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THE CALIBRATION OF CELLS FOR CONDUCTANCE MEASUREMENTS. II. THE INTERCOMPARISON OF CELL CONSTANTS

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Introduction

Although several new methods have been introduced within the last few years, by means of which information regarding the state of electrolytic substances in solution may be obtained, conductivity measurements still remain the only method whereby concordant results may be obtained in the most dilute solutions. It seems well, then to examine these measurements critically to see whether the assumptions underlying them are justified, and whether the apparent concordance of these results is really a measure of their trustworthiness. The length of time during which conductance measurements have been in vogue and the great number of investigations which have made use of this method seem to have predisposed the acceptance of the results without such a critical examination. Without a continual effort to increase the absolute accuracy, as well as the precision of this method, it is evident that these measurements will be superseded by those from the more recently developed methods.

There have been but few modern attempts to improve the conductance method, and these, while contributing greatly to the increase of the precision of the measurements, have for the most part left the inherent accuracy of the method unquestioned. No investigator can long work with a modern conductance outfit, however, without finding a number of possible sources of error and perplexing phenomena, many of which have never been even mentioned in the literature. A sufficient variety of these sources of error will be discussed in the later sections of this article to show that there exists abundant evidence to warrant an extended investigation into the accuracy of the method. That attempts at such investigations have been so infrequent and so few of the results have been published is due, undoubtedly, to the numerous difficulties encountered, to the mass of conflicting material obtained and the complexity of the problem as a whole.

The present investigation was undertaken to compare 2 conductivity cells over a large range of concentrations in order to obtain a knowledge of the range through which reliable measurements might be obtained with a given cell. The ultimate intention was the determination of the absolute value of the specific conductance of certain solutions, which could then be used as standards in order to obtain the "cell constants" of other cells, since the first paper of this series[2] had shown that the data in general

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[1] National Research Fellow in Chemistry.

[2] Kraus and Parker, THIS JOURNAL, 44, 2422 (1922).

use, given by Kohlrausch and Holborn are not satisfactory for this purpose. A new method for the intercomparison of cell constants was devised, and several types of electrodes were intercompared, in this preliminary work.

Work of Previous Investigators.—An extended intercomparison of conductivity cells over a large range of concentrations has apparently never before been undertaken.

In Kohlrausch and Maltby's work[3] there occur three such intercomparisons but only through a limited range of concentration.

To form a basis of comparison, it will be assumed, for their measurements, that the cell in which the spacing of the electrodes is greater gives the more correct value for the specific conductance of a given solution. This assumption seems justified for these concentrations and resistances. In this case, we see from the intercomparison of their Cells XXXV and R_2 (using the data for the potassium chloride solutions[4]) that the "cell constant" of the latter cell apparently increases by 0.03% between the concentrations of 1.0 *N* and 0.2 *N*. In the intercomparison between R_1 and R_4b (using the data for potassium and sodium chloride solutions) the "constant" of the latter is found to be 1.9298, 1.93035 and 1.93023 at the concentrations of 0.1 *N*, 0.05 *N* and 0.01 *N*, respectively. In the intercomparison between cells R_1 and R_2 with R_{12}, the latter of which has electrodes spaced the closest, the average values determined for the "cell constant" are 0.099020, 0.098982 and 0.099005 as the resistance is increased from 80 to 165 ohms.

In an intercomparison given by Taylor and Acree,[5] Cell III has the larger electrodes with the greater spacing and if this is assumed to give the more correct value for the specific conductance of the solutions, the constant of the other cell is proportional to the numbers, 1.1360, 1.1358 and 1.1361 at the concentrations of 0.2 *N*, 0.1 *N* and 0.05 *N*, respectively.

In these intercomparisons it is evident that there is a distinct indication that the constant of the cell, whose electrodes are positioned the closer, increases in the more dilute solutions, if the other "cell constant" is assumed to remain fixed. If the intercomparisons are carried to low enough resistances there is another rise, due to polarization, thus producing a minimum value at moderate resistances.

These appear to be the only examples in the literature where two cells are intercompared, one of which may be safely assumed to give the more nearly correct value of the specific conductance of the intercomparison solutions.

Preliminary Measurements

It is realized that the nature of the results in the experimental section of this article is such as to cause skepticism regarding their accuracy. It seems well, therefore, to outline briefly the series of tests which were developed in order to insure that the resistance measurements in this

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[3] Kohlrausch and Maltby, *Wiss. Abh. Phys.-Tech. Reichsanst.*, **3**, 162, 173 (1900).

