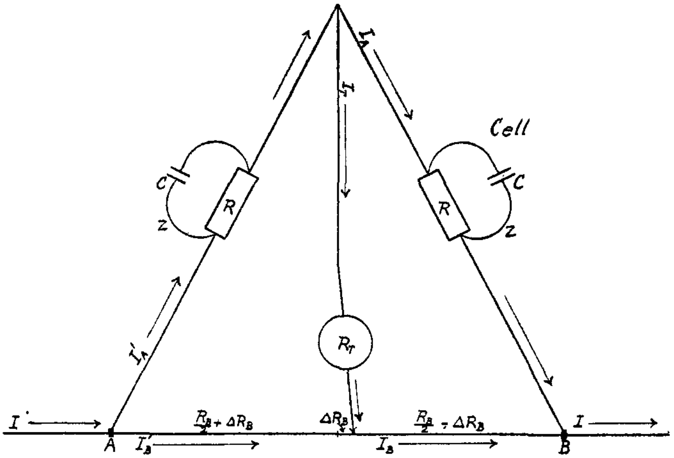

Fig. 1.—Diagrammatic representation of the ideal Wheatstone-bridge network containing a conductivity cell free from polarization.

A tuned telephone having the resistance R_T connects the sliding contact with a point between the cell and the resistance box as indicated. By the term "tuned telephone," is meant a telephone which is substantially free from reactance for the frequency employed and whose diaphragm has a natural period of vibration, for its fundamental, which is the same as that of the current.

The resistance of that portion of the bridge wire between the center of the bridge and the position of the sliding contact will be denoted by ΔR_B. This resistance is just sufficient to cause an audible sound in the telephone and the current flowing through the telephone under these conditions will be its "audibility current," I_T.

3. The Distribution of the Current in the Bridge Network.—With the aid of Kirchhoff's laws, the following expression for the total current I through the bridge may be readily obtained in the same manner as for direct currents:[3]

$$I = \frac{I_T}{2\,\Delta R_B}\left[\frac{(R_B/2 + Z)^2 + 2R_T\,(R_B/2 + Z)}{Z}\right] \tag{1}$$

where the impedence Z is, of course, a complex quantity, which in the present instance is expressed by the equation

$$Z = \frac{-jR}{2\pi fCR - j}. \tag{2}$$

If we substitute this expression into Equation 1 and separate the resulting expression into its real and imaginary parts, we find for the real part

$$I = \frac{I_T}{2\,\Delta R_B R}\sqrt{\left[{}^1\!/_4 R_B^2 + RR_B + \frac{R^2}{\dfrac{f^2k^2}{324.10^{22}\overline{L}^2} + 1} + 2R_TR + R_TR_B\right]^2 + \frac{f^2k^2}{324.10^{22}\overline{L}^2}\left[{}^1\!/_4 R_B^2 + R_TR_B - \frac{R^2}{\dfrac{f^2k^2}{324.10^{22}\overline{L}^2} + 1}\right]^2} \tag{3}$$

where k is the dielectric constant of the liquid in the cell and $\overline{L}$ is its specific conductance.

An inspection of this equation shows that for good conductors it reduces to

$$I = \frac{I_T}{2\,\Delta R_B R}\left[\left(\frac{R_B}{2} + R\right)^2 + 2R_T\left(\frac{R_B}{2} + R\right)\right]. \tag{4}$$

As the value of $\overline{L}$ decreases and the resistance of the cell increases, however, the two expressions differ from each other more and more. If we put $\overline{L} = 10^{-7}$ and $R = 10^5$, then if f is not greater than 1000 cycles and k is not greater than 80, Equation 3 does not differ from Equation 4 by more than 10% of the value of I. Within this degree of accuracy, therefore, we may use Equation 4 in place of Equation 3 as long as we are dealing with solutions whose specific conductance does not fall below 10^{-7} reciprocal ohms.

It will be noticed that this range includes all aqueous solutions down to and including the best "conductivity water" that can be prepared and handled in contact with the atmosphere, even under the most favorable

---

[3] Maxwell, *Electricity and Magnetism*, 1, 477.

conditions.[4] For the large majority of investigators engaged in conductivity measurements with solutions of electrolytes the above range is sufficiently ample to include all the cases which they meet with in practice. For this reason it seems best in the interest of simplicity to restrict the present discussion to liquids whose specific conductances fall within the range mentioned, since the relations obtained will be much simpler if we can employ Equation 4 instead of the more general and more complex Equation 3. Moreover the applications of the general equation to cases which lie without the above range are of more interest in connection with measurements of dielectric constants than in connection with conductance measurements because, when the specific conductance of the material begins to drop below 10^{-8}, it becomes possible in most instances to use the direct current and galvanometer for the conductance measurements and under these conditions Equation 4, of course, becomes rigorously exact for all cases. The author hopes at some future time to discuss the subject of dielectric constant measurements in the light of Equation 3, particularly with reference to the problem of determining the dielectric constant of salt solutions, a problem which was taken up experimentally in this laboratory last year but which will now have to be dropped.

4. The Theory of Cell Design.—In the process of determining the correct bridge setting, the portion of the bridge-wire over which the "minimum" extends will evidently have a resistance equal to $2\Delta R_B$ ohms (see Fig. 1). Within this range *no sound* will be heard in the telephone. The uncertainty in judging the exact center of this minimum will evidently be larger the larger $2\Delta R_B$ is, but with properly designed apparatus this uncertainty should never amount to as much as one-fourth of the total range, that is, to as much as $^1/_2\Delta R_B$, and this would produce an error of $p\%$ in the resistance of the cell. We shall, therefore, be conservative, if we write

$$2\Delta R_B = \frac{pR_B}{100} \qquad (5)$$

where p is the allowable percentage error from the bridge setting.

The relation between the Current I_A and the Current I (see Fig. 1) is evidently

$$\frac{I_A}{I} = \frac{R_B}{2R + R_B} \qquad (6)$$

If we combine Equations 4, 5 and 6 we have

$$I_A = \frac{50 I_T(R_B/2 + R + 2R_T)}{pR}. \qquad (7)$$

For the purposes of the present discussion we shall assume that the

---

[4] Cf. J. E. Bell, Univ. of Ill. Thesis, 1913, p. 16,

conductivity cell contains two parallel electrodes of approximately equal areas. These electrodes will be l centimeters apart and the area of the *uniform* cross-section of the solution between them will be A square centimeters. The electrodes may be either two metal disks closing the ends of a cylindrical tube containing the solution, or they may be two sufficiently large coaxial cylinders. The area of each electrode must be substantially equal to or larger than the effective area of the cross-section of the solution between them. The heat capacity of the solution between the electrodes will be $Alds$, where d is the density of the solution and s its specific heat capacity.

If during the operation of determining the bridge setting the temperature of the solution between the electrodes rises $\Delta T°$ because of the current I_A passing through the cell, the energy thus liberated will be $Alds\,\Delta T\cdot 4.2$ Joules. Equating this to the electrical energy, we have

$$Alds\,\Delta T\cdot 4.2 = I^2_A \frac{lt}{A\overline{L}} \qquad (8)$$

where $\overline{L}$ is the specific conductance of the solution and t is the time required to obtain the final correct bridge setting.

If α is the temperature coefficient of the conductance of the solution in the cell, a rise of $\Delta T°$ in the temperature during the measurement will produce a percentage error

$$p_T = 100\alpha\Delta T. \qquad (9)$$

Now there is no particular advantage to be gained by attempting to make the error from this source less than that arising from the uncertainty in the bridge setting. We shall, therefore, equate these two sources of error.

$$p_T = p. \qquad (10)$$

We can now write

$$\Delta T = \frac{p}{100\alpha}. \qquad (11)$$

and Equation 8 becomes

$$\frac{Aldsp\cdot 4.2}{100\alpha} = I_A{}^2 \frac{lt}{A\overline{L}}. \qquad (12)$$

Combining this with Equation 7 so as to eliminate I_A and solving for A, we have the condition

$$A \geqq \frac{50 I_T[R_B/2 + R + 2R_T]t^{1/2}}{R\overline{L}^{1/2}\sqrt{\frac{p^3ds}{\alpha}\cdot 0.042}} \qquad (13)$$

If we put

$$R = \frac{l}{A\overline{L}} \qquad (14)$$

in Expression 13 and again solve for A, we obtain the important condition

$$A^2 \geqq \frac{6 \cdot 10^4 \cdot I_T^2 l^2 t}{\bar{L}[l\sqrt{p^3 ds/\alpha} - 120 I_T \sqrt{t\bar{L}} \cdot (R_B + 4R_T)]^2}. \tag{15}$$

This relation gives the minimum allowable value for the cross-section of the cell, if the two sources of error indicated are not to exceed $p\%$ each. By solving this equation for l, we obtain a similar relation giving the maximum allowable value for the distance between the electrodes for the same condition.

