[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Measurement of the Conductance of Electrolytes. V. A Redetermination of the Conductance of Standard Potassium Chloride Solutions in Absolute Units

BY GRINNELL JONES AND BENJAMIN C. BRADSHAW

After Kohlrausch had developed his method of measuring the electrical conductance of solutions by means of an alternating current bridge, he undertook with the aid of Holborn and Diesselhorst[1] the determination of the specific conductance of seven standard reference solutions in absolute units in order that the results might be available to himself and to other experimenters for the calibration of conductance cells. For this purpose they used two cells whose cross sectional areas, *a*, and length, *l*, were determined mechanically. The cell constant, l/a, could then be computed in absolute units (cm.$^{-1}$) from the measured dimensions.

The cell constants of a considerable number of other cells with sealed-in electrodes of the usual type were determined electrically by comparison with the primary cells by measurements of resistance when filled with a common solution. These cells, whose cell constants were thus determined indirectly, were then used for the determination of the specific conductance of the seven standard reference solutions at approximately 0, 9, 18, 27 and 36°. The specific conductance of each of these solutions for every degree between 0 and 36° was obtained by interpolation. No actual measurements were made at either 20 or at 25°. The water-bath used to fix the temperature of the cells was not provided with an automatic thermostatic control. The majority of the data on conductance in the literature are based on the values ascribed to these standard reference solutions by Kohlrausch, especially the 1 *N* and 0.1 *N* potassium chloride solutions.

In the original paper by Kohlrausch, Holborn and Diesselhorst it is stated that the normal potassium chloride solution was prepared by dissolving 74.555 g. of potassium chloride weighed in air and making up to 1 liter at 18°. The 0.1, 0.02, and 0.01 normal solutions were prepared by dilution by volume. The book "Das Leitvermögen der Elektrolyte" by Kohlrausch and Holborn,[2] which was published in the same year as the paper referred to, contains alternative directions for the preparation of these solutions by weight. This book has probably been used by other experimenters more than the original paper because it is more generally available.

Kraus and Parker[3a] have pointed out that the alternative instructions for preparing the 0.1, 0.02 and 0.01 normal solutions given by Kohlrausch and

---

(1) F. Kohlrausch, L. Holborn and H. Diesselhorst, *Wied. Ann.*, **64**, 417–455 (1898).

(2) F. Kohlrausch and L. Holborn "Leitvermögen der Elektrolyte." Teubner, Leipzig.

(3a) C. A. Kraus and H. C. Parker, THIS JOURNAL, **44**, 2422 (1922).

Holborn are inconsistent and in part erroneous. They estimate that in the case of the 0.01 normal solution the difference between the alternative volume and weight method is 0.54%. Kraus and Parker recommend that the weight method be used and that the values for the specific conductance of 1.0, 0.1 and 0.01 normal potassium chloride at 18° as determined by Kohlrausch and Maltby[3b] be used as standards for the calibration of cells. Kohlrausch did not recommend that these data, which are based on the earlier absolute measurements, should be used in place of those of Kohlrausch, Holborn and Diesselhorst.

Parker and Parker[4] made new absolute measurements of specific conductance of several standard reference solutions. The method used was in principle identical with that of Kohlrausch, Holborn and Diesselhorst. They used four cells whose linear dimensions were determined by the method used by Kohlrausch. The primary measurements were all made at 0°. Three different concentrations were used, 1 demal, 0.1 demal and 0.01 demal. They point out that the specific conductance of a normal solution as usually defined is expressed in a hybrid unit since the dimensions of the cell are expressed in centimeters whereas the concentration is expressed in gram molecules per liter and the liter is not defined as 1000 cubic centimeters but as the volume of a kilogram of water; and according to the best available measurements the liter is actually 1.000027×10^3 cubic centimeters.[5] They therefore proposed to avoid this logical inconsistency by defining a demal solution as one containing a gram molecule of salt dissolved in one cubic decimeter of solution at 0°.

Three different 0.1 demal and two different 1.0 demal and 0.01 demal solutions were placed in the primary cells, packed in ice, the resistance measured and the specific conductance computed. Then four cells with sealed-in electrodes of the pipet type were sealed together by means of their filling tubes and the cell constant of each determined at 0° by means of the 0.1 demal solution. These cells were then used to determine the specific conductance of each of the new standard solutions at intervals of 5° from 0 to 30°, inclusive, and also at 18°. The variation of the cell constant with temperature was computed from the known coefficient of expansion of the glass. These cells were then also used to determine at 0 and 25° the values of 1 N, 0.1 N and 0.01 N potassium chloride prepared according to the directions of Kohlrausch, Holborn and Diesselhorