[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, THE UNIVERSITY OF CHICAGO]

THE CALIBRATION OF CELLS FOR CONDUCTANCE MEASUREMENTS. III. ABSOLUTE MEASUREMENTS ON THE SPECIFIC CONDUCTANCE OF CERTAIN POTASSIUM CHLORIDE SOLUTIONS

BY HENRY C. PARKER[1] AND ELIZABETH W. PARKER

RECEIVED OCTOBER 19, 1923

Introduction

In a recent article[2] Kraus and Parker showed the presence of an error in the data given by Kohlrausch and Holborn[3] which have commonly been used for the purpose of calibrating cells for conductance measurements. They likewise showed that there were in the literature several indications of inaccuracy in the relative as well as the absolute values of these measurements. There had been several suggestions in the literature[4] before this as to the advisability of a redetermination of these absolute values, but the necessity for such a redetermination was now finally established.

That these measurements were not repeated at a much earlier date is due to the fact, undoubtedly that relative are much more important than absolute values. If there was a single solution at a single temperature upon which all the measurements were based, the necessity for a redetermination would not be urgent. The use of these original data was such, however, that any one of five different electrolytes might be used at any temperature within a considerable range and in the case of one of the electrolytes at any one of four different concentrations, as a basis for the determination of cell constants. Since modern refinements in the Kohlrausch method, mostly of American origin, have increased the precision of conductance measurements many fold, it was evident that future determinations could not be given to the degree of accuracy justified by their precision until a better and more accurate cell constant basis had been established. Such was the purpose of the present investigation.

System of Units

Since the investigation of Kohlrausch, Holborn and Diesselhorst,[5] conductance measurements have been based on the ohm and the hydrogen temperature scale. Recently, however, the more precise determina-

---

[1] National Research Fellow in Chemistry.

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

[3] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," Teubner, Leipzig, **1916**, p. 76.

[4] (a) Washburn, THIS JOURNAL, **38**, 2459 (1916). (b) Eastman, *ibid.*, **42**, 1655 (1920).

[5] Kohlrausch, Holborn and Diesselhorst, *Ann. Phys.*, **64**, 440 (1898).

tion of the relation between the liter and the cubic decimeter[6] has entered to complicate the other units upon which these measurements have been based. This is due to the fact that concentrations have been based upon the liter as a unit of volume, while the specific conductance and the cell constants have been based, presumably, upon the centimeter. This has caused the equivalent conductance to be expressed in a hybrid unit.[7]

The precision of conductance measurements at the present time is just sufficient to make the small difference between the cubic decimeter and the liter of significance. If the precision of the measurements is increased this difference will become of greater importance and in any case an incorrect basis of units can only result in confusion.

It is evident that the proper procedure would be to select either the liter and the $\text{ml.}^{1/3}$ as units of volume and length, respectively, or on the other hand to choose the cubic decimeter and the centimeter for the same purpose. In order that the true specific conductance of the solutions may be obtained, in the same units in which all other specific conductances are expressed, and since the centimeter is a more fundamental unit of length than the $\text{ml.}^{1/3}$ it seems evident that the latter choice is the better. When an electrical measurement is involved, confusion would be certain to result if the $\text{ml.}^{1/3}$ were to be introduced as a unit of length.

The adoption of the cubic decimeter and the centimeter as units of volume and length, respectively, requires the concentrations to be expressed in equivalents per cubic decimeter rather than in equivalents per liter.[8] The concentrations could no longer be called "molal" or "normal" but a new expression could readily be adopted. The letter D has been adopted in this article to indicate concentrations which are expressed in equivalents per cubic decimeter. To take the place of the word "normal" the expression "*demal*" is suggested.

In terms of these units we then have the cell constant, K, expressed as $K = (l^2/v)\ \text{cm.}^{-1}$, where l is the length in centimeters and v the volume in cubic centimeters. The specific conductance, L, becomes $L = (l^2/vR)\ \text{cm.}^{-1}$, ohm^{-1}, where R is the resistance in ohms. If the concentration C is expressed in equivalents per cubic decimeter and if V cu. dm. contain D gram equivalents the concentration is $C = (D/V)\ \text{dm.}^{-3}$, gram equivalent. The equivalent conductance Λ is then, $\Lambda = \dfrac{1000\,L}{C} = \dfrac{1000\,l^2}{R\,D}\ \text{ohm}^{-1}$ cm.^2 gram equivalent^{-1}.

---

[6] Benoit, *Trav. Mem. Bureau Intern. des P. et. M.*, **14,** 1910.

[7] Dr. E. W. Washburn, private communication.

[8] The best way to obtain this transformation would, undoubtedly, be to express the volume of the solution in cu. dm. in calculating the concentration. When the volume of the solution is determined from its weight and density (if based on the density of H_2O at 4°) the volume is expressed in liters but may be transformed to cu. dm. by multiplying by the factor 1.000027.

It has been customary to *state* conductance results in terms of reciprocal ohm, square centimeters per gram equivalent while in reality they have been *expressed* in reciprocal ohm milliliters per gram equivalent per centimeter. If the proposed change in units is adopted the results will be correctly expressed in terms of the customary units, and will be placed on a rational foundation.

Accuracy of the Measurements

At the beginning of this investigation it was hoped that the sum of all the errors in these measurements might be kept below 0.01%. It was found, however, that the best accuracy which could be obtained under the conditions of measurement was about half that desired. The principal factor which caused this discrepancy was the fact that it was found necessary to correct the specific conductances on account of the presence of electrode effects, a procedure which considerably reduced the precision of the resistance measurements. It was also found that the resistance measurements were not quite as consistent at 0° (at which temperature the absolute measurements were made) as they have proved to be at room temperatures. This was probably caused by temperature effects, since the majority of the measurements were made while the room temperature was in the neighborhood of 32° (90°F). The other measurements such as the calibration of the standard cells, the making of standard solutions, etc., were kept well within the limits which would be consistent with a final accuracy of about 0.02%.

Measuring Apparatus

Bridge Assembly.—A commercial drum-wound slide-wire bridge with extension cells was used in the resistance measurements, the capacity of the cell being balanced out by means of air condensers. The bridge was connected and grounded according to the method used by Washburn.[9] The assembly was enclosed in a box having a grounded lead lining and all wires were lead-covered and grounded. The bridge and the Curtis resistance box were calibrated against resistance standards bearing a 1922 Bureau of Standards certificate.

Source of E.m.f.—A Siemens-Schuckert high frequency generator was used as the source of alternating current. The normal frequency of 1000 was employed throughout the final measurements, although this frequency was varied in order to be sure that the change of the apparent resistance with the frequency was reduced as far as possible. The peculiar effect mentioned by Schlesinger and Reed[10] when using this generator was examined and eliminated by a method which will be described in a subsequent article.

[9] Washburn and K. Parker, THIS JOURNAL, **39**, 244 (1917).

[10] Schlesinger and Reed, *ibid.*, **41**, 1727 (1919).

Measuring Cells.—Four conductivity cells were used in the absolute measurements. They were made from two tubes of Pyrex glass, one of which had an internal cross section about twice that of the other. The wall was about 3mm. thick. The tubes were ground by lapping to insure an interior which would closely approximate a ruled surface, and were polished with rouge in order to remove surface effects as far as possible. They were then cut into two tubes, one of which was about twice the length of the other. The ends were then ground flat and true. The method of applying the electrodes is shown in Fig. 1.

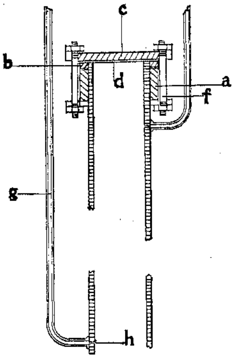

Fig. 1.