For many purposes, however, a more convenient expression is obtained by solving the equation for $\bar{L}$ giving us

$$\bar{L} = \frac{l^2 p^3 ds/\alpha}{6 \cdot 10^4 I_T^2 t(R_B + 4R_T)^2}\left[1 \pm \sqrt{1 - \frac{1.2 \cdot 10^5 I_T^2 t(R_B + 4R_T)}{Alp^3\, ds/\alpha}}\right]^2. \tag{16}$$

This equation gives two values for $\bar{L}$. These two values represent the limits between which it is safe to use the cell in question if the two sources of error indicated are not to exceed $p\%$ each. These two limiting values of $\bar{L}$ determine what we shall call the *ultimate range* of the cell. No conductivity cell should ever be used for solutions with specific conductances which do not lie within the *ultimate range* of the cell as defined by the above equation.

In determining the actual *working range* of a given cell, however, another factor must also be taken into account, and that is the range of resistances within which it is practicable or desirable to make measurements. If $R_{\text{max.}}$ is the highest and $R_{\text{min.}}$ the lowest resistance which it is desirable to undertake to measure, then in addition to the above condition, the following must also be fulfilled:

$$\frac{l}{AR_{\text{max.}}} > \bar{L} > \frac{l}{AR_{\text{min.}}} \tag{17}$$

Before proceeding further with the discussion of the use of the principles thus far derived, it will be convenient to simplify the nomenclature somewhat. We shall introduce the following abbreviations:

$$p^3\, ds/\alpha = a \tag{18}$$

$$I_T^2 t = b \tag{19}$$

and

$$R_B + 4R_T = c \tag{20}$$

Furthermore, if $\bar{L}_1$ and $\bar{L}_2$, respectively, represent the upper and lower limits of the range of the cell, then the *range ratio* r will be defined by the expressions

$$\frac{\bar{L}_1}{\bar{L}_2} = r \text{ and } r \leqq \frac{R_{\text{max.}}}{R_{\text{min.}}}. \tag{21}$$

Equation 16 can now be written

$$\overline{L} = \frac{l^2a}{6 \cdot 10^4bc^2}\left[1 \pm \sqrt{1 - \frac{1.2 \cdot 10^5bc}{Ala}}\right]^2 \qquad (22)$$

and Expression 13 may be written

$$A \geqq \frac{122 \cdot b^{1/2}(2R_{\text{max.}} + c)}{R_{\text{max.}}\, \overline{L}_2^{1/2}a^{1/2}} \qquad (23)$$

where $R_{\text{max.}}$ is the resistance of the cell when filled with a liquid having the specific conductance $\overline{L}_2$.

If $R_{\text{max.}}$ is more than ten times c, which will practically always be the case when $R_{\text{max.}}$ is not less than 10,000 ohms, c may be neglected in comparison with $R_{\text{max.}}$ and the above expression reduces to the simple form

$$A \geqq \frac{244 \cdot b^{1/2}}{\overline{L}_2^{1/2}a^{1/2}} \qquad (24)$$

or in words, the minimum allowable value for the cross-section of the cell is determined by the audibility current of the telephone, the specific conductance of the liquid having the maximum desired resistance in the cell, the density, heat capacity and conductance temperature-coefficient of this liquid, and the percentage accuracy demanded in the measurement. It does not, however, depend upon the distance between the electrodes, that distance being fixed (after the value of A has been decided upon) by means of the equation

$$l = \overline{L}_2AR_{\text{max.}}\,. \qquad (25)$$

Expressions 23 and 25 together, therefore, fix a minimum volume for the cell. There is, however, another relationship involving the product Al which must also be satisfied. That is the relationship involved in Expression 22 which we will now proceed to examine more closely.

The Volume Factor of a Conductivity Cell.—From Equations 19 and 20 we obtain

$$\frac{\overline{L}_1}{\overline{L}_2} = r = \left[\frac{1 + \sqrt{\left(1 - \frac{1.2 \cdot 10^5bc}{Ala}\right)}}{1 - \sqrt{\left(1 - \frac{1.2 \cdot 10^5bc}{Ala}\right)}}\right]^2 \qquad (26)$$

and if we solve this equation for the product Al, we obtain the following expression which determines the minimum allowable value for what we shall call the *volume factor* of our cell.

$$Al \geqq \frac{(r^{1/2} + 1)^2 \cdot 1.2 \cdot 10^5bc}{4r^{1/2}a} \qquad (27)$$

Since it will not ordinarily be desirable to restrict the range ratio of a cell to a value less than 10^3, Expression 27 can for most purposes be written

$$Al \geqq \frac{3.10^4 \cdot bcr^{1/2}}{a} \text{ approx.} \tag{28}$$

It will be noticed that for a series of cells having the same range ratios, the minimum allowable value for the volume factor of the cells is the same for all the cells independent of their particular ranges.

Now if a cell is designed in accordance with the principles set forth in Expressions 23 and 25 a minimum value for its volume factor is also determined thereby. It is necessary, therefore, to ascertain whether this minimum is greater or less than the one fixed by Expression 27. If it is always greater, then Expression 27 need not be considered in designing cells, for the condition which it lays down would always be met if Expressions 23 and 25 are satisfied. We shall proceed to discover the conditions under which the minimum volume factor given by Expressions 23 and 25 shall always be greater than the value demanded by Expression 27.

We proceed as follows: From Expressions 23 and 25 we find

$$Al \geqq \frac{1.5 \cdot 10^4 \cdot b(2R_{\text{max.}} + c)^2}{R_{\text{max.}}\, a}. \tag{29}$$

The condition desired is, therefore, expressed by the relation

$$\frac{1.5 \cdot 10^4 \cdot b(2R_{\text{max.}} + c)^2}{R_{\text{max.}}\, a} \geqq \frac{(r^{1/2} + 1)^2 3 \cdot 10^4 bc}{ar^{1/2}}. \tag{30}$$

Putting $R_{\text{max.}} = rR_{\text{min.}}$ in this relation and solving it for c, we find the two alternative conditions

$$c \geqq R_{\text{min.}} [r^{1/2}(r + 1) + \sqrt{r(r + 1)^2 - 4r^2}] \tag{31}$$

or

$$c \leqq R_{\text{min.}} [r^{1/2}(r + 1) - \sqrt{r(r + 1)^2 - 4r^2}]. \tag{32}$$

Of these two conditions the first one may ordinarily be disregarded because it usually gives values for c which are very much greater than any which would be met with in practice. Expression 32 then describes the condition which must be fulfilled if Expression 29 is to take precedence over Expression 27 in determining the dimensions of a conductivity cell. In nearly all cases which will be met with in actual practice, it will be found that the above condition will be fulfilled and that hence no attention need be paid to Expression 27 in designing conductivity cells. In a few very special cases, however, account must be taken both of Equation 31 and Equation 27. As an illustration of such an instance we shall at this point consider briefly the problem of designing a conductivity cell which shall have a minimum volume factor.

To Design a Conductivity Cell Having a Minimum Volume Factor.— It is sometimes necessary to determine the conductivity of a liquid of which only a very small quantity is available. This is the case in studies of the conductivity of the sap of plants, for example. In such cases it is important to employ a cell which requires a minimum amount of liquid to fill it.

To take a concrete example suppose the specific conductances of different samples of a certain group of plant saps lie within the limits $\bar{L}_1$ and $\bar{L}_2$ and that it is desired to measure the specific conductances of these saps with an accuracy of $p\%$. Let us suppose further that

$$r = \frac{\bar{L}_1}{\bar{L}_2} \ngtr 10. \tag{33}$$

Applying the criteria in Expressions 31 and 32 we find the two *alternative* conditions

$$6.3\ R_{\text{min.}} \geqq c \geqq 63\ R_{\text{min.}}\,. \tag{34}$$

If, as would normally be the case, $100 \nless R_{\text{min.}} \nless 20$, we would usually find that neither of these conditions was satisfied. This would mean that the volume factor of our cell would be determined by Equation 27 which in this case would become

$$Al \geqq 1.65 \cdot 10^5\ bc/a. \tag{35}$$

After having determined the minimum volume factor from this relation, the values of A and l would then be separately obtained by combining with the equation

$$l = A\bar{L}_1 R_{\text{min.}}\,. \tag{36}$$

We shall complete this discussion in the numerical form after considering some typical numerical values of a, b and c (see Sec. 7 below).