[4] The necessity for using the data for the same or closely related salts, in their intercomparisons, will become evident in the later sections of this article.

[5] Taylor and Acree, THIS JOURNAL, **38**, 2421 (1916).

investigation should represent the true resistance of the cells, as found by the Kohlrausch alternating current method. A description of the bridge, resistance boxes, thermostat, etc., which were used in this investigation, is given in an article by Kraus and Parker.[6]

Testing the Conductance Outfit with Known Resistances.—In order to test the bridge equipment for any possible source of error a complete series of measurements was made upon known resistances with the outfit in its final form and with both alternating and direct current. These measurements would evidently have revealed any possible source of error such as would have been eliminated by a direct substitution method, and in reality they are seen to have constituted such a method. A series of non-inductive resistances[7] as well as a standardized Curtis resistance box were used as the known resistances. A condenser was placed in parallel with these resistances and balanced out by means of the capacity in the regular bridge equipment. Resistance measurements were made at a series of frequencies ranging from 350 to 1750 and at two different voltages (0.2 and 10 volts). The condenser in parallel was likewise varied in order to show any influence upon the apparent resistance. The resistances found by direct current were assumed to be correct.

The maximum variation from the *correct resistance* found in these measurements was about 0.05%. This occurred at low frequencies and the lower voltage. It was found that the *correct resistance was obtained*, with the higher voltage, at frequencies over 1000 and with the lower voltage at frequencies in the neighborhood of 800. Consequently, in the actual conductance measurements, these were the two adjustments utilized.[8]

Testing the Bridge.—The bridge was calibrated by means of 2 standardized Curtis resistance boxes, with both alternating and direct current. The frequency of the alternating current used was 1200. The two calibration curves were identical for the lower readings of the bridge (with extension coils in circuit) and considerably past the center, but they began to diverge at a bridge reading of about 700, until at a reading of 1000 the discrepancy was 0.02%. The calibration was made with a resistance of about 10,000 ohms on both sides, but it was found that the discrepancy mentioned was not altered when this resistance was increased. This was the only indication which the writer obtained of the possibility

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[6] Kraus and Parker, This Journal, **44**, 2432 (1922).

[7] Three silvered quartz fibers ranging in resistance from 600 to 2000 ohms were used, besides a series of film resistances which reached 3000 ohms. A standardized Curtis resistance box was used in the regular bridge equipment.

[8] It was the usual practice to employ the higher voltage and a frequency of 1200 throughout a conductance run, since it was found that the variation with the voltage caused an effect *in the cell*, which varied with the electrolyte being measured, as well as the resistance.

of any error caused in the measurements by the inductance and capacity in the slide wire of the bridge, such as suggested by Taylor and Acree.[9] It is evident that the measurements obtained in the center of the bridge will not be influenced by even this small error. The Kelvin method of calibration gave a curve which agreed very closely with that obtained by means of the direct current and the 2 resistance boxes.

Testing the Conductivity Cell.—When the electrolyte was measured in the cell, during a conductance run itself, only the two adjustments were used which had been shown to give the *correct resistance* (assuming that a conductance cell acts like a non-inductive resistance with a capacity in parallel). In order to determine the manner in which the resistance of the electrolyte itself varied when measured in the cell, however, its resistance was determined at a series of frequencies when a series of non-inductive resistances, as well as the Curtis resistance box, was used as known resistance in the bridge arrangement. The form of curve showing the variation with the frequency agreed for the two types of known resistance (from 300 to 3000 ohms), so it is thought that the form found for the Curtis box alone at the still higher resistances is correct. The film resistances alone were used at the lower voltage.

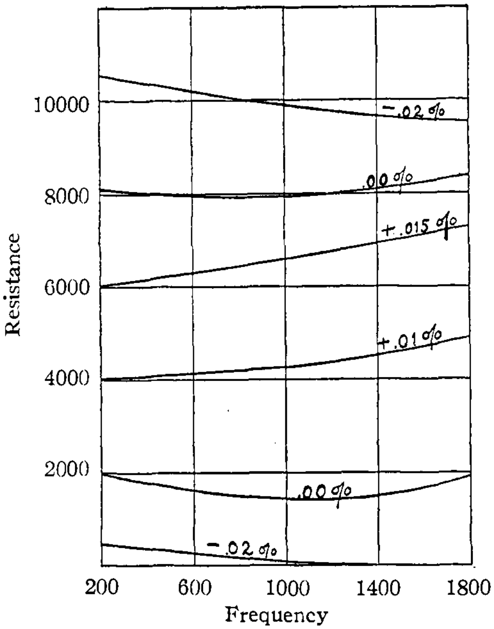

Fig. 1.