The outer ends of the tubes were platinized for a short distance and a ring of tin, a was cast on and subsequently turned down to make room for the rubber washer b. The platinum electrode d, was supported by the brass disc c, which in turn was fastened to the end of the cell by means of the bolts f. The holes h were blown in the tubes by employing a tiny gas-oxygen flame and about $1^{1}/_{3}$ atmospheres of air pressure on the inside of the cell. These holes were somewhat less than 1 mm. in diameter and caused only a slight indentation on the interior of the tube. The walls of the cell were so thick that the tubes g could be sealed on without causing any deformation. The holes were blown and short tubes sealed on before the tubes were ground, in order to insure a true interior surface. After the length and diameter had been measured, the ends were fastened on and tested for leaks under a vacuum. The insulation was obtained by coating with de Khotinsky cement and finally numerous layers of paraffin were applied, just before the cell was used.

The four pipet cells which were used to obtain a comparison with Kohlrausch's measurements were described in a recent article.[11]

Thermostat.—A modification of the usual ice thermostat was used which, it is believed, removes the necessity for an expensive stirring device as well as uncertainty in the temperature secured. The writers' experience has indicated that the actual temperature obtained in the usual type of ice thermostat depends to a large extent upon the granulation of the ice, the height of the water and the efficiency of the stirring. During the density measurements, when the pycnometer served as a very sensitive thermometer, it was found that great reproducibility could be obtained when the pycnometer was well packed in finely chopped ice. When the water began to rise around the pycnometer the readings indicated that the temperature was rising and to reproduce these readings it was necessary to maintain the water at the same height. Consequently it was decided to provide drainage for the water and rely entirely upon the ice to produce the desired temperature. The same arrangement proved to be successful with conductivity measurements. This simplifies the apparatus and reduces its cost to within the reach of the most modest pocket book.

---

[11] Parker, THIS JOURNAL, **45**, 2020 (1923).

A convenient form is shown in Fig. 2. The outside container a is preferably covered with felt. Within this is placed a cylinder b which need not reach entirely to the bottom of the container a but may be supported by the ice around and under it. Coarsely chopped ice may be put outside of this cylinder, for economy of labor, while within, the ice must be very finely shaved in order that it may be well packed without danger of injuring the cell which is embedded in it. Drainage may be provided for the water at the bottom or by means of an aspirator and a tube running to the bottom of the container. The leads a were connected to the bridge through test-tubes c dipping into the ice, according to the method described by Washburn—an important precaution for such low temperatures.

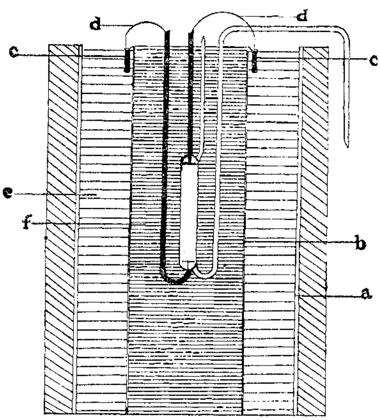

Fig. 2.

Preparation of Materials

Potassium Chloride.—It had been shown by a previous investigation that the purity of the potassium chloride could be relied upon after two crystallizations from conductivity water, so in these measurements this was the procedure adopted. Samples of potassium chloride from three different commercial sources were employed, but it was impossible to distinguish any consistent variation in the measurements due to the use of the different purified samples.

Water.—The conductivity water used in these measurements was prepared by distilling laboratory-distilled water over alkaline permanganate in a 60-liter still with a block tin condenser. Part of the vapor was allowed to escape, the water being collected hot. No great care was taken to obtain the very best water, since the principal object was to obtain results which could be reproduced by the average investigator. The results were corrected for the conductance of the water in each case.

Preliminary Measurements

Calibration of Bridge and Resistances.—The resistance box was calibrated by employing another box and calibrating both simultaneously, with direct current. The 100-ohm dial was calibrated as follows. The 100-ohm position on the dial was checked directly against the 100-ohm standard. The 200-ohm position was measured against the standard plus the first coil in the second box and so on, and the 1000-ohm position on this dial was checked against the 1000-ohm standard, as well as against the 900-ohm position on the second box plus the 100-ohm standard. The 100-ohm dial on the second box was then checked by making the same measurements on its 100-ohm dial with the resistance boxes in the same arm of the bridge but with the position of the 100-ohm standard reversed. The two resistance boxes were then interchanged and the 100-ohm standard again checked on either side. A total of four sets of measurements was thus made, and two independent checks were obtained at the beginning and end of each series, against the standard coils of higher and lower resistance. It was found that there was an average difference of 0.3 bridge units (0.012%)

when the same reading was taken with the resistance in opposite arms of the bridge. This was of course explained by the presence of 0.15 unit correction on the bridge at its center point. When this correction was added to all the bridge readings the measurements gave two independent values for each setting of the dial on each of the two boxes. The average of these two was taken to be the resistance of that setting of the dial. When both boxes were completely calibrated, the bridge was finally calibrated by putting the 10,000-ohm standard on one side and taking the bridge setting for various resistances of the calibrated box. The two resistances were then reversed in order to obtain a check on the measurements. When this was finished the two calibrated boxes were introduced and alternating current used to check out several points on the bridge-correction curve and to test the accuracy of the assembly as a whole. In no case were discrepancies obtained greater than 0.008%, while the average was considerably less. When the conductance cell is introduced in place of this calibrated resistance it is evident that this method has all the accuracy of a substitution method.

Length of Cells.—The length of the standard cells was determined by using the large comparator in the Ryerson Physical Laboratory. The length was compared directly with a standard meter to the nearest millimeter, the fractions being read upon the vernier of the comparator, which was shown to have a negligible correction for this purpose. A 1922 certificate from the Bureau of Standards gave the length of the standard meter as 1.00032 meters at 20°, so the measurements were multiplied by this factor.

The length of each cell was measured four times, the cell being rotated through an angle of 90° after each measurement. The data obtained are given in Table I. Each length given represents the average of several readings at the same position of the cell. The temperature at which the

TABLE I

LENGTHS OF STANDARD CELLS

Cells	Length[a] l_t in cm.		Temp. t °C.	Length at 0°[b] l_0 in cm.
I	31.6678	31.6693		
	31.6672	31.6711	26.2	31.6661 ± 0.0014
II	18.1518	18.1520		
	18.1547	18.1488	26.2	18.1503 ± .0015
III	26.5859	26.5847		
	26.5831	26.5889	26.2	26.5835 ± .0018
IV	13.3511	13.3515		
	13.3511	13.3508	26.2	13.3500 ± .0002

[a] Found by comparison with a standard meter, 1.00032 meters long at 20° (Bureau of Standards 1922 Certificate).

[b] Linear expansion coefficient of the glass is 3.2×10^{-6} (private communication from the Corning Glass Co.).

measurements were made was taken and the lengths were reduced to 0° by using 3.2×10^{-6} as the temperature coefficient of Pyrex glass.[12]

The accuracy of these measurements is indicated by the average deviation from the mean, which is given in the last column. This is rather misleading, however, since the measurement at any one position of the cell could be reproduced to about 0.0002 cm. The deviations must be looked upon, therefore, as being primarily due to the ends not being ground quite truly. The average of the apparent length at the four positions of the cell thus gives the true length to a greater degree of accuracy than is indicated.