5. The Adjustment of the Total Current through the Bridge for a Conductance Measurement.—In the theory of cell design presented above, one of the principal features is the entire elimination of any appreciable heating of the cell during the measurement. It is obvious, however, that *any* cell *could be* appreciably heated if a large enough current is employed for the measurement. The regulation of the current through the bridge is, therefore, an important element in the use of the cells.

It will be noticed, however, that the value of I, the total current through the bridge, does not appear in any of the final equations which control the cell design. Stated in words this means that a knowledge of the actual value of the current through the bridge is unnecessary either for the purpose of designing the cells or for using them afterwards. By looking back to Sec. 4 it will be noticed that at the beginning of the development of our theory a definite restriction was as a matter of fact placed upon the value of I. This restriction is involved in writing Equation 5 and the rule for adjusting the current through the bridge for the final measurement may, therefore be formulated as follows: Increase the current from the generator until the following condition is fulfilled:

$$\Delta R_B \nleqq \frac{pR_B}{200} \text{ approx.} \tag{37}$$

where p is the maximum percentage accuracy which the cell is designed to give with the telephone employed with it, and R_B is the approximate resistance of the bridge. Or stated in another way, p may have any desired value, not less than $100\alpha\Delta T'$, provided the cell is not used outside of the conductance range fixed by Equation 22.

6. Summary.—The results of the foregoing discussion may be summed up as follows:

Given the problem, *To construct a conductivity cell with a range ratio* $r = \frac{R_{\text{max.}}}{R_{\text{min.}}} = \frac{\bar{L}_1}{\bar{L}_2}$, *where* $R_{\text{min.}}$ *is the resistance of the cell when filled with a liquid of specific conductance* $\bar{L}_1$ *and* $R_{\text{max.}}$ *is the resistance of the cell when filled with a liquid of specific conductance* $\bar{L}_2$.

The answer is: *1. Determine the minimum allowable value for the area of the cross-section between the electrodes with the aid of Expression 24; 2. Choose any convenient value larger than this; and then, 3. Determine the distance between the electrodes by means of Equation 25.*

Stated in other words, *The area of the cross-section between the electrodes of a conductivity cell must not be less than a certain minimum value which is completely fixed and determined by the audibility current of the telephone, the time required to make the bridge setting, the lowest specific conductance which it is desired to include within the range of the cell and the percentage accuracy demanded in the measurements.*

This practically means that conductance cells should be designed to fit the telephone which is to be employed with them. The audibility current of the telephone is the chief controlling factor and every investigator making conductance measurements should determine for himself the audibility current of his telephone because the value of this important quantity is a function both of the construction of the telephone and of the observer's ear. The audibility current can be conveniently determined by methods which will be described in the second paper of this series, which will appear very shortly.

7. Numerical Values of the Variables which Control the Cell Design.—Before proceeding to the discussion of the application of the above principles to concrete cases, it will be necessary to assign appropriate numerical values to the variables involved. The factors governing the selection of these values will now be considered.

The Resistance of the Slide-wire.—The theoretical and practical principles which govern the selection and arrangement of the resistance or resistances which make up that portion of the Wheatstone bridge included between the points A and B of Fig. 1, will be considered in detail in a later paper. For our present purposes, it will be sufficient to note that according to Equation 1, the best value for R_B is given by the equation

$$R_B = 2\sqrt{Z(Z + 2R_T)} \qquad (38)$$

or for aqueous solutions

$$R_B = 2\sqrt{R(R + 2R_T)}. \qquad (39)$$

As a matter of fact, except for very small or very large values of R it is not necessary to pay much attention to fulfilling the condition expressed by this equation because sufficient accuracy can be obtained with a single bridge wire over a wide range of resistances. One of the slide-wire bridges in extensive use at the present time for measuring the conductances of electrolytes has a slide-wire which with its extension coils has a total resistance in the neighborhood of 250 ohms. This is an appropriate value for general use and in the following illustrative calculations we shall accordingly assume

$$R_B = 250 \text{ ohms}. \qquad (40)$$

The Resistance and Sensitivity of the Telephone.—Theoretically, other things being equal, a high-resistance telephone should be employed for measuring high resistances and a low-resistance telephone for low resistances but practically the sensitivity is at present the only determining factor in the choice of a telephone. A very satisfactory telephone on the market at present has an audibility current[5] not greater than 2.10^{-9} ampere and a resistance of 150 ohms. We shall assume these values in the following calculations and write

$$I_T = 2.10^{-9} \text{ ampere} \qquad (41)$$

and

$$R_T = 150 \text{ ohms}. \qquad (42)$$

Density and Heat Capacity of the Solution.—In the following calculations we shall assume

$$ds = 1. \qquad (43)$$

This assumption will not be far from the truth in the case of aqueous solutions of electrolytes and in cases where this assumption is not sufficiently exact the ecessary modifications of the equations will be obvious.

Time Required to Obtain the Bridge Setting.—This factor will vary with the observer, the apparatus he is using and a variety of conditions prevailing at the time of observation. Experiments in this laboratory have shown that a trained observer working in quiet surroundings with good apparatus can, if necessary, make the final bridge setting in about five seconds, even when measuring resistances as high as 50,000 ohms. In designing cells, however, it is better where possible to allow a somewhat longer time than this. We have found that a period of 10 seconds is usually ample to make a leisurely bridge setting if good apparatus is employed. We shall accordingly write

$$t = 10 \text{ seconds}. \qquad (44)$$

For any given cell the maximum allowable value for t can be calculated

---

[5] Determined for the writer's ear.

from Equation 15. It is well to know this maximum value for t before measurements are begun with a new cell. Moreover if for any reason an observer wishes a longer time than 10 seconds, the design of the cell can, of course, be made to meet his condition. The following numerical calculations are given only as illustrations.

Maximum and Minimum Values for the Resistance of the Cell.—To a considerable extent the values of $R_{\text{max.}}$ and $R_{\text{min.}}$ may be chosen arbitrarily and the dimensions of the cell made to correspond with the values chosen. In the following illustrative calculations we shall assume

$$R_{\text{min.}} = 100 \text{ ohms.} \tag{45}$$

This value is sufficiently large to make the elimination of errors due to lead resistances and contact resistances comparatively easy. Moreover it will always be practicable to construct the cell to meet this condition even for solutions of the highest specific conductance. For $R_{\text{max.}}$ we shall employ the value 10,000 ohms as long the dimensions of the cell will conveniently permit, but for cells to be used for poorly conducting liquids we shall include the case $R_{\text{max.}} = 100{,}000$ ohms.

Temperature Coefficient of Conductivity.—In the following calculations we shall write, for salt solutions,

$$\alpha = 0.02 \tag{46}$$

as an average value. In the case of conductivity water, however, we shall employ $\alpha = 0.05$.

Percentage Accuracy Desired in the Measurement.—With the apparatus now available for measuring the conductivity of electrolytes, the degree of precision attainable in the measurement is entirely determined and limited by the magnitude of the unavoidable variation of the temperature of the bath containing the cell. All other sources of variable error are now entirely negligible in comparison with this one. If therefore, $\Delta T'$ represents the temperature range covered by the fluctuations of the "constant temperature" bath containing the cell, it is obvious that the maximum attainable percentage accuracy, that is, the minimum percentage error in the conductivity measurement is given by the equation

$$p_{\text{min.}} = 100\alpha\Delta T' \tag{47}$$

Now there will obviously be no advantage in making the other sources of error much smaller than this one. We shall, therefore write

$$p = p_T = {}^1/_2 p_{\text{min.}} = 50\alpha\Delta T'. \tag{48}$$

For solutions of electrolytes where $\alpha = 0.02$ and $\Delta T'$ is taken as 0.001° this becomes

$$p = \Delta T' = 10^{-3} \tag{49}$$

and for conductivity water where $\alpha = 0.05$, it becomes

$$p = \text{approximately } 3 \cdot 10^{-3} \tag{50}$$

which are the values which we shall employ in the following calculations.