Variation with Frequency.—The general trend of the data obtained at the higher voltage in this investigation is shown in Fig. 1. The data obtained at low voltages show somewhat greater variations than those recorded on the figure, but in the same direction through most of the resistance range. The apparent resistances of the cell are indicated as ordinates, and the frequencies as abscissas. The variation of the resistances are, of course, exaggerated, the true variations being indicated on the individual curves. Below 300 ohms the variation rapidly increases as the resistance is decreased, due undoubtedly to the effect of polarization. The form of the curve in this region is shown to justify the expedient of

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[9] Ref. 5, p. 2407, where it is stated that errors of 1% may arise from this cause, with certain bridge arrangements.

Taylor and Curtis[10] who recommend extrapolation to "infinite frequency" to eliminate polarization. As for such an extrapolation applied to all conductance measurements, as recommended by Taylor and Acree,[11] it would be difficult to see what the significance would be if it were applied to such curves as occur at resistances between 2000 and 8000 ohms. Above 8000 ohms it is possible that such a correction would again become significant.

Between the resistances of 2000 and 8000 ohms there is a region where the apparent resistance of the cell *increases* with the frequency. It is indicated that this is the normal trend of the variation for well platinized electrodes in iodic acid at high voltages and at resistances at which the measurements are not influenced by polarization or some similar effect.

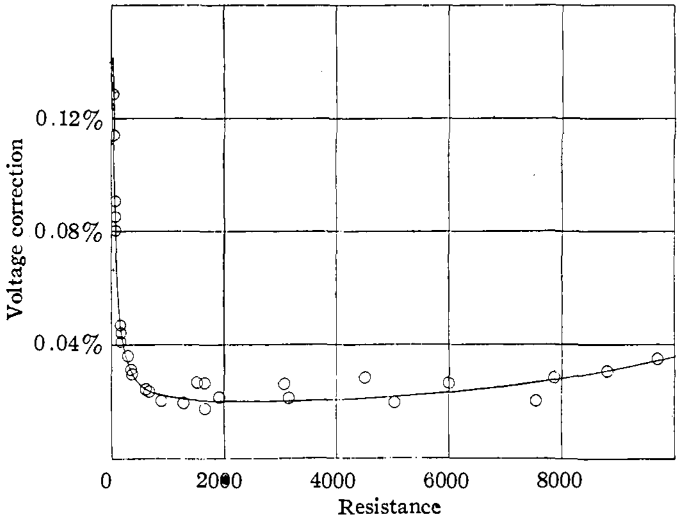

Fig. 2.

The variations found in this region are so small, however, that confirmation can come only by means of an investigation covering a considerably greater range of frequencies. It may be mentioned that this variation is opposite in direction to that predicted by Eastman.[12]

Variation with Voltage.—The variation of the apparent resistance of an electrolyte in a cell is likewise complex. It was mentioned that the variation with the frequency went in the same direction at the two voltages, but that the variation at the lower voltage was greater than that at the higher voltage. This is further complicated by the fact that the variation with the voltage, *at moderate resistances*, may actually change

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

[11] Ref. 5, p. 2409. Acree, *Trans. Faraday Soc.*, **15**, 176 (1919).

[12] Eastman, THIS JOURNAL, **42**, 1648 (1920).

sign with the electrolyte being measured, as mentioned by Kraus and Parker.[13] This fact shows that this effect is intimately connected with overvoltage and kindred electrode phenomena.

In Fig. 2 are plotted data obtained with potassium chloride solutions, in which case the higher voltage gives the higher resistance throughout the curve. The differences in percentages between the two voltages are plotted against the resistances. It is seen that, at lower resistances where polarization has a controlling influence, this variation with the voltage reaches enormous proportions. The same tendency is found at the higher resistances, where there is also a distinct rise in the curve.