Diameter of Cells.—The diameter of the standard cells was determined by weighing an equal volume of mercury. The side tubes were first sealed off at a short distance from the cell. One of the ends was fastened to the cell and then the cell was filled with mercury, under a vacuum, which filled the side tubes and prevented the possibility of any bubbles of air being left on the sides of the cell. The last few cubic centimeters of mercury were then added and the excess mercury was discarded by pressing the top of the cell against ground plate glass, care being taken that the air was entirely eliminated. The mercury was then poured into a beaker, its temperature was taken and then its weight. Upon being poured out, the mercury was prevented from leaving the side tubes by the small capillary hole connecting to the cell, but was removed from the slight depression caused by blowing out this capillary hole. It is believed that this method of determining the volume gave the correct allowance for these slight depressions. It is to be noted that, on account of the grinding operation, it was not necessary to determine the diameter at different points along the cell, since it was assured that the inside of the cell was a ruled surface. The densities of the mercury at the different temperatures were taken from the "Physikalisch-Chemische Tabellen,"[13] which are expressed in grams per milliliter.

The mercury was purified by the method of Hulett.[14] A check was obtained upon the diameter by changing the ends on the cell and weighing the mercury a second time. This also gives a check upon the reproducibility obtained by the described method of fastening the electrodes. The data obtained in these measurements are given in Table II. In the last column are given the cell constants which were calculated from the values obtained for the volumes and lengths of the cells.

In regard to the accuracy of these measurements, sources of error might be found in determining the temperature and the weight of the mercury. From the expansion coefficient of mercury, however, it is seen

---

[12] Courtesy of the Corning Glass Co.

[13] Landolt, Börnstein and Roth, 4th ed., p. 45.

[14] Hulett, *Phys. Rev.*, **33**, 307 (1911).

that the temperature needed only to be determined to an accuracy of 0.25° to keep this source of error below 0.005%. It was assumed that the *mean* temperature of the mercury could be determined to this accuracy by pouring it into a beaker and taking its temperature, care being taken to have the mercury, cell, beaker and thermometer all at room temperature (by using thick gloves, etc.). The smallest volume (20 sq. cm.) of mercury weighed 278 g. and it is evident that the error in weighing this quantity could be kept below 0.005% by only ordinary precautions. The weight was obtained in a Pyrex beaker which was wiped with a damp cloth and left for 45 minutes to come to equilibrium. The weight of the beaker was obtained by pouring out the mercury and weighing according to the same procedure. The largest deviation from the mean volume when this was obtained by pouring from opposite ends of the cell, was 0.004%.

TABLE II

VOLUMES AND CONSTANTS OF STANDARD CELLS

Cells	Wt. of Hg (in air) G.	Temp. t °C.	Density assumed d g./ml.	Vol. at 0°[a] in ml.	Vol. at 0°[b] V_0 in cm.^{2}	Cell constant $\left(\frac{l_0^2}{V_0}\right)$ in cm^{-1}
I	1072.676	26.7	13.5298	79.2578	79.2593 ± 0.0006	12.651_4
	1072.697	26.5	13.5303	79.2566		
II	603.521	25.9	13.5317	44.5870	44.5901 ± .0019	7.388_{04}
	603.564	26.0	13.5315	44.5908		
III	545.285	28.4	13.5256	40.3018	40.3035 ± .0006	17.534_0
	545.319	28.2	13.5261	40.3029		
IV	278.284	27.6	13.5276	20.5650	20.5663 ± .0007	8.665_{75}
	278.274	28.2	13.5261	20.5664		

[a] Calculated from equation $V_0 = (m/d)\ (1 - \gamma t)$, where V_0 is the volume at 0°, m is the weight of the Hg (in a vacuum) and d is its density. γ is the cubic expansion coefficient of the glass (9.6×10^{-6}) and t is the temperature of the Hg. In the reduction of the weight of Hg to a vacuum the density assumed for the brass weights was 8.4 and for the air 0.0012.

[b] One ml. was assumed to be 1.000027 cm.^{3}

Calibration of Weights.—The set of weights[15] (reading from 1 mg. to 100 g.) used in weighing the potassium chloride for the standard solutions bore a 1921 certificate from the Bureau of Standards and had been placed in Class "A." The corrections employed were the "apparent mass corrections based on apparent weight in air against brass standards." Against this set, another set was calibrated for the purpose of weighing the water and mercury.

The balance used in weighing the potassium chloride was a special balance sensitive to 0.01 mg. This was tested for inequality in length of the balance arms and it was found that weights of less than 20 g.

---

[15] Kindly loaned by Professor W. D. Harkins.

could be checked on either pan to about 0.02 mg. The balance used in weighing the water and mercury had a capacity of 3 kg. and was sensitive to about 0.5 mg. In calibrating the large set of weights the standard set was placed on the *left* pan, making the weighings equivalent to a substitution method.

Densities.—It was necessary to obtain the density for the new standard solutions, in order to make them up by weight methods. For the 0.1 *D* and 0.01 *D* solutions this was obtained with a new pycnometer which will be described in a separate article. The density of the demal solution was obtained by using two volumetric flasks. The flasks were first filled with boiled distilled water and packed for 90 minutes in ice, the volume in cubic decimeters being determined by the weight of the water and the data for the density given by Thiesen, Scheel, and Diesselhorst.[16]

To 1 cu. dm. of volume 74.518 g. of potassium chloride (weight in air) were then weighed into the flasks and they were filled with nearly the required amount of water and packed in ice for 90 minutes again, the last few drops of water were then added, and the contents weighed. This gave the data required for calculating the density. The values obtained for these solutions are given in the second column of Table IX.

Resistance of Leads.—The resistance of the leads was determined by clamping the ends of the cells together and immersing them in ice, measuring the resistance by direct current and a galvanometer. The values obtained were as follows: Cell I, 0.018 ohms; Cell II, 0.019 ohms; Cell III, 0.019 ohms; Cell IV, 0.019 ohms. When two of the cells were measured in parallel the corresponding leads resistance was 0.016 ohms, and when in series 0.026 ohms. The resistance of the wires leading to the resistance box was subtracted from the resistance measured, in determining the above values.

Variation of Resistance with Frequency and Voltage.—In the absolute measurements the variation of the apparent resistance with the frequency of the alternating current was always less than 0.01% between 500 and 1000 cycles. The variation with the voltage was likewise extremely small and in fact at the lower resistances, where this effect becomes the most pronounced,[17] the difference between readings at approximately 5 and 0.5 volts was less than the experimental error due to the heating effect at the higher voltages.[18] The lower voltages, therefore, were used in measuring the *D* potassium chloride solutions.

---

[16] Thiesen, Scheel and Diesselhorst, *Wiss. Abh. Phys.-Tech. Reichsanst.*, **3,** 68 (1900); (assuming 1 liter = 1.000027 cu. dm.).

[17] Parker, This Journal, **45,** 1370 (1923).

[18] A previous experience had also indicated that the variation of the apparent resistance of a KCl solution with the voltage was reduced or eliminated when the solutions were handled in *laboratory air*. When purified air was blowing through the solution such a variation was present.

Care of the Electrodes.—In a recent article[19] Morgan and Lammert described the precautions they found necessary to take when using *unplatinized* electrodes in order to obtain consistent results. Although the writer's experience with *platinized* electrodes has indicated that the effects obtained with *dried cells* and mentioned by them may be eliminated by Ostwald's suggestion[20] of washing the electrodes with alcohol or replatinizing, it was thought well for the sake of safety to follow their directions regarding the short-circuiting of the electrodes when the cells were being cleaned and brought to temperature.[21]

The cells were cleaned with cleaning mixture, rinsed with alcohol and washed with running distilled water for several hours between every two sets of measurements. They were allowed to stand for one hour, filled with the solution to be examined, then rinsed with this solution several times before being finally filled and brought to temperature. From Morgan and Lammert's experience it would seem that this was a method most certain to give consistent results.[22] The electrodes were platinized with the Lummer-Kurlbaum solution of platinum chloride and lead acetate.