It will be noted that the choice of the above values imposes the condition that the rise in the temperature of the solution produced by the current which passes through it during the measurement shall not exceed 0.0005°. This requirement is evidently sufficiently exacting for all practical purposes. A more exacting requirement in this respect would be useless unless the fluctuations of the constant temperature bath could be made considerably less than 0.001°.

Using the above numerical values we have

$$a = p^3\, ds/\alpha = 5\cdot10^{-8} \text{ (or for conductivity water } = 54\cdot10^{-8}\text{) calories per cc.} \tag{51}$$

$$b = I_T^2 t = 4\cdot10^{-17} \text{ coulomb-amperes.} \tag{52}$$

$$c = R_B + 4R_T = 850 \text{ ohms} \tag{53}$$

and the set of expressions derived above may be written:

Equation 22

$$\bar{L} = 2.9\cdot10^{-2}\, l^2\left[1 \pm \sqrt{1 - \frac{8.2\cdot10^{-2}}{Al}}\right]^2 \tag{54}$$

Expression 24

$$A \geqq \frac{6.9\cdot10^{-3}}{\bar{L}^{1/2}} \tag{55}$$

or for conductivity water ($\bar{L} = 10^{-7}$)

$$A \geqq 7.0 \tag{56}$$

Expression 25

$$Al \geqq \frac{(r^{1/2}+1)^2}{r^{1/2}}\cdot 2\cdot10^{-2} \tag{57}$$

or for $r = 10^3$

$$Al \geqq 0.665 \tag{58}$$

Furthermore, if we apply the test imposed by Expression 32 using $r = 10^3$, we find the condition

$$c \leqq 60R_{\text{min.}} \tag{59}$$

a condition which is evidently fulfilled. We must, therefore, employ Expression 24, or in this instance 55, in determining the minimum value for A. For this purpose it will be most convenient to construct a graph of this equation. Such a graph is shown in Fig. 2, Curve A. The ordinates represent values of A in square centimeters and the abscissae, corresponding values of $\bar{L}_2$ expressed as powers of ten. The point corresponding to $\bar{L}_2 = 10^{-7}$ is that given by Expression 56. The corresponding curve for D, the diameter of the cross-section of the cell, is shown on the same diagram.

This diagram can also be employed in designing cells for use with a telephone for which $I_T \ngtr 6\cdot10^{-8}$, if $p \nless 10^{-2}$ or for which $I_T \ngtr 2\cdot10^{-6}$, if $p \nless 10^{-1}$.

We shall now proceed to illustrate the use of this diagram in designing a set of conductivity cells to cover the whole range of specific conductances between 1 and 10^{-7} reciprocal ohms.

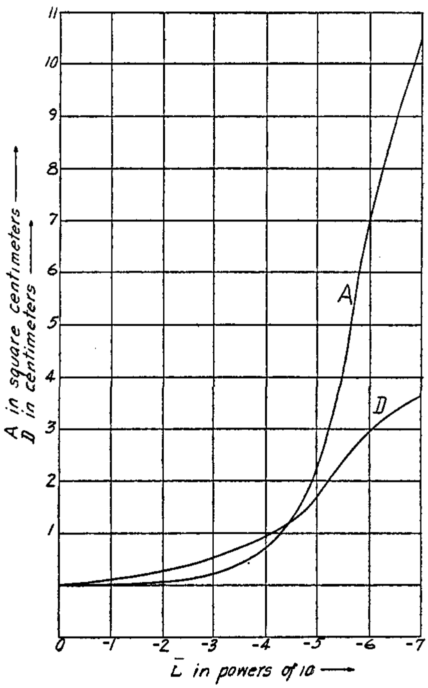

Fig. 2.

8. Types of Conductivity Cells. *General Features.* — Every conductivity cell designed for accurate work should fulfill the following obvious conditions:

1. It should be so formed that the operation of filling it with the solution to be measured and its subsequent use exposes the solution as little as possible to the action of the atmosphere.

2. The material of which it is constructed should not contaminate the solutions to be used in it.

3. The electrodes should be of such size and weight that when fixed firmly in one position the cell constant will not change with use, and the electrodes should be so placed that the cell constant does not depend upon the height to which the cell is filled. The electrode stems should be as short as the conditions of manufacture and of filling and washing the cell will permit.

A cell constructed in the form of a pipet[6] probably fulfills the first condition most satisfactorily. Types[7] of pipet cells which have been in use in this laboratory for a number of years are shown in Figs. 3, 4, 5 and 6.

Type A.—This type is for use with conductivity water and very dilute solutions. For use with conductivity water the electrodes may be placed vertically since they are so close together that no appreciable number of lines of flow will reach the surface of the liquid, if the precaution is taken to fill the cell up to the level of the arrows *A* and *D*. The right-angled

---

[6] The writer is not aware of the origin of the pipet form for a conductivity cell. Such a cell is pictured and mentioned in Ostwald-Luther's *Handbuch*, 1902 Ed., and a cell of this form was constructed in this country in 1907 by Kraus (THIS JOURNAL, 31, 732 (1909)).

[7] In the case of Type *A* the figure is drawn so as to exhibit a form of construction which will permit a minimum electrode stem length, which may be desired in some cases for the reasons explained in Sec. 13. If this is not required the body of the cell is most easily made in the globular form shown in THIS JOURNAL, 35, 752 (1913), Fig. 1.

turn in the tube above the electrodes is an additional precaution against the escape of lines of flow to the surface of the liquid. The electrodes are constructed of the purest platinum alloyed with enough iridium to render them stiff. Each electrode is in the shape of a disk about 0.15 mm. thick and supported at the center by a rod of the same material about 1.5 mm. in diameter. The end of this rod may be slightly flanged before it is welded on to the disk in order to increase the strength of the joint and insure perfect rigidity after the electrode has been sealed into position. The inside surfaces of both electrodes should be roughened with a sand blast.

For use with dilute solutions the electrodes are lightly platinized and are preferably placed in a horizontal position (Fig. 4).

Type B.—This type is for use with moderately good conductors. The electrode specifications are the same as for Type *A*, except that a lighter weight platinum may be employed. The electrodes should be covered with a sufficiently heavy coating of platinum black to insure the elimination of polarization (see Sec. 14 below) but the coating should not be any heavier than necessary to accomplish this purpose.

Type C.—This type is for use with good conductors. The electrode specifications are the same as for Type *A* except that the electrodes may be made in the shape of a bowl as shown in the figure and the lower electrode should have a circular perforation at least 2 mm. in diameter near the center of the bottom. The diameter of the bowl may be about 5 centimeters and the depth about 7 millimeters. Both electrodes should be heavily platinized. The electrodes may be placed with their convex sides towards each other as shown in the figure, or they may be placed with their concave sides facing each other. The second arrangement makes a somewhat more efficient use of the electrode surface but it is necessary to guard carefully against the inclosure of a bubble of air underneath the upper electrode in this arrangement. A bubble of air below the lower electrode in the arrangement shown in the figure will do much less harm.

9. A Series of Cells Covering the Complete Conductance Range for Aqueous Solutions.—*Cell No. 1. For Conductivity Water.*—This cell will have nonplatinized electrodes and will be employed for solutions with specific conductances ranging from $1.6 \cdot 10^{-7}$ reciprocal ohms up to a value which will be determined by the appearance of a poor minimum due to the influence of polarization. From Fig. 2 we find $A = 10.4$ square centimeters. For circular electrodes this would correspond to a diameter of 3.65 centimeters. Suppose we choose 4 centimeters as the maximum diameter which we wish to employ for this type of electrode. This would mean an area of 12.6 square centimeters. Suppose moreover that it is undesirable to place these electrodes nearer together than 2 millimeters. If we put $R_{\text{max.}} = 10^5$ ohms we find from Equation 25, $\overline{L}_2 = 1.6 \cdot 10^{-7}$.

In other words such a cell could be used for conductivity water down to a specific conductance of $1.6 \cdot 10^{-7}$ reciprocal ohms. This is practically the purest water which can be prepared in contact with the atmosphere[4] and hence the above cell would fill all requirements for conductivity water which is to be handled in contact with the atmosphere. The cell would be of Type *A*, Fig. 3.

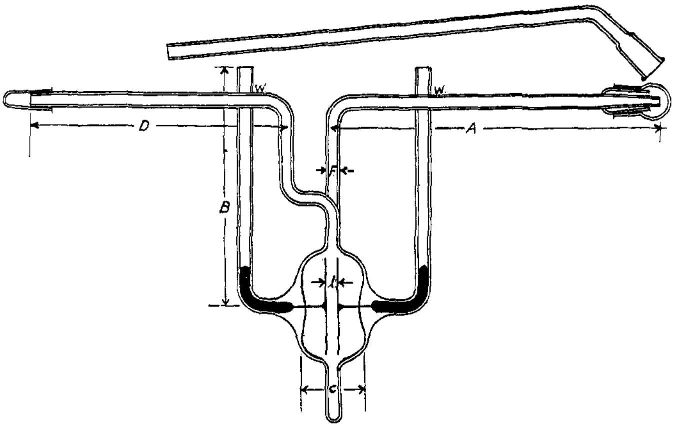

Fig. 3.—Water cell. Type *A*

For measuring conductivities less than $1.6 \cdot 10^{-7}$ it is convenient to use electrodes in the form of two coaxial cylinders.[8] A pair of such electrodes about 4 centimeters long, 4 centimeters across and 3 millimeters apart could be employed for specific conductances down to $0.6 \cdot 10^{-7}$ without the resistance rising above 10^5 ohms. A study of the conductivities of dilute solutions in water having an initial conductivity of $0.6 \cdot 10^{-7}$ reciprocal ohms at 18° is now in progress in this laboratory.

Cell No. 2. For Dilute Solutions.—This cell will have lightly platinized electrodes and will be designed to cover the range between 10^{-6} and 10^{-4} reciprocal ohms. From Fig. 2 we find $D \geq 3$ centimeters. We shall choose the value 4 centimeters for the diameter of the electrodes and of the cross-section of the cell. For the distance between the electrodes we shall take 3 millimeters. The cell will be of the same type as No. 1 and when filled with a liquid of specific conductance 10^{-6} reciprocal ohms will have a resistance of 24,000 ohms.

It will be noticed that the ranges of Cells 1 and 2 overlap to a considerable extent. This is desirable in the case of these cells because the upper limit of Cell No. 1 will be determined by the appearance of polarization influences and recourse will then have to be had to Cell No. 2. Needless to say it is advantageous to employ Cell No. 1 as long as possible because contamination of the solution by materials adsorbed by platinum

[8] A form of electrode originated by Pfeiffer [*Wied. Ann.*, 25, 232 (1885)].

black need not be feared with this cell. Cell No. 2 will require careful washing on account of this source of error. (In this connection cf. Sec. 14*b* below.)

Cell No. 3. Range 10^{-4} *to* 10^{-2}.—This cell will have well platinized electrodes. The diameter of the cross-section of the cell will be 1.5 centimeters and the distance between the electrodes 1.8 centimeters. It will be noticed that these dimensions fulfill the conditions shown by the diagram and give the cell a resistance of 10^4 ohms at the lower limit of the above range. The cell will be of Type *B*, Fig. 5.

Cell No. 4. Range 10^{-2} *to* 10^{0}.—This cell will have heavily platinized electrodes and will be of type *C*, Fig. 6. The diameter of the cross-section of the cell will be 0.36 centimeter and the length of the connecting tube 10.1 centimeters, which accords with the diagram.

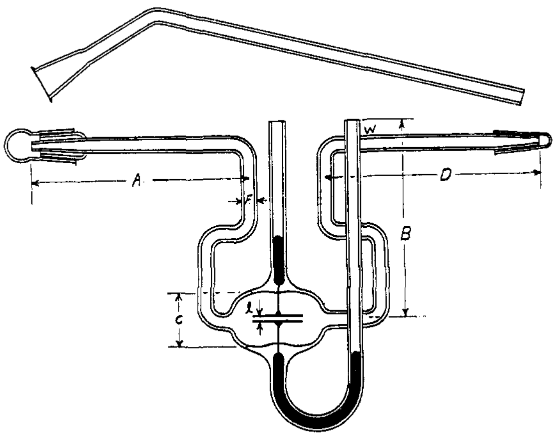

Fig. 4.—Cell for dilute solutions.

Discussion.—These four cells will cover the total conductance range between 1 and 10^{-7} reciprocal ohms. It is obvious that a greater number of cells could be employed if desired and that considerable variation in the dimensions is possible within the limits set by the diagram. It will be noted that with the above set of cells it is not necessary to employ a resistance greater than 10,000 ohms until the specific conductance of the liquid falls below $1.6 \cdot 10^{-6}$ reciprocal ohms. The whole range could be covered with three cells by taking $R_{\max.} = 10^5$ for each cell. Where it can be done conveniently, however, it is desirable to keep the value of $R_{\max.}$ not greater than 10^4 ohms since there is then less trouble in obtaining a sufficiently close balance of the capacities in the two arms

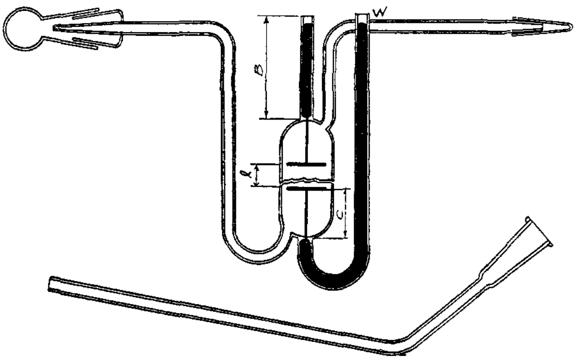

Fig. 5. Type *B*

of the bridge and in securing the necessary symmetrical distribution of condensive and inductive reactance throughout the bridge net-work.

It is, of course, possible to impose the condition, $R_{\text{max.}} = 10^4$ ohms, upon all of the cells. In the case of the water cell this would mean an electrode area of about 125 sg. cm. At the present price of platinum this would be rather expensive, but the 10^5-ohm dial in the resistance box is fairly expensive also, so that the expense of the platinum would have to be balanced against the expense of the extra dial on the resistance box and the greater ease in making the measurements at the lower resistance. Moreover it seems probable that a little investigation would result in the discovery of some other electrode material (possibly gold- or platinum-plated silver) which could be substituted in place of the platinum in the water cell. There are no particular difficulties in constructing the cell with the larger electrodes. We have found that very satisfactory cells with electrodes of the coaxial cylinder type can be constructed, if the electrodes are supported in a quartz frame-work to insure rigidity. A water cell with two electrodes of this type could be readily constructed after the manner indicated in Fig. 7 and this cell would have a resistance of 10,000 ohms when filled with water having a specific conductance of $1.6 \cdot 10^{-6}$. All in all much may be said in favor of imposing the condition $R_{\text{max.}} = 10^4$ ohms, in designing conductivity cells.

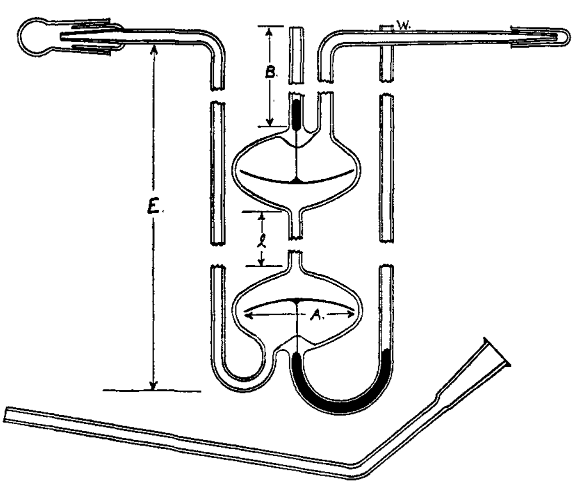

Fig. 6.—Cell for good conductors Type C.

10. A Cell with a Minimum Volume Factor.—Returning for a moment to a further consideration of the problem discussed in the last part of Sec. 4 we find, on combining Equations 51, 52 and 53 with Expression 35,

$$Al \geq \frac{1.65 \cdot 10^5 \cdot 4 \cdot 10^{-17} \cdot 850}{50p^3} \geq \frac{1.12 \cdot 10^{-10}}{p^3} \qquad (60)$$

If $p = 10^{-3}$, or 10^{-2}, respectively, the corresponding values of Al, the minimum volume factor, would be 0.1 cc. and 0.0001 cc., respectively. If the telephone employed had an audibility current of 10^{-8} amperes, and most investigators have worked with telephones no more and in many cases less sensitive than this, the corresponding values of Al would be 2.8 cc. and 0.003 cc., respectively.