It is to be noted that the curves of Figs. 1 and 2 both show the presence of *two* auxiliary effects, the one whose influence is felt at resistances above 7000 ohms and the other below 300 ohms. Both of these figures indicate that *there is an effect, similar in some respects to polarization, which occurs at the higher resistances.*

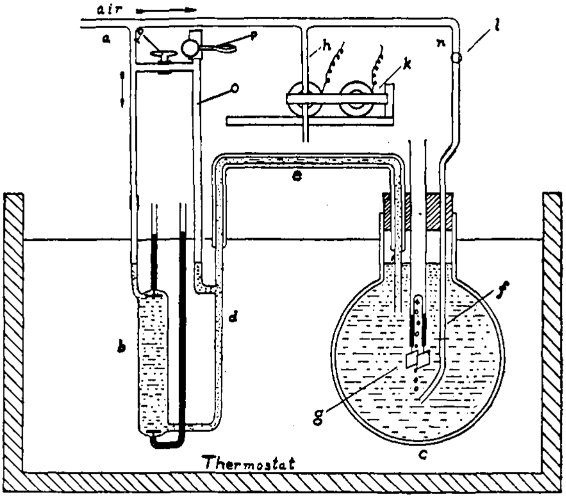

Fig. 3.

It is to be emphasized that these variations were found on a single type of electrode (shown in Fig. 3 at *g*) and with a single electrolyte. These effects are undoubtedly influenced by these factors, but it is believed that the two important phenomena occurring at very low and also at high resistances, are common to all well-platinized electrodes and electrolytes, although varying in extent and position in the curve with the disposition of the electrodes.

Apparatus and Manipulation

Apparatus.—It was evident that, in order to obtain a good intercomparison between cell constants, some method of mixing the solutions

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[13] Ref. 6, p. 2438.

must be used that would work automatically and insure identical concentrations in the cells. The apparatus, as finally perfected, is shown in Fig. 3.

The cells used as standards to be compared with the other electrodes were of the pipet type such as is shown at *b*. Different types of electrodes were placed in the large quartz flask *c* and these were compared with the pipet cells by measuring the resistances after thorough mixing had occurred. Purified air is blown through the rubber tube *a*, which divides into 3 paths. When the electromagnet *k* is open, the air goes through the by-pass at *h*, and no pressure is produced in the rest of the system. When *h* is closed by the electromagnet, however, the pressure rises and blows the solution in the pipet cell into the quartz flask, at the same time stirring the solution in the flask by bubbling through the tube *f*. The relative pressure in the 2 branches is governed by the stopcock *n*. The stopper in the quartz flask has another hole in it, not shown in the drawing, which permits the air to escape. When the pressure is released, the solution siphons back into the pipet cell and thus thorough mixing occurs between the 2 cells. The temperature is kept identical in the 2 cells by the vacuum jacket *e*. In this way complete equilibrium is obtained, in the more concentrated solutions, in about half an hour. The current operating the electromagnet *k* is interrupted by means of a contact, formed by a strip of copper running on the edge of a worm-screw reducing gear. The tubes at *o* and *q* were introduced later, in order to break the column of liquid through the siphon, and were not used in the measurements recorded in this article. The measurements with this apparatus showed that consistent results may be obtained to much higher dilutions than cell constants have ever before been intercompared.

Manipulation.—The method of carrying out a run, with this apparatus, was as follows. The 2 cells to be intercompared were first cleaned inside and out with cleaning mixture, hot water and steam. The electrodes were washed with alcohol, in order to remove the adsorbed acid. Then the 2 cells were filled with distilled water of approximately 1.5×10^{-6} specific conductance, placed in the thermostat and the potassium chloride was introduced in the form of a concentrated solution, from a pipet, a small amount at a time. This solution was not made up carefully, since it was necessary only to have equilibrium between the 2 cells, the absolute value of the concentration not being necessary. The approximate value of the concentration may be obtained by calculating the specific conductance from the "cell constant" and comparing this with the known values for potassium chloride at 25°.

The resistance was measured in the pipet cell and in the large cell, and the ratio calculated, at each measurement. The mixing of the solution and the measurements were continued until this ratio became reproducibly constant for a considerable length of time.

Results

The results of the intercomparison measurements with this apparatus are given in Tables I and II. The data are plotted in Figs. 4 and 5.

In the first and third columns of Table I are given the resistances of the electrodes of the type shown at *g* in Fig. 3, found with a series of concentrations of potassium chloride. The ratios of this resistance to the resistance of the pipet cell, *for the same concentration*, are given in Cols. 2 and 4. These ratios are proportional to the values of the cell constants of Cells II_a and II_b which may be found by multiplying these ratios by the constant of the pipet cell (assuming that the latter remains fixed at 3.67117 over this concentration range), although this value was determined with the standard 0.1 *N* solution. The resistance found in the pipet cell, at each concentration, may be determined by dividing the resistances in the first and third columns by the corresponding ratio.

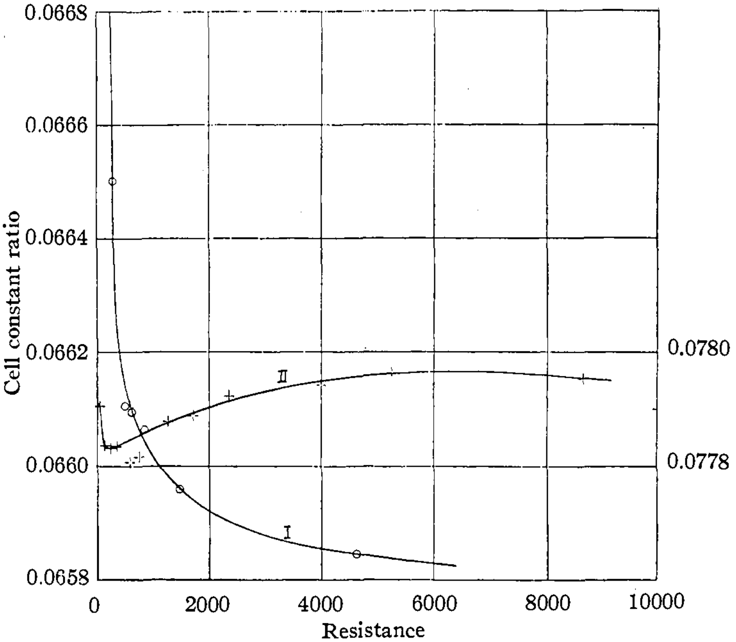

Fig. 4.

In Cells II_a and II_b the electrodes are nearly identical, except that in the latter case they have been platinized. The electrodes were broken and repaired after this process, so the curves cannot be compared regarding

TABLE I

INTERCOMPARISON OF CELL CONSTANTS

Curve I[a] (unplatinized)		Curve II (platinized)	
R of Cell II_a	Cell const. ratio II_a/I	R of Cell II_b	Cell const. ratio II_b/I
4,619.9$_0$	0.065843$_6$	8,675.0$_5$	0.077953$_8$
1,460.2$_9$	.065958$_7$	5,243.9$_0$	.077962$_8$
840.19$_0$	.066064$_1$	3,989.6$_9$	.077942$_4$
610.10$_0$	.066095$_2$	1,708.6$_4$	.077887$_3$
490.09	.066104	1,257.0$_9$	.077878$_7$
280.04	.066501	748.21$_6$	.077816$_0$
150.04	.06711$_8$	586.86$_7$	.077807$_1$
		350.90$_9$	.077835$_0$
		242.92$_9$	.077831$_9$
		133.89$_9$	.077836$_1$
		42.68$_4$	.077905$_3$

[a] These data were taken by Mr. Harold Heiser.