Temperature Coefficient of Conductivity Water.—In order to determine the conductance of the solutions at 0° it was necessary to obtain the specific conductance of the water at that temperature. It was most convenient to determine the latter at room temperatures and reduce to 0°. For this purpose the equation given by Kohlrausch and Holborn[23] was transformed to $L_t = L_o\,(1 + .0360^t + .000215^{t^2})$ where L_o is the specific conductance

---

[19] Morgan and Lammert, THIS JOURNAL, **45,** 1692 (1923). There are several interesting correlations which may be made between the effects observed by these writers and those mentioned in Ref. 12, p. 1369. Thus, the differences between the apparent resistances at 500 and 1000 cycles were found by Morgan and Lammert to pass through a minimum at moderate resistance with *unplatinized* electrodes, while with the *platinized* electrodes used by the writer this difference not only passes through a minimum but actually changes sign at moderate resistances. Both investigations indicate the presence of a disturbing effect in the dilute solutions. This is also indicated by the observations of Haworth, *Trans. Faraday Soc.*, [2] **16,** 372 (1921).

[20] Ostwald-Luther, "Physiko-Chemische Messungen," 3rd ed., Akademische Verlagsgesellshaft, Leipzig, **1920**, p. 466.

[21] No change of the resistance could be detected when this precaution was omitted.

[22] The explanation given for the effects observed by Morgan and Lammert is that the two electrodes act like dissimilar pieces of metal, forming in reality a voltaic cell. They may be explained equally well by the writers' suggestion of taking into account not only the effect of an adsorption (positive or negative, of the electrolyte on the surface of the electrodes) upon the resistance of the body of the solution but also upon the resistance of the (*adsorbed*) layer in proximity to the electrodes. The former explanation is said to account for the variation of the resistance with the voltage (Ref. 19, p. 1705). Unless the resistances of the adsorbed layers are taken into account, however, the cause for a variation in the resistance of a voltaic cell by change of voltage of an *alternating current* is difficult to explain.

[23] Ref. 3, p. 123.

at 0° and L_t is that at the room temperature. The value determined for the latter is substituted in the equation and L_0 is solved for. In case the correction is desired for 0.1 *D* solution, one may safely assume that for temperatures in the neighborhood of 24.5° the resistance of the water is one-half that at at 0°. When correction for the 0.01 *D* solution is desired this is not quite accurate enough. This equation was checked with several samples of water and good agreement was obtained.

Experimental Procedure and Results

Manipulation.—In order to standardize partially the method of preparing the 0.1 *D* solution (which was used as a primary standard) the method used in this investigation will be outlined in some detail. The 0.01 *D* solution was prepared in a similar manner, but two cu. dm. was employed. The potassium chloride was twice crystallized from conductivity water by filtering the boiling saturated solution into a Pyrex filter flask and cooling in ice water. The water was extracted from the crystals by repeated shaking and decantation or by leaving the flask tilted in such a manner that the water would drain. The crystals were dried by heating in the same flask under a vacuum.

The procedure adopted in making up a solution was as follows. The conductance of the water (which was kept in 3-liter Pyrex flasks) was first determined by drawing the water through a cell of very low constant by means of a siphon. The resistance was taken while the water was running through the cell. The temperature of the water was taken and by means of the equation given in a previous paragraph, the specific conductance was calculated at 0°. About 1000 g. of this water was weighed (after rinsing) into a Pyrex florence flask which had been carefully cleaned by using cleaning mixture, hot water, steam and by frequent rinsings with conductivity water, and finally dried with purified air. The weight of potassium chloride, required for the solution, was calculated from this weight of water by using the data given in the fourth column of Table IX. In the meantime about 12 g. of the purified potassium chloride had been placed in a small porcelain crucible and heated over a Meker flame so regulated that about half of the chloride melted within 30 minutes. (The melt clings to the top crust and the whole may be removed without difficulty.) The crucible had been cooled over sulfuric acid in a desiccator, the cover of which was free from grease. A watch glass was now weighed carefully and the extra weights required for the calculated potassium chloride were placed on the pan. The crust of potassium chloride was removed from the crucible and broken into a few large pieces in an agate mortar. The exact quantity required was quickly weighed into the watch glass and finally added to the conductivity water which had been kept stoppered with a clean rubber stopper.

The solution was transferred to the cell by means of a siphon and allowed to stand for 60 minutes while the ice thermostat, described in a previous paragraph, was being prepared. The cell was again rinsed with the solution, filled and allowed to stand in ice water for 30 minutes before being packed in the ice. The resistance became constant in about 60 minutes. The ice was repacked around the cell when the resistance commenced to decrease and the process was repeated until assurance was obtained that the cells were in equilibrium. This usually occurred in 60 minutes, but always after the first repacking. When the manipulation was perfected, the solutions were so uniform that one check was found to be sufficient. Resistance measurements were taken upon the individual cells and also when they were connected in parallel.

0.1 *D* Solution.—In Table III are given the data for the specific con-

TABLE III

SPECIFIC CONDUCTANCE OF NEW STANDARD POTASSIUM CHLORIDE SOLUTION 0.1 *D*[a] AT 0°

Cell		$L \times 10^3$ Sol. 1	$L \times 10^3$ Sol. 2	$L \times 10^3$ Sol. 3	Av.
		Cells of Large Diameter			
I		7.129_6	7.130_2	7.130_7	7.130_2
II		7.129_9	7.130_0	7.131_1	7.130_3
I + II parallel		7.127_7	7.129_2	7.130_6	7.129_2
		Cells of Small Diameter			
		Sol. 4	Sol. 5	Sol. 6	Av.
III		7.124_7	7.125_1	7.125_2	7.125_0
IV		7.122_7	7.121_2	7.122_0	7.122_0
III + IV par.		7.120_1	7.120_9	7.119_2	7.120_1
		SPECIFIC CONDUCTANCES BY DIFFERENCES			
		Cells of Large Diameter			
		Sol. 1	Sol. 2	Sol. 3	Av.
I − II		7.129_1	7.130_4	7.130_0	7.129_8
I − par.		7.130_7	7.130_8	7.130_9	7.130_8
II − par.[b]		7.133_8	7.131_6	7.132_4	
	Av.	7.129_9	7.130_6	7.130_5	7.130_3
		Cells of Small Diameter			
		Sol. 4	Sol. 5	Sol. 6	Av.
III − IV		7.126_9	7.129_1	7.128_3	7.128_1
III − par.		7.127_1	7.127_6	7.128_2	7.127_6
IV − par.[b]		7.127_9	7.122_9	7.127_7	
	Av.	7.127_0	7.128_3	7.128_3	7.127_9
Accepted value[c]					7.129_5

[a] 7.4789_6 g. of KCl to 1000 g. of H_2O (weighed in air). Molecular weight assumed is 74.553. Concentrations are expressed in equivalents per cu. dm.

[b] Not included in the averages, on account of large experimental error in this difference.

[c] The results with the cells of large diameter and those with the cells of small diameter are weighed as 2:1. Only the specific conductances obtained by "differences" are employed in determining this quantity.

ductance of the 0.1 *D* solutions as determined in the different cells. It is evident from a comparison of the results obtained in the cells of small and large diameter that the same electrode effects are present in the measurements which were first mentioned in a recent article.[24] In order to make some correction for these effects, which would be free from all objection, the specific conductances were determined by "differences," that is, the cell constants of two cells were subtracted and the corresponding resistances of the two cells were subtracted. The differences of the constants divided by the differences in the resistances give the specific conductances required and partially corrected for any effect occurring at the electrodes. It is evident that this method will give the same correction as would have been obtained by putting the cells in opposite branches of the bridge, a method which has been frequently used for such a purpose.[25] This method reduces the precision somewhat. The results having the greatest precision will naturally be those having the greatest differences in the cell constants. The two cells connected in parallel were treated as a separate unit, the constant for this unit being determined by calculation from the individual cells. When the resistances are subtracted, three differences are obtained, only two of which are independent. The lack of precision in the "difference" Cell IV − (III and IV parallel) caused this difference to be discarded in the averages, while the other two "differences" are averaged. It is seen that in spite of this correction there is still a discrepancy between the cells of larger and smaller diameter. It seems probable from the writers' experience with this effect that the results in the larger cells are the more nearly correct and should be given greater weight. The results in the cells of larger diameter are also seen to agree excellently with the results by "differences." For these reasons these measurements were given twice the weight accorded those obtained with the cells of smaller diameter. The 0.1 *D* solution is the most convenient concentration for the purpose of determining cell constants, and the value for the specific conductance of this solution is probably more accurate than that for the *D* or 0.01 *D* solution.