Evidently these values are so low that there is practically no danger in falling below them in constructing cells for small quantities of liquids unless a larger range ratio than 10 is demanded for the cell. They are so low in fact that the total volume of the cell would in most cases be practically determined by the space necessary to inclose electrodes of sufficient size to eliminate polarization, unless the method described in Sec. 14*b* were employed for this purpose.

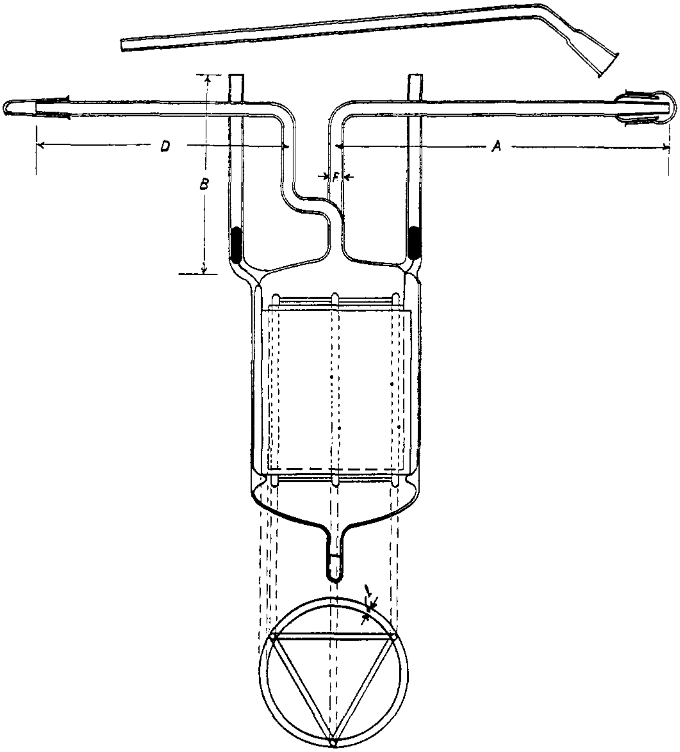

Fig. 7.—Scale: 1 inch = 3 inches. $l = 0.2$ cm.

11. Connecting the Cell to the Bridge.—In accurate work the conductivity cell should never be directly connected to the lead wires coming from the bridge but instead a pair of mercury cups *dipping into the bath containing the cell* should always be employed as an intermediary, as illustrated in Fig. 8. The reason for this is, of course, to prevent the exchange of heat between the electrodes and the room, along the connecting wires. For the same reason the distance B in Figs. 3–7 should be long enough to permit the submersion of all of the body and a good part of the connecting tubes of the cell, below the surface of the bath. Insulated wires with amalgamated ends are used for bridging across between the cell and the intermediate mercury cups as shown in Fig. 8.

Twisted lamp cord No. 11 is, in practically all cases, of ample size[9] for connecting the intermediate mercury cups with the bridge and if the same length of this cord is employed in connecting the bridge with the resistance box, it will *never* be necessary to determine or apply any correction for lead resistance, as long as the distance between the bridge setting and the center of the bridge is not greater than $n/10000$ of the total bridge length, n being given by the expression

$$n = \frac{5000Rp_L}{Rp_L + 200R_L} \quad (61)$$

where R_L is the resistance of each pair of leads.

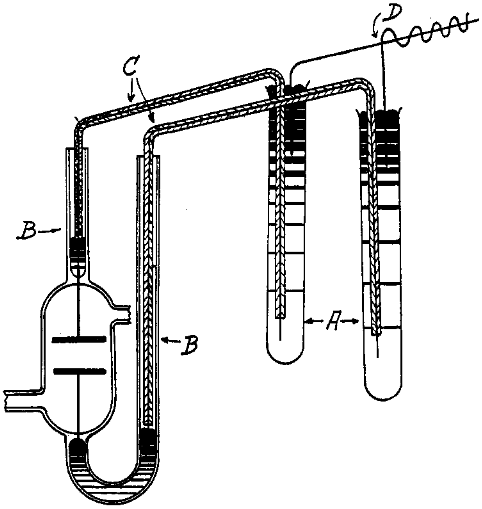

Fig. 8.

The resistance of the wires used to bridge across from the cell to the intermediate mercury cups as well as the resistance of the mercury and of the platinum stems of the electrodes are counted as part of the total lead resistance, R_L, of the cell.

12. The Temperature Coefficient of the "Cell Constant" of a Conductivity Cell.—As is well known, the Cell Constant of a conductivity cell changes with the temperature. The rapidity with which it changes, however, varies with the manner in which the cell is constructed and depends upon the nature of the materials which compose it. The nature of this dependence can be deduced as follows:

Cells of Types A and B.—For simplicity let us assume that the lines of flow are all perpendicular to the surface of the electrode, that is, we shall neglect the "edge effect," which will be smaller the more tightly the electrodes fit the cell and the smaller l is. For the Cell Constant of such a cell we will then have

---

[9] This size of lead wire is calculated as follows: From Equation 61 we find our limiting condition

$$\underline{R} \geq \frac{(5000 - n)R_{\text{min.}}p_L}{400\,nh}$$

where $\underline{R}$ is the resistance of the wire in ohms per foot, and h is the distance between the cell and the bridge. Putting $n = 200$, $R_{\text{min.}} = 100$, $h = 2$ ft. and $p_L = 5 \cdot 10^{-4}$, we find $\underline{R} = 15 \cdot 10^{-4}$ ohms per foot = about No. 11 B. & S. copper wire. Similarly for $h = 1$ ft. and $p_L = 5 \cdot 10^{-3}$ we find $\underline{R} = 3 \cdot 10^{-2}$ ohms per foot = about No. 25 B. & S. copper wire, etc., for any conditions which may be demanded.

$$K = \frac{l}{A} \tag{62}$$

and therefore,

$$A\frac{\mathrm{d}K}{\mathrm{d}t} = \frac{\mathrm{d}l}{\mathrm{d}t} - \frac{l\,\mathrm{d}A}{A\mathrm{d}t} \tag{63}$$

For the two derivatives of l and A we have

$$\frac{\mathrm{d}l}{\mathrm{d}t} = \beta(l + s) - \gamma s \tag{64}$$

and

$$\frac{\mathrm{d}A}{\mathrm{d}t} = 2\gamma A \tag{65}$$

respectively, where s is the total length of the two platinum rods which support the electrodes, γ is the linear coefficient of expansion of platinum and β the coefficient of linear expansion of the material of which the cell is constructed. Combining these two expressions with Equations 62 and 63, we have the desired expression for the temperature coefficient of the Cell Constant, namely,

$$\frac{1\mathrm{d}K}{K\mathrm{d}t} = (\beta - 2\gamma) + \frac{s}{l}(\beta - \gamma) \tag{66}$$

from which it is evident that the shorter the electrode stems the smaller will be the temperature coefficient of the cell.

Cells of Type C.—If the diameter of the cross-section of the connecting tube is small in comparison with its length, we have approximately

$$\frac{\mathrm{d}l}{\mathrm{d}t} = l\beta \tag{67}$$

and

$$\frac{\mathrm{d}A}{\mathrm{d}t} = 2A\beta \tag{68}$$

and hence from Equation 63

$$\frac{1}{K}\frac{\mathrm{d}K}{\mathrm{d}t} = -\beta \tag{69}$$

Cells of the Arrhenius Type.—For this type we have

$$\frac{\mathrm{d}l}{\mathrm{d}t} = l\beta \tag{70}$$

and

$$\frac{\mathrm{d}A}{\mathrm{d}t} = 2\gamma A \tag{71}$$

and on combining with Equation 63 we have

$$\frac{1}{K}\frac{\mathrm{d}K}{\mathrm{d}t} = \beta - 2\gamma \tag{72}$$

Typical Illustrations.—The value of γ between 0° and 100° is $9\cdot10^{-6}$. For s we may safely put 2 cm. as the maximum value which the requirements of manufacture or of filling and cleaning will ever demand. Using these values Equation 66 may be written

$$\frac{1}{K}\frac{\mathrm{d}K}{\mathrm{d}t} = (\beta - 18\cdot10^{-6}) + \frac{2}{l}(\beta - 9\cdot10^{-6}). \tag{73}$$

For materials such as fused quartz where $\beta < 0.5\cdot10^{-6}$, this reduces to

$$\frac{1}{K}\frac{\mathrm{d}K}{\mathrm{d}t} = -18\cdot10^{-6}(1 + \frac{1}{l}). \tag{74}$$

For Jena Apparatus Glass for which[10] $\beta = 6\cdot10^{-6}$, it becomes

$$\frac{1}{K}\frac{\mathrm{d}K}{\mathrm{d}t} = -6\cdot10^{-6}(2 + \frac{1}{l}). \tag{75}$$

In Table I are given the values of $\frac{100}{K}\frac{\mathrm{d}K}{\mathrm{d}t}$, the percentage increase in the Cell Constant per degree rise in temperature, for some typical cells constructed of quartz and of Jena Apparatus Glass, respectively. It will be noticed that these coefficients are very small and that they are all negative. By making s smaller than 2 cm., they could be decreased still further.