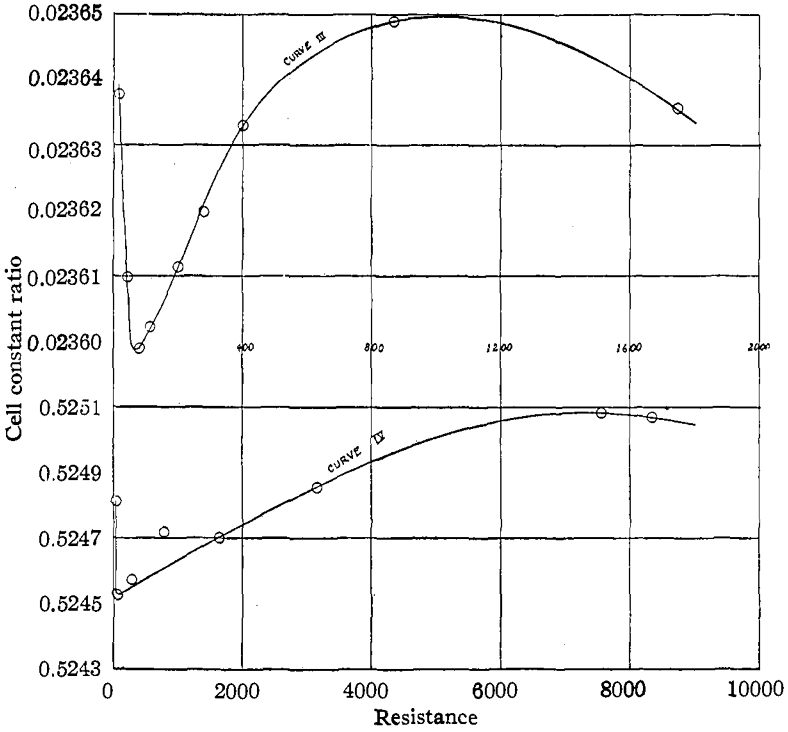

Fig. 5.

TABLE II

INTERCOMPARISON OF CELL CONSTANTS

Curve III		Curve IV	
R of Cell II_c	Cell const. ratio II_c/I	R of Cell I	Cell const. ratio I/IV
$1,748.0_5$	0.023635_7	$8,342.4_6$	0.52506_6
869.00_4	$.023649_0$	$7,556.5_6$	$.52508_3$
400.93_0	$.023633_1$	$3,156.4_3$	$.52485_5$
279.87_9	$.023619_8$	$1,636.7_4$	$.52469_9$
201.91_8	$.023611_8$	785.25_2	$.52472_6$
111.44_3	$.023602_1$	279.05_6	$.52457_1$
78.58_1	$.023598_9$	50.27_7	$.52453$
44.84_0	$.023609_8$	31.73_0	$.5248_1$
18.62_3	$.023638$		

the change in the value of the constant due to platinization. These electrodes have an area of 1.55 sq. cm. and are 2.3 cm. apart. In Cell II_c (Curve III) the electrodes have an area of 1.59 sq. cm. but are only 0.25 cm. apart. Cell I, the pipet cell, with which the above cells are intercompared, and whose ratios are plotted in Fig. 5, Curve IV, has electrodes with an area of 1.5 sq. cm. which are about 10 cm. apart. Cell IV is shown in Fig. 3 of the paper by Kraus and Parker.[14] This has electrodes of about the same area but 30 cm. apart.

Discussion

It is evident from a glance at the curves in Figs. 4 and 5 that one of the most fundamental of the assumptions underlying conductance measurements is considerably at fault. Every conductance measurement is based on the assumption that the value of the so-called "cell constant" is maintained throughout the concentration range which may be used in that cell. Hence, when two "cell constants" are intercompared over this range of concentrations, a constant ratio should result. No two of these cells exhibit this constant ratio. The possible factors which might cause the failure of this condition are numerous, and there are few facts which would indicate the true nature of the cause for this failure.

In measuring the lower resistances, where polarization enters, it may be safely assumed that the cell having the greater distance between its electrodes and exhibiting the greater resistance, will give the more reliable readings. At the higher resistances, the choice of the cell giving the more reliable readings is more difficult. It is evident from the direction of the effect in the more dilute solutions that, if the correction which should be applied to the resistances to give a constant ratio, is *relatively* greater for the shorter cell, then the correction is negative. If the longer cell has the *relatively* greater correction, the correction is positive. Whether the correction is to be positive or negative depends upon this choice. The cause for the effect might be in the resistance box, in the bridge, in connection with the thermostat or in the cell itself. The facts gathered thus far indicate that the effect is in the cell itself and that the correction is negative, that is, that the resistances, R, should be corrected by an amount ΔR, which should be subtracted from the apparent resistance. The facts leading to this choice will be presented in more detail in the next article of this series.