D **Solution.**—Before the *D* solution was measured Cell I was broken, which removed probably the most accurate of all the cells from the measurements. It was seen that with the 0.1 *D* solution Cells I and II agreed very closely and presumably they would have done likewise at the *D* concentration. For this reason in the final average in Table IV, the results with Cell II are given equal weight with the average of the differences III − parallel and IV − parallel. It is to be noted that the differences between the cells of large and small diameter are somewhat reduced in the measurements with the *D* solution. Solution 1 was made by weight

---

[24] Ref. 17, p. 1376.

[25] Ref. 5, p. 440.

methods and Solution 2 by volume. For this reason it is probable that the former is the more accurate.

TABLE IV

SPECIFIC CONDUCTANCE OF NEW STANDARD POTASSIUM CHLORIDE SOLUTION

1.0 D^a at 0°

	Cell II	Cell III	Cell IV	Cell III + IV parallel
Sol. 1				
$L \times 10^3$	0.06512_2	0.06508_2	0.06506_0	0.06504_4
Sol. 2				
$L \times 10^3$	$.06509_4$	$.06504_6$	$.05601_8$	$.06500_0$
Av.	$.06510_8$	$.06506_4$	$.06503_9$	$.06502_2$

SPECIFIC CONDUCTANCES BY DIFFERENCES

1.0 N Solution

	III−IV	III−par.	IV−par.	
Sol. 1				
$L \times 10^3$	0.06510_4	0.06510_1	0.06509_2	
Sol. 2				
$L \times 10^3$	$.06507_3$	$.06506_7$	$.06505_3$	
Av.	$.06508_9$	$.06508_4$	$.06507_3$	
Accepted value[b]				0.06509_8

[a] 76.627_6 g. of KCl to 1000 g. of H_2O (weighed in air). Molecular weight assumed is 74.553. Concentration expressed in equivalents per cu. dm.

[b] The results with Cell II are given equal weight with the average obtained from the differences III−IV and III−parallel.

0.01 D Solution.—The differences between the cells of large and small diameter had so increased in the 0.01 D solution that a considerable error would have been introduced even by the method of differences. It was impossible to use this method, likewise, since the two short cells had been chosen for the measurements before it was realized that the results would have to be corrected. These cells had constants so nearly alike that the differences contained a large experimental error. If two other cells had been used with the 0.1 D solution the specific conductance of the latter would have been assumed to be 7.1295×10^{-3} and the constants would have been calculated from the resistances obtained at that concentration. It was decided to use Cells II and IV in this manner and to use the new values for the constants (obtained in that manner) in determining the specific conductance of the cells at 0.01 D. This was found equivalent to multiplying the observed specific conductances by the factors 0.99989 and 1.00105, respectively. This method corrects the results in Cell IV by approximately the amount which the results in that cell *should have been* corrected at 0.1 D (to remove the electrode effects) leaving only the increase between the two concentrations uncorrected. In the final average of Table IV only the results converted in this manner are used.

The errors (due to electrode effects) in the *uncorrected* specific conductances found in Cells II and IV at the concentrations of D, 0.1 D and 0.01 D

are 0.106%, 0.116% and 0.144%, respectively. It is evident from this increase that if these two cells had been intercompared a cell constant curve for Cell IV would have been obtained similar to those found previously[26] for other cells.

TABLE V

SPECIFIC CONDUCTANCE OF NEW POTASSIUM CHLORIDE SOLUTION

0.01 D^a at 0°

	Cell II	Cell IV	Cells II + IV parallel	Cell II converted	Cell IV converted
Sol. 1					
$L \times 10^3$	0.7730_7	0.7718_4	0.7724_7	0.7729_9	0.7726_5
Sol. 2					
$L \times 10^3$	$.7729_9$	$.7720_0$	$.7725_2$	$.7729_0$	$.7728_1$
Av.	$.7730_3$	$.7719_2$	$.7725_0$	$.7729_5$	$.7727_3$
Accepted value[b]					$.7728_4$

[a] 0.74625_3 g. of KCl to 1000 g. of H_2O (weighed in air). Molecular weight assumed is 74.553. Concentrations are expressed in equivalents per cu. dm.

[b] Only the converted results are included in this value, obtained by multiplying the results in Cols. 2 and 3 by 0.99989 and 1.00105, respectively, which factors were obtained from the ratios of the specific conductances *accepted* for the 0.1 D solution to the value *obtained* for that solution, in the corresponding cells.

Specific Conductance of Kohlrausch and Maltby's 0.1 N Solution

In order to obtain accurate temperature coefficients for the new standard solutions it was decided to determine the specific conductance of Kohlrausch and Maltby's 0.1 N potassium chloride solution, whose specific

TABLE VI

SPECIFIC CONDUCTANCE OF KOHLRAUSCH AND MALTBY'S POTASSIUM CHLORIDE SOLUTION

(0.1 N AT 18°)[a] AT 0°, 18° AND 25°

	Cell A	Cell B	Cell C	Cell D	Av.
Sol. 1					
$L \times 10^3$ at 0°	7.140_6	7.139_7	7.139_0	7.142_9	7.140_6
Sol. 2					
$L \times 10^3$ at 0°	7.141_9	7.140_2	7.143_1	7.145_1	7.142_5
Av. at 0°	7.141_3	7.140_0	7.141_1	7.144_0	7.141_6
Sol. 3					
$L \times 10^3$ at 18°	11.188_1	11.187_7	11.186_5	11.186_5	11.187_2
Sol. 4					
$L \times 10^3$ at 18°	11.188_4	11.187_2	11.186_1	11.186_3	11.187_0
Av. at 18°	11.188_3	11.187_5	11.186_9	11.186_4	11.187_1
Sol. 3					
$L \times 10^3$ at 25°	12.880_5	12.879_0	12.878_1	12.879_1	12.879_2
Sol. 4					
$L \times 10^3$ at 25°	12.881_4	12.879_5	12.878_6	12.878_5	12.879_5
Av. at 25°	12.881_0	12.879_3	12.878_4	12.878_8	12.879_4

[a] 7.4945 g. of KCl to 1000 g. H_2O (weighed in air). Kohlrausch and Maltby's value for the molecular weight is 74.60.

---

[26] Ref. 11, p. 2022.

conductance at 25° had been accurately determined in terms of its value at 18° upon the older basis of measurement.[27] This served the double purpose of determining the relation between the two bases of measurement and giving accurate data for the temperature coefficients between these temperatures. The same four cells were used with which the older measurements were made. The correct specific conductances for this solution, as obtained in this investigation, are given in Table VI.

It is seen that the measurements are not as consistent at 0° as those at the higher temperatures. Most of these measurements were made when the room temperature was about 32°C., so this lack of precision is easily explained. The four pipet cells with which these measurements were made constituted about as delicate a piece of apparatus as can easily be imagined. This was packed in the finely shaved ice 18 times and except for breaking one of the connecting rods which held the cells together, the first time it was packed, no harm came to the apparatus.

Comparison between the New and Old Bases of Calibration

The cell constants of Cells A, B, C and D were determined with the new standard solutions at 0° as given in Table VII. The constants which had previously been determined at 18° with Kohlrausch and Maltby's 0.1 *N* solution were reduced to 0° by assuming 8.4×10^{-6} for the expansion of the lead glass between these temperatures. The difference between these quantities gives a direct comparison between the two bases of calibration. The difference is seen to vary for the different cells from 0.134 to 0.152%, and to average 0.145%. The new measurements give a *lower* value for the cell constant and for the specific conductance. The new values for the constants found in this table are those which were used in determining the specific conductance of Kohlrausch and Maltby's solution at 0° (Table VI).

The values in Table VII were the first to be determined with these cells. Some measurements which were made at the end of the investigation indicated a value for these constants about 0.02% lower than the values given here. It was expected that the rather severe treatment of repeatedly

TABLE VII

COMPARISON OF NEW AND OLD BASES OF CALIBRATION

Cell	Cell consts. new basis Sol. 1	Cell consts. new basis Sol. 2	Av.	Cell consts. at 0° calcd. from K. and M. (18°)	Diffs. in %
A	11.643_4	11.643_6	11.643_5	11.659_2	0.13_4
B	5.470_{62}	5.469_{40}	5.470_{01}	5.477_{85}	$.14_2$
C	5.707_{86}	5.706_{13}	5.707_{00}	5.715_{75}	$.15_2$
D	3.1467_7	3.1460_6	3.1464_1	3.1512_2	$.15_1$
Av.					$.14_5$

---

[27] Ref. 2, p. 2426.

changing the temperature from 32° to 0° would cause a change in the constants of the cells and when this was demonstrated care was taken to include only the earlier measurements with these cells.

The calibration at 18° and measurements at 25° had been made just a year previously. The writers' experience has indicated that a cell of the pipet type which has been *well aged* and which *has not been in use* may be relied upon to about 0.02% for that length of time. One cell had been checked to that precision after a period of two years. These four cells were twelve months old when the measurements at 18° and 25° were made. During the previous eight months they were shown to have decreased an average of about 0.02%, while during the first four months they decreased 0.04%. In these measurements it was indicated that the relative as well as the absolute values for the constants of the four cells had changed. The cells were not in use during the year previous to the present measurements and the relative value of the constants (compare Table VII) have evidently remained very constant during that time. An allowance of 0.01% was made for the decrease in the constants, however, and it seems probable that these results are accurate to at *least* 0.02%. When these measurements are used for transforming older data to the new basis, an error of this amount is of small moment since there are few conductance measurements in the literature in which the accuracy would require a closer determination of this relation. The data for higher temperatures given in Table X are also based on these results and when greater accuracy than this is desired the cells should be calibrated at 0° to avoid this uncertainty.

In order to obtain a further check upon this comparison between the two bases of calibration the measurements were made whose results are given in Table VIII. Kohlrausch, Holborn and Diesselhorst's 0.1 N solution[28] was made by weight methods, after calculation of the *correct* weight of potassium chloride[29] to be added to 1000 g. of water. From this table

Table VIII

Specific Conductance of Kohlrausch, Holborn and Diesselhorst's 0.1 N Solution[a] at 0° (New Basis)

Cell	Sol. 1 $L \times 10^3$	Sol. 2 $L \times 10^3$	Av.	Diff. in %[b] from K. H. and D.
A	7.142_4	7.139_3	7.140_9	-0.12_6
B	7.143_2	7.142_1	7.142_6	$.10_3$
C	7.141_7	7.140_6	7.141_2	$.12_2$
D	7.144_4	7.140_2	7.142_3	$.10_7$
Av.	7.142_9	7.140_7	7.141_8	$.11_4$

[a] 7.4931_3 g. of KCl to 1000 g. of H_2O (weighed in air). Kohlrausch, Holborn and Diesselhorst's value for the molecular weight is 74.59.

[b] The specific conductances obtained in this investigation are *lower*.

---

[28] Ref. 5, p. 440.

[29] Ref. 2, p. 2424.

it is seen that the differences between the two investigations range from 0.103% to 0.126%, averaging 0.114%. It is evident, therefore, that the results in Table VII give the correct order of magnitude of the difference between the two bases of calibration and since the work of Kohlrausch and Maltby is of considerably greater accuracy than that of Kohlrausch, Holborn and Diesselhorst (given to only 3 places) it is believed that Table VII gives a more accurate value. It will be shown (Table XI) that the values of the specific conductances for the latter's N, 0.1 N and 0.01 N solutions on the new basis average about 0.15% higher than the values given by them. This confirms the use of the value 0.145% for the true difference between the two bases of calibration.

The Determination of a Cell Constant

Introduction.—From the earliest investigations upon the conductance of electrolytes to the present, two methods have been used for the determination of the so called "cell constant." By the first or absolute method the "constant" was obtained by measurement of the dimensions of the cell and the value so determined was a "constant" in so far as the dimensions of the cell were constant. By the second method, which has almost entirely superseded the first, the constant was obtained by measuring in the cell the resistance of a standard substance or solution the value of whose specific conductance had been determined, more or less accurately, in a previous investigation. The substance whose resistance in the cell was determined, has varied from a primary standard such as mercury to a varied assortment of "normal" solutions. Experimental difficulties have almost entirely eliminated the use of the absolute method as well as the use of a primary standard, and the choice has thus unfortunately fallen upon a method whose accuracy depends entirely upon the accuracy of an investigation which was made long before modern precision was introduced.

This latter method at best may be said to give only an *apparent* cell constant since the values determined in this manner have been found to vary with the voltage and frequency of the measuring current and even with the electrolyte used in the measurements. If there were but a single standard solution upon which these measurements were based the absolute value of this solution would be of secondary interest, since accurate *relative* values are of the most importance. Unfortunately, however, conductances of a number of standard solutions were examined in this original investigation, and other investigators have chosen indiscriminately among a series of values whose relative as well as absolute accuracy is limited to that obtained in the original investigation.

It was primarily for the purpose of *limiting* the number of standard solutions upon which the "cell constant" is based, that the present investigation was undertaken. That only three concentrations of a single electrolyte were chosen as standards was for this reason. It is hoped that only one of these (0.1 *D*) will be generally accepted as a primary standard upon which to base the determination in the future. The standard cells were made especially for this concentration and more care was taken in the determination of its specific conductance so it is believed that the data for the 0.1 *D* solution have the greatest accuracy of the three.

Direct Determination of a Constant.—The reasons for the choice of the 0.1 *D* solution as a primary standard were, first, that this solution is nearly as dilute as a solution can be made and handled in the laboratory air without special precautions against contamination, and second, that it is sufficiently dilute so that by one accurate intercomparison with a reference cell (whose constant has been determined directly with the 0.1 *D* solution) the constant of another cell can be determined which would be sufficiently small for use in the most dilute solutions.

A suitable reference cell must be chosen for this purpose and it is recommended that a pipet cell similar to that of Washburn,[30] Type *B*, or Acree,[31] Type II, having electrodes of about 2 sq. cm. cross section and a constant of about 2.5–3.5 be used.[32]

This cell may be directly calibrated by means of the 0.1 *D* solution at 0°. It is most convenient and accurate to make up the solutions for this purpose by the weight method, although sufficient data for making up the solutions by volume are likewise given in Table IX. The manipulation used for the former method has been carefully outlined in a previous paragraph.