It seems reasonable to suppose that the coefficients calculated in this way will usually justify the use of two significant figures in expressing them; that is, the influence of the "edge effect" will in most cases not introduce an error as large as 10% in the calculated coefficient. If this statement is true, then it will be apparent that if the cell constant is known for one temperature, its value at another temperature may be safely calculated by means of the above relationships, from the equation

$$K_2 = K_1(1 + (t_2 - t_1)\frac{1}{K}\frac{\mathrm{d}K}{\mathrm{d}t}) \tag{76}$$

provided that p_{K_2}, the permissible percentage error in K_2, fulfills the relation

$$p_{K_2} \geqq \frac{10(t_2 - t_1)\frac{1}{K}\frac{\mathrm{d}K}{\mathrm{d}t}}{1 + (t_2 - t_1)\frac{1}{K}\frac{\mathrm{d}K}{\mathrm{d}t}} \tag{77}$$

it being, of course, also true that p_{K_2} cannot be less than p_{K_1}.

A check on the above considerations by means of an experimental study of the variation of Cell Constants with the temperature has not been made.

---

[10] A value kindly given me by Dr. E. C. Sullivan of the Corning Glass Works.

TABLE I.

Values of $\frac{100}{K}\frac{dK}{dt}$, the percentage increase in the cell constant per degree rise in temperature, for different types of cells in which the length of each electrode stem is taken to be 1 cm.

Type of cell. (See Sec. 8.)	l in cms.	$100/K\ dK/dt$. Quartz $\beta = 0.44 \cdot 10^{-6}$.	$100/K\ dK/dt$. Jena App. Glass $\beta = 6 \cdot 10^{-6}$.
A	0.2	—0.0103	—0.0042
A	0.3	0.0067	0.0032
B	1.8	0.0027	0.0015
B	$\nless 10$	0.0018	0.0012
C	*	0.000044	0.0006
Arrhenius	All values	0.0018	0.0012

* For all cases where l is large in comparison with D, the diameter of the cross-section.

13. The Choice of the Material for Constructing a Conductivity Cell.—The material of which the cell is composed must first of all be practically insoluble in the liquids to be used in the cell. For most aqueous solutions,[11] at temperatures not greater than 100° and at atmospheric pressure, fused quartz and a number of varieties of glass fulfill this condition satisfactorily. Fused quartz and Jena Apparatus Glass are the materials which have been most extensively used in this laboratory for conductivity work and a brief comparison of their relative merits is perhaps worth while.

The quartz is, of course, more resistant to the attack of water than is the glass, but Kohlrausch's investigation of the solubility of Jena Glass[12] demonstrated that it is sufficiently resistant for all purposes where the solutions are to be made up and handled in contact with the atmosphere. This is confirmed by our own experience with it.[4] Conductivity water with a specific conductance of $0.21 \cdot 10^{-6}$ ohm has been kept in Jena Apparatus Glass for 12 hours without any appreciable change in its conductance and after several weeks' standing the conductance did not rise above $0.6 \cdot 10^{-6}$ and in this case the contamination undoubtedly came from the atmosphere.

From the standpoint of cost of material and ease of construction the glass is, of course, to be preferred. A tight seal between the glass and the platinum is comparatively easy to make and is not likely to fracture if handled with ordinary care, and good cells can be made by any skilled glass blower. The manufacture of quartz cells, on the other hand, re-

---

[11] Such cases as solutions of hydrofluoric acid, solutions at very high temperatures and pressures and solutions of strong alkalies and acids, especially when hot, represent special cases which require individual treatment and they are, therefore, not included here.

[12] Kohlrausch, *Ber.*, **26**, 2915, 2998 (1893).

quires the services of a skilled quartz worker and the operation of sealing in the platinum electrodes is covered by patents.

From the standpoint of the magnitude of the effect of temperature on the cell constant, quartz is superior to Jena Apparatus Glass for constructing cells of Type C. As shown in Table I, the cell constant of a quartz cell of this type changes only 0.004% for a 100° change in temperature. From the same point of view the glass is superior to the quartz in the case of cells of Types A and B, as shown by the data in the Table. By choosing a glass with the proper coefficient of expansion it is theoretically possible to construct cells of these types in which the cell constant will be practically independent of the temperature. The necessary condition is obtained by equating the right hand member of Equation 66 to zero, giving

$$\beta = \frac{2 + \frac{s}{l}}{1 + \frac{s}{l}} \gamma \tag{78}$$

or putting $s = 2$ and $\gamma = 9 \cdot 10^{-6}$

$$\beta = \frac{2 + \frac{2}{l}}{1 + \frac{2}{l}} \gamma. \tag{79}$$

According to the value of l, β varies between $18 \cdot 10^{-6}$ and $9\ 10^{-6}$. Glass can be manufactured[13] with almost any coefficient of expansion between $3 \cdot 10^{-6}$ and $14 \cdot 10^{-6}$, so that the above conditions could be met if desired.

Aside, however, from the desirability of having a cell constant with a small temperature coefficient, it is essential that the cell constant shall not exhibit appreciable thermal hysteresis. With respect to this quality, quartz would be superior to any glass and for this reason quartz is to be greatly preferred for all very accurate work at temperatures greatly removed from room temperature. For the same reason glass cells should be very carefully annealed and aged for a period before being put into use.

14. The Elimination of Polarization. (*a*) *By Platinization and Increase of Frequency.*—The elimination of the effects of polarization in conductivity measurements is usually effected by control of the frequency of the current and of the size and the extent and degree of platinization of the electrode surfaces. In all cases where the presence of platinum black is permissible it has been our experience that polarization can always be eliminated, even when using comparatively low frequencies ($f \ngtr 1000$) by the usual process of platinizing the electrodes. It sometimes happens, however, that the solution under investigation contains a substance which

---

[13] Sullivan, *J. Soc. Chem. Ind.*, 35, 513 (1916).

undergoes a slow decomposition or oxidation in contact with platinum black. Under these circumstances, provided the solution is not too concentrated, the effect of polarization may frequently be eliminated by simply increasing the frequency until a sharp minimum is secured.

The effect of uncompensated polarization always manifests itself by the appearance of a poor minimum, silence never being obtained and a different quality of tone usually being apparent on the two sides of the minimum. In eliminating polarization by the customary device of platinizing the electrodes it should be remembered that the heavier the coating of platinum black the more difficult and tedious will the operation of washing the cell be. The platinum black coating should only be of sufficient thickness to accomplish the elimination of polarization in the solutions for which the cell is to be employed. At present this can only be determined by trial since the problem of the degree of platinizing as a function of the frequency of the current and the nature of the solution, its concentration and temperature is one which still awaits systematic investigation.[14]

In eliminating polarization by increase of frequency, the frequency employed should not be greater than necessary to accomplish the desired result owing to disturbances arising from capacity and inductive influences, which disturbances increase with increasing frequency. For frequencies between 1000 and 5000 cycles the sensitivity of the human ear is approximately constant.

For use in investigations in which it is necessary to eliminate polarization by increase of frequency, it is convenient to have available, telephones tuned to one or two of the higher frequencies, say 1800 and 3000 cycles. It is, of course, also necessary to employ a cell designed to fit the telephone at the particular frequency which is to be employed.