Effect of Platinization and Disposition of Electrodes.—Several interesting facts can be derived at once from Figs. 4 and 5. The cell-constant ratios are plotted against the corresponding resistances of the electrodes. It is seen that in each curve there is a sharp rise of the cell-constant ratio at the lower resistances. This is due undoubtedly to the effect of polarization. The entrance of this effect in Curves II, III and IV causes a sharp break in the curve, while in Curve I, in which the electrodes are unplatinized, the rise is gradual over the entire extent of the curve, becoming extremely steep at the lower resistances. The polarization is seen to affect the entire shape of the curve and to obscure a second effect which is exhibited in the other curves. At resistances above 3000 ohms, this curve

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[14] Ref. 2, p. 2433.

shows a constant value of the ratio, and this is the only region in which the use of these electrodes is justified without the use of some method for the correction or elimination of this effect. From the statement of Kohlrausch[15] it would be inferred that these electrodes (area 1.5 sq. cm.) could be used to measure a resistance of 160 ohms, but at this resistance we should have a correction of 1.7%, if the only constant value of the ratio were assumed to be correct.[16]

The effect of the disposition of the electrodes upon the shape of the curve likewise becomes evident from these 2 figures. Thus, Curves II, III and IV all have the same general characteristics, but the sharp minimum exhibited in Curve III (electrodes 0.25 cm. apart) is less pronounced in Curve II (electrodes 2.3 cm. apart) and has broadened out to a considerable extent in Curve IV (electrodes 10 cm. apart). The total variation in the curve is likewise reduced upon increasing the distance between the electrodes. This fact would indicate that *the cell having the electrodes at the greatest distance gives the most nearly correct value for the specific conductance of a given solution.*

A Disturbing Effect in the More Dilute Solutions.—The rise shown in the cell-constant ratios of Curves II, III and IV at the higher resistances indicates the presence of a disturbing effect which apparently has never before been mentioned in the literature.[17] These curves indicate that the relative size of this effect is reduced by moving the electrodes to a greater distance. It is possible that the absolute amount of the correction, at a given concentration, is identical for the different cells, but since the resistance is greater in those cells having electrodes at the greater distance, the *relative* effect would be less. These curves likewise indicate that the closer the electrodes, the lower the resistance at which this effect enters. It is possible, however, that the effect enters at the *same concentration* in the different cells, but at this concentration it is evident that the resistance would be lower in the cell having the electrodes at the least dis-

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[15] Ref. 3, p. 10, where it is stated that unplatinized electrodes may be used where the area is $250/w$ sq. cm., where w is the resistance expressed in ohms.

[16] It is evident that the effect of the polarization is much greater than usually supposed or that an additional factor, such as the distance apart of the electrodes, must be introduced into Kohlrausch's expression. The writer's experiments indicate that the expression $R = 160\sqrt{d}/A$ holds fairly well as an indication of the critical resistance at which polarization enters, *for well platinized electrodes*, where R is the critical resistance in ohms, d is the distance apart of the electrodes in centimeters and A is the area of 1 electrode in sq. cm. It is possible that the similar expression which should hold for unplatinized electrodes is $R = 2500\sqrt{d}/A$ as would be derived from this one determination.

[17] The apparent bending back of these curves at the highest resistances is not to be relied upon, since the later measurements, made when the column of liquid through the siphon tube, *e*, Fig. 3, had been broken, do not exhibit this feature. The other characteristics of the curves are still present.

tance. These questions cannot be satisfactorily answered without a more complete investigation in these dilute solutions.

Authenticity of Effect.—Although this effect in the more dilute solutions has never been mentioned before, it was shown in a previous section that the intercomparisons recorded in the literature which were likely to disclose an effect of this nature, actually did show an indication of an increasing cell constant in the more dilute solutions. It was likewise shown that the variation in the apparent resistance of a series of solutions, by change of frequency and voltage, indicated the presence of a disturbing effect in the more dilute solutions. Hence the authenticity of this disturbing effect can scarcely be doubted. It may be mentioned that the range of concentrations over which these measurements have been taken is about 25 times that employed by Kohlrausch and Maltby and 50 times that used by Taylor and Acree. Without such an accurate method for the intercomparison, it is evident that these investigators could not have been certain of the presence of such an effect.

It is indicated that the presence of this effect is revealed only when there is a considerable difference in the disposition of the electrodes. This explains why various investigators may have obtained remarkable agreement in the more dilute solutions, since it is certain that in these solutions the dispositions of the electrodes have been very similar. If such an effect had been indicated, the predisposition would have been to lay it to experimental error.