TABLE IX

NEW BASIS FOR CALIBRATION[a] AT 0°

Conc. of KCl *D*[b]	Density[c] at 0°. g./cm.^{3}	Wt. of KCl to 1 cu. dm. sol.	Wt. of KCl to 1000 g. of H_2O	Spec. cond. at 0°, *L*
1.0	1.0480_4	74.518_4	76.627_6	0.06509_8
0.1	1.00488_7	7.4518_4	7.4789_6	$.007129_5$
.01	1.00037_2	0.745184	0.74625_3	$.0007728_4$

[a] The concentrations are based upon a molecular weight for KCl of 74.553. The weights given in the table are weights in air.

[b] Equivalents per cu. dm.

[c] Based upon a density of water at 0° in g./cm.^{3} = 0.999841.

If work of the utmost accuracy is not required it is possible to simplify this procedure to a considerable extent. Thus, it may be safely assumed that one crystallization of the potassium chloride will give results accurate to 0.04% and a very improvised thermostat may be used. Use may also

---

[30] Ref. 4a, p. 2449. It has been found more convenient for intercomparison measurements to have the filling tube sealed on the cell and protected from the bath by a closely fitting tube sealed at the lower end.

[31] Robertson and Acree, *J. Phys. Chem.*, **19**, 396 (1915).

[32] A cell of 1.8 cm. internal diameter with electrodes 1.6 cm. in diameter and about 6.5 cm. apart will be found suitable.

be made of Table X which contains the calculated specific conductances for the new standard solutions at a series of temperatures.[33]

The values found in this table have been corrected for changes in the cell constants with the temperature.

Cell Constants by Intercomparison.—The lower limit of resistances at which a cell constant may be determined directly by means of the primary standard is rather difficult to set. There is evidently a relation between the resistance at which polarization first becomes appreciable, the area of the electrodes, the degree of platinization, the frequency and probably the current density. Neglecting the effect of changes in the last three variables Kohlrausch[34] makes the statement that with "well platin-

---

[33] The method of calculating the specific conductances for Table X was rather involved. It was assumed that the *relative* specific conductances obtained by Kohlrausch and Maltby (at 18°) for their N, 0.1 N, and 0.01 N solutions were correct, but that the *absolute* values should be corrected by 0.145% as found in Table VII. The corrected values are found in Table XI. The value for their 0.1 N solution at 25° was taken from Table VI. The value for their 0.01 N solution at 25° was obtained from its value at 18° by the use of the ratio 1.1538 which had been determined for this temperature change by Bray and Hunt [THIS JOURNAL, **33,** 784 (1911)]. The value for their N solution at 25° was obtained by assuming the same ratio between the values for their N solution and that of Kohlrausch, Holborn and Diesselhorst's N solution at 25° as found by them at 18°. These data together with the values found for the solutions used in the present investigation at 0° gave a series of three specific conductances at each of these three temperatures. As a first approximation a quadratic equation was assumed to hold for the three values found at each of the three temperatures and the grams of potassium chloride per 1000 g. of water (weight in air) used in making the solutions. The equations obtained at the temperatures of 0°, 18° and 25° are as follows.

$$L_0 = 0.0007728_4\,[1 + 1.2336\,(g. - 0.74625) - 0.001805\,(g. - 0.74625)^2]$$
$$L_{18} = 0.0012225_5\,[1 + 1.2243\,(g. - 0.74766) - 0.0024124\,(g. - 0.74766)^2]$$
$$L_{25} = 0.0014105_2\,[1 + 1.2224\,(g. - 0.74766) - 0.0025736\,(g. - 0.74766)^2]$$

where L_{18} is the specific conductance at 18° and $g.$ the grams of potassium chloride per 1000 g. of water (weight in air). From these equations were calculated the specific conductances of Kohlrausch and Maltby's, Kohlrausch, Holborn and Diesselhorst's, and the writers' solutions at *each* of three concentrations and temperatures.

In order to test the correctness of this first approximation the results of Kohlrausch and Maltby at 18° were plotted on a large scale and after the concentrations corresponding to Kohlrausch and Maltby's atomic weights were calculated, the specific conductances of Kohlrausch, Holborn and Diesselhorst's and the writers' solutions were interpolated. A difference of 0.012% was indicated for the writers' 0.01 D solution and 0.023% was indicated for the writers' D solution. These values were used to correct the first approximation at the temperatures of 18° and 25°. The first approximation was found sufficiently precise for the writers' 0.1 D solution and at all concentrations for Kohlrausch, Holborn and Diesselhorst's solutions. The values given for the writers' solutions in Table X were calculated from the equations found at the bottom. The equations were obtained from the observed values at 0° and those calculated (as above) at 18° and 25°. The results calculated for Kohlrausch, Holborn and Diesselhorst's solutions were used to obtain the data found in Table XI.

[34] Ref. 3, p. 10.

ized" electrodes polarization may be assumed to be absent if the resistance expressed in ohms is greater than $50/q$ or $100/q$, where q is the cross section of the electrodes in square centimeters. Ostwald gives the same numerical values.[35] It is probable that with a frequency of 1000 or over it may be safely assumed that resistances above $200/q$ are accurate to 0.01%. This makes 100 ohms the lowest resistance measurable with the pipet cell described and since, for measurements below this, the resistance of the leads and other factors interfere with accurate measurements, this limit seems a convenient one. The only certain method by which to determine this lower limit for a given cell is by intercomparison measurements with a cell of higher constant and if possible with larger electrodes.

TABLE X

SPECIFIC CONDUCTANCE OF NEW POTASSIUM CHLORIDE SOLUTIONS[a] AT DIFFERENT TEMPERATURES

°C.	1.0 *D*[b] at 0°	0.1 *D*[c] at 0°	0.01 *D*[d] at 0°
0	0.06509_8	0.007129_5	0.0007728_4
5	$.0738_{76}$	$.00820_{55}$	$.000892_{03}$
10	$.0828_{86}$	$.00931_{58}$	$.001015_{13}$
15	$.0921_{32}$	$.01046_{03}$	$.001142_{15}$
18	$.09779_0$	$.011163_6$	$.0012202_3$
20	$.1016_{07}$	$.011639_3$	$.001273_{07}$
25	$.1113_{22}$	$.012852_4$	$.0014078_9$
30	$.1212_{67}$	$.01409_{96}$	$.001546_{61}$

[a] 76.627_6, 7.4789_6 and $.74625_3$ g. of KCl to 1000 g. of H_2O (weighed in air). The molecular weight assumed is 74.553. Concentrations are expressed in equivalents per cu. dm.

[b] The equation is $L = 0.06509_8 + 1.7319 \times 10^{-3} t + 4.681 \times 10^{-6} t^2$.

[c] The equation is $L = 0.007129_5 + 2.1178 \times 10^{-4} t + 6.850 \times 10^{-7} t^2$.

[d] The equation is $L = 0.0007728_4 + 2.3448 \times 10^{-5} t + 7.816 \times 10^{-8} t^2$.

When the constant of a cell is such that the resistance of the primary standard will be *lower* than that calculated from the above relation, it is necessary in accurate measurements to use a reference cell which is calibrated directly and intercomparison measurements between the two cells to establish the constant of the former. When the constant is very small it is necessary to use some such accurate method for intercomparison as that described in a recent article.[36] Morgan and Lammert's[37] suggestion of using the potassium chloride solutions diluted with alcohol, may simplify the intercomparison somewhat, although new complications may be introduced by changing the solvent.

After the reference cell is calibrated at 0° the intercomparison measurements may be made at any convenient temperature. In accurate measure-

---

[35] Ref. 21, p. 465.

[36] Ref. 17, p. 1371.