As an illustration of the effect of increasing the frequency, some results obtained in connection with a recently completed investigation in this laboratory, may be mentioned. It was necessary to measure the conductance of a 0.002 N salt solution containing organic substances which decomposed in contact with platinum black. Using a cell of Type B provided with sand blasted electrodes, the minimum obtained with 1000 cycles was not satisfactory but by increasing the frequency to about 1800 cycles it became perfectly sharp.

In eliminating polarization by increase of frequency it should, of course, be remembered that the presence of polarization is not the only factor which causes a poor minimum and before attributing a poor minimum to this cause, one should make sure that the resistances and the condensive and inductive reactances are properly balanced and symmetrically dis-

---

[14] A few experiments along this line using a solution of platinum chloride as the electrolyte have been made by Wien (*Ann. Phys.*, 58, 57 (1896)).

tributed in the bridge net work, and that the electromagnetic shielding has been properly carried out. A quick way of deciding whether a poor minimum is due to the incomplete elimination of polarization or not is to substitute in place of the cell in question a second cell[15] having heavily platinized electrodes and filled with a solution which will give it about the same resistance as the original cell. If the minimum does not become perfectly sharp it indicates that causes other than polarization are responsible. A discussion of some of these other causes and their elimination will be taken up in the third paper of this series which will deal with the details of bridge construction and assembly.

In this connection it should also be remembered that not only will the minimum be poor when polarization is present, but the center of that minimum, even if it can be accurately determined, does not represent the correct bridge setting, but differs from it by an amount $\Delta R_B'$ which in our nomenclature is expressed by the equation[16]

$$\Delta R_B' = \frac{{}^1/{}_2 R_B}{(2\pi f C_p R)^2} \tag{80}$$

where C_p is the capacity equivalent of the polarization. As f increases C_p also increases and hence $\Delta R'$ rapidly decreases. The elimination of polarization is thus not merely for the purpose of bettering the minimum but also for the purpose of obtaining a correct bridge reading.

(*b*) *By Compensation and Increase of Frequency.*—For the measurement of the specific resistance of a *good* conductor in which for any reason the presence of platinum black is not allowable, the method of merely increasing the frequency ceases to be practicable owing to the lack of sensitivity of the telephone for the very high frequencies which would be required. In such a case, however, a method originally suggested by Kohlrausch and later developed and used by Wien is available. This method is based upon the electrical compensation of the polarization.

In so far as polarization acts like a pure condensive reactance in series with the cell it should be possible theoretically to eliminate it either by the insertion of a variable *pure* inductance in series with the cell, as was early suggested by Kohlrausch; or by the insertion of a variable capacity in series with the resistance box, as in the dielectric-constant method of Nernst.[17] Since the second method is impracticable for good conductors, owing to the magnitude of the capacity required, Wien took up the experimental study[18] of the first method, and he soon discovered that the

---

[15] A cell with heavily platinized readily adjustable electrodes would be convenient for this test.

[16] For the deduction and discussion of this equation and a number of experiments illustrating the magnitude of $\Delta R'$ for different frequencies see Wien, *Wied. Ann.*, **47,** 627 (1892).

[17] Nernst, *Z. physik. Chem.*, **14,** 622 (1894).

[18] Wien, *Loc. cit.*, **1896,** p. 37. See also Neumann, *Ibid* **67,** 499 (1899).

effect of polarization is not solely that of a pure condensive reactance but that an increase in effective resistance accompanies it. In other words the compensation of the condensive reactance arising from the polarization, while it improved the minimum, did not give the correct bridge setting but gave a value which corresponded to an apparent increase in the resistance of the cell. This apparent increase in resistance he found to be the smaller, the larger the electrodes and the higher the frequency, and he suggested the very plausible hypothesis that it arises from the incomplete reversal of the electrode reaction. Such a failure of the electrode reaction to reverse itself would mean the consumption of energy and in an alternating current circuit this would play the same role as ohmic resistance. Moreover, it would become less and less as the frequency increased.[19]

By Wien's device, therefore, of electrically compensating for the condensive reactance of the polarization and increasing the frequency so as to eliminate as far as possible the energy loss, arising probably from the incomplete reversal of the electrode reactions, he was able to secure very satisfactory measurements of good conducting solutions with unplatinized electrodes. These results of Wien have been recently reproduced with modern apparatus at the Bureau of Standards by Curtis and Taylor[20] who found that the above method applied to 0.1 *N* and 0.05 *N* solutions of NaCl gave, within 0.02%, the same ratio of specific conductances as was obtained with platinized electrodes.[21]

In concluding this discussion of the conductivity cell, it seems worth while to call attention to the need of a new determination of the absolute specific conductance of some solution. For the purpose of obtaining cell constants we are at present dependent upon Kohlrausch's determination of the specific conductance of potassium chloride solutions. It is doubtful if his values are as accurate as 0.05%. With modern apparatus the accuracy with which these values can be determined is limited only by the accuracy with which the salt could be purified and the solutions made up. It is to be hoped that some institution, such as our National Bureau of Standards for example, will before long undertake the repetition of Kohlrausch's measurements of the specific conductance of the material best suited for use as a standard in determining cell constants.

In conclusion I wish to acknowledge the assistance of Mr. H. J. Weiland and Mr. J. M. Braham in checking the algebra and arithmetic involved in the calculations given in this paper. Most of these calculations have

---

[19] In this connection the thought naturally occurs that the efficiency of platinum black in eliminating polarization in conductivity measurements is not due solely to the increase in the area of the electrode but arises in part from its catalytic powers.

[20] Curtis and Taylor, *Phys. Rev.*, **6**, 64 (1915).

[21] A third method for diminishing the influence of polarization has been described by Wolcott, *Ann. Phys.*, **12**, 1653 (1903).

been checked by both men and it is believed that the values given are correct.

URBANA, ILLINOIS.

REVIEW: THE PREPARATION OF CONDUCTIVITY WATER.[1]

BY JAMES KENDALL.

Received June 30, 1916.

Water so nearly corresponds to the universal solvent sought by the alchemists that it is a matter of extreme difficulty, whatever methods of purification are adopted, to obtain a sample which may be shown to be practically free from all conducting impurities. Still more onerous is the task of preserving such a specimen when once prepared, since solution from the containing vessel inevitably introduces some contamination. The final and practical object—to maintain the sample at its original purity while actually in use in conductivity determinations—borders closely upon the unattainable.

By repeated distillations *in vacuo* Kohlrausch and Heydweiller,[2] working in Strasbourg,[3] succeeded in obtaining, in a glass conductivity cell, water with a specific conductivity of 0.043×10^{-6} reciprocal ohms at 18°, or 0.015×10^{-6} reciprocal ohms at 0°.[4] These values are certainly very near to those which would be given by perfectly pure water at the corresponding temperatures. This has been proved by the employment of several distinct indirect methods for determining the ionization constant of water.[5] Kohlrausch and Heydweiller themselves estimate the specific conductivity of absolutely pure water at 18° to be 0.0384×10^{-6} reciprocal ohms.[6]

If it were possible to reproduce this work conveniently and, after obtaining in quantity water of such extreme purity, to employ it in actual conductivity work, then it is obvious that we should never need to apply to our results any water correction at all.[7] In order to do this, however,

---

[1] Nearly all chemists have occasion at some time to employ especially pure water in their investigations, and find that the usual methods often fail to give the anticipated results. It is difficult to collect from the references in the literature (since the work is generally only incidental) satisfactory suggestions in such a case. Perhaps the most frequent mistake made is to persist in the attempt to prepare water beyond the laboratory's limit of purity. In the following pages the previous work on the subject is summarized and the utmost degree of purity attainable under ordinary conditions indicated.

[2] Kohlrausch and Heydweiller, *Z. physik. Chem.*, **14**, 326 (1894).

[3] After each reference which follows, the place where the investigation was carried out will be indicated. The difficulty in obtaining good conductivity water varies considerably in different localities, as will be seen below.

[4] One millimeter of this water at 0° possessed a resistance equal to that of forty million kilometers of copper wire of the same sectional area, or a length of wire capable of encircling the earth a thousand times.

[5] Landolt-Börnstein, *Tabellen*, **1912**, p. 1187.

[6] This is often incorrectly quoted as *the experimental value* of Kohlrausch and Heydweiller. The results are also usually given without conversion from the Siemens units in which they were published to the units now employed.

[7] A general discussion of the water correction in conductivity determinations will