Magnitude and Direction of Effect.—The importance of this effect in the more dilute solutions cannot be exaggerated. Most of the investigations upon the accuracy of the conductance method have been made upon the concentrated solutions, where the effect of polarization was early discovered and means found for its elimination. The agreement of various investigators and the relationships found holding between the ion mobilities have constituted the greater part of the proof for the accuracy of the measurements in the more dilute solutions. The importance of this effect may be seen when it is mentioned that Curve II shows an apparent variation in "cell constant" of 0.17% while the resistance changes from 200 to 6000 ohms. Curve III shows a change in "cell constant" of 0.22% when the resistance is changed only from 100 to 1000 ohms. Curve IV, showing the "cell constant" of the pipet cell, which had been assumed fixed in the intercomparison with these other cells, shows a variation of 0.11% while the resistance is changed from 200 to 8000 ohms. It is evident that this latter variation will have to be added to the variation of the other curves. In Curve III, this additional variation must be added at a resistance of only 160 ohms, since this is the resistance of Cell II_c, when Cell I gives a resistance of 8000 ohms. Thus we have a demonstrated error of 0.33% in the "cell constant" of

Cell II_c occurring at resistances far below those which are used in measurements upon the most dilute solutions. The shape of the curve and the value of the "cell constant" at these higher resistances can only be conjectured. The value of the "cell constant" and the disposition of the electrodes of Cell II_c are very similar to those used in the measurements of Kohlrausch and Maltby upon dilute potassium chloride solutions,[18] which have, up to the last few years, been considered the standard of accuracy in conductance measurements.

The application of a series of corrections to the "cell constant," the necessity for which has been indicated in these measurements, will evidently increase the values of the equivalent conductance in the dilute solutions. The values at infinite dilution may be affected to a considerable extent, reducing the calculated values for the "ionization" correspondingly. It is believed that the new values found for the salts will be unchanged *relatively*, and will still retain the valuable inter-relationships found for these electrolytes. If the writer's theory of the cause of these corrections should prove correct, however, the values for the acids and bases are likely to be changed relatively to the salts.

Theory.—The most logical cause for such a correction is to be found in the adsorbed layer at the surface of the electrode. If this layer contains a defect of the conducting species, as is probable with potassium chloride, all of the effects described in this article could be reasonably accounted for. The effect of the alternating current upon this adsorbed layer would probably be similar to a wave motion upon an adsorbed surface layer, causing a spreading out of the excess or defect to a considerable distance. The sign of the effect would be partially determined from the sign of the adsorption coefficient. It is evident, of course, that a positive adsorption would have to be "spread out" to a considerable extent to cause a reduction in the apparent resistance, while the decrease in concentration in the body of the solution might even cause the actual correction to be of the opposite sign. An increase of voltage, besides causing an increase in the "spreading out" of this layer, would probably be similar in effect to an increase of pressure upon the system.

Summary

1. A series of preliminary measurements is outlined, which were made to insure the accuracy of the results found in this investigation. The general trend of the variations in the apparent resistance of a series of solutions, by change of frequency and voltage of the impressed current, is indicated.

2. A new method is described for the accurate intercomparison of cell constants over a great range of concentrations, and the results of four such

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[18] Ref. 3, pp. 170–173.

intercomparisons are given. The range of concentrations through which these intercomparisons were made is 25 times greater than that used previously.

3. The effect of platinization and the disposition of the electrodes upon a "cell constant" is shown by the intercomparison curves. It is indicated that there is a gradual transition in the shape of curve as the electrodes are placed farther apart, the farthest apart giving a curve showing the most nearly constant value. None of the electrodes intercompared gives what could be considered a *fixed* value for the derived "cell constant."

4. A new effect, similar in some respects to polarization, is found to occur at high dilutions with all types of cells which have been used in this intercomparison. This effect is *demonstrated to amount to at least* 0.33% *at moderate dilutions*, in the case of one type of electrode which has been used in many accurate conductance measurements.

5. The existence of this effect at high dilutions is shown to be supported by the results of other investigators over a more limited range of concentrations. It is also supported by the writer's observations upon the variation of the apparent resistance of a cell with the voltage and frequency, at high dilutions.

6. Correction of the existing conductance data for this effect would tend to increase the values of the equivalent conductance at the higher dilutions. The limiting values would probably be affected to a considerable extent, the values of the calculated degree of ionization being reduced in like proportion.

7. A theory to account for this effect, at high dilutions, is outlined. This theory accounts for the effect by the assumption of an adsorbed layer in contact with the electrodes. The correction for the resistance of this layer is assumed to be positive or negative according to whether the adsorbed layer contains an excess or a defect of the conducting species.

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