[37] Ref. 19, p. 1693.

ments the change of the cell constant with the temperature becomes significant. This may be calculated with sufficient precision from the coefficients of expansion of the electrodes and the material from which the cell is constructed.[38]

Transferring Older Measurements to the New Basis.—In Table XI are given the values, calculated by the method outlined in a footnote, for the correct specific conductances of the solutions which have been most commonly used as standards in previous investigations. The value for Kohlrausch, Holborn and Diesselhorst's 0.1 *N* solution at 0° was checked directly (Table VIII) and likewise the values for Kohlrausch and Maltby's 0.1 *N* solution at 18° and 25° (Table VI) and 0.01 *N* at 18°.[39] The value given for maximum conducting sulfuric acid is that found by Eastman[40] with direct current. The percentage differences between the two bases of calibration are given and it is these percentages by which the measurements, based upon the original values of these solutions, are to be corrected. The specific conductance on the new basis is *lower* in every case.

Table XI

Factors for Transferring Older Data to New Basis

Correct *L* for Kohlrausch, Holborn and Diesselhorst's Potassium Chloride Solutions[a] (Calculated)[b]

Temp. °C.	*N*	% diff.[c]	0.1 *N*	% diff.	0.01 *N*	% diff.
0	0.6531_2	-0.15_0	0.007141_6	-0.11_8	0.007742_2	-0.22_9
18	$.09811_6$	$.10_8$	$.011184_6$	$.04_8$	$.0012223_8$	$.21_4$
25	$.1116_{87}$	$.10_1$	$.012876_5$	$.02_7$	$.001410_{37}$	$.18_6$

Correct Value for Kohlrausch and Maltby's Solutions[d] at 18°

Temp.	*N*	% diff.	0.1 *N*	% diff.	0.01 *N*	% diff.
18	0.09812_8	-0.14_5	0.011187_1	-0.14_5	0.0012225_2	-0.14_5

Correct *L* for Kohlrausch's Maximum Conducting H_2SO_4 at 25°[e]

L at 25°	% diff.
0.8242	−0.18

[a] 76.915_3, 7.4931_3 and 0.74756 g. of KCl to 1000 g. of H_2O (weighed in air). The molecular weight is 74.59.

[b] See footnote.

[c] The new values for *L* are lower in each case.

[d] 76.925, 7.4945 and 0.74766 g. of KCl to 1000 g. of H_2O (weighed in air). The molecular weight is 74.60.

[e] From Eastman's work with direct current.

From Table XI it is seen that the maximum *absolute* error in any of the former measurements amounts to 0.229% while the maximum *relative* error amounts to 0.202%. When conductance measurements are being made at present to a precision of a few hundredths of 1% it is evident that the older measurements constituted an unsatisfactory basis. It is note-

[38] Ref. 4a, p. 2452.

[39] Ref. 2, p. 2426.

[40] Ref. 4b, p. 1651.

worthy that Kohlrausch and Maltby's measurements (upon which the relative values at 18° are based) check the discrepancy found by the writers' between the *relative* values by Kohlrausch, Holborn and Diesselhorst at N, 0.1 N, and 0.01 N. The value determined by Eastman[41] for their N solution at 25° (0.11168) by his direct current method, gives a close check upon the calculated value found in Table XI. Since Eastman's cell was calibrated against mercury as a primary standard, his measurements can be considered absolute and furnish a valuable check upon the present investigation.

In conclusion, the writers desire to express their appreciation of the facilities afforded them at the University of Chicago by Professor Stieglitz and Professor Harkins and also to Dr. Washburn for checking the numerical results and giving valuable suggestions.

Summary

1. The absolute values for the specific conductance of three potassium chloride solutions, D, 0.1 D and 0.01 D (equivalents per cubic decimeter) at 0° have been determined. The solutions were made by adding 76.627_6, 7.4789_6 and 0.74625_3 g., respectively, of potassium chloride to 1000 g. of water, both weighed in air. The values found are 0.065098, 0.0071295 and 0.00077284 ohms^{-1}, cm.$^{-1}$, respectively.

2. It has been suggested that the value (0.0071295) for the 0.1 D solution be used as a primary standard for the determination of cell constants in future conductance measurements.

3. It has been suggested that in the future the concentrations used for conductance measurements be expressed in equivalents per cubic decimeter in order to avoid the present hybrid unit of equivalent conductance, which would *then* be expressed in terms of the ohm^{-1}, cm.^{2}, gram equivalent.

4. It has been suggested to call a concentration, expressed in equivalents per cubic decimeter, "*demal*," and indicate this by the letter "*D*."

5. The values obtained by Kohlrausch and Maltby at 18° are found to be 0.145% too *high*. Measurements based on their values may be reduced to the new basis by the use of this factor.

---

[41] In his most accurate comparison between the alternating current method and direct current method, Eastman found an average difference of 0.018%. If this is corrected by 0.004% (the percentage to which he found his measurements on metallic resistances to be in error) a difference of only 0.014% is found in the two methods. This shows that, if there is any difference between the two methods, as Eastman assumes, it is slight. His direct current measurements appeared to be the more reproducible of the two. However, if there is any true difference between the resistances obtained by direct and alternating current (1000 cycles), it will not affect the accuracy of a cell constant determination made with the results in this article, if a.c. is used in the determination. Since the alternating current method was used in this investigation, the constant of any cell which is calibrated by alternating current on the new basis will be correct, any such difference canceling out.

6. The values obtained by Kohlrausch, Holborn and Diesselhorst for potassium chloride solutions are shown to *average* about 0.15% high but the relative values are also in error. The maximum *absolute* error (in their 0.01 *N* solution at 0°) is shown to be 0.23% and the maximum *relative* error determined is 0.20%.

7. Values for the new solutions have been calculated to include temperatures as high as 30°, but for accurate measurements it is recommended that cells be standardized at 0°.

8. A new ice thermostat was used in these measurements where the cells were embedded and thoroughly packed in finely shaved ice, drainage being provided for the water.

RESEARCH DEPARTMENT,
THE LEEDS AND NORTHRUP COMPANY,
PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON AND LEE UNIVERSITY]

RUTHENIUM DICHLORIDE

BY JAS. LEWIS HOWE, JAMES L. HOWE, JR.,[1] AND S. C. OGBURN, JR.[1]

RECEIVED NOVEMBER 8, 1923

The blue color produced by the action of reducing agents on solutions of ruthenium appears to have been first noticed by Vauquelin[2] in 1804, and was later[3] attributed by him to the presence of the recently discovered osmium.

Thirty years later Claus discovered ruthenium, and noted this reaction as one of the most characteristic of this metal.[4] Since the blue color was produced by reducing agents, especially by zinc and by hydrogen sulfide, it was assumed by Claus and by later workers that it was occasioned by a lower chloride, $RuCl_2$, and as such has passed into the literature.

It may be noted that Claus[5] succeeded in chlorinating metallic ruthenium by heating in a current of dry chlorine, and considered that his analytical results substantiated this formula (then considered as RuCl).

Later, Joly[6] found that ruthenium could be more readily chlorinated by heating in a current of chlorine to which carbon monoxide was added. Under these conditions a very voluminous dark brown to black finely divided mass is obtained, to which Joly ascribed the formula $RuCl_3$. The chloride thus formed is insoluble in water, absolute alcohol, acids and alkalies, but dissolves readily in dil. alcohol, best about 25%, giving

---

[1] This communication is an abstract of theses submitted by James L. Howe, Jr., in partial fulfilment of the requirements for the degree of Master of Arts (1921), and by S. C. Ogburn, Jr., in partial fulfilment of the requirements for the degree of Master of Science in Chemistry (1923) at Washington and Lee University.

[2] Vauquelin, *Ann. chim.*, **49**, 188, 219 (1804); **50**, 5 (1804).

[3] Vauquelin, *Ann.*, **89**, 150, 225 (1814).

[4] Claus, *Ann.*, **56**, 260 (1846).

[5] Claus, *Ann.*, **59**, 238 (1846).

[6] Joly, *Compt. rend.*, **114**, 291 (1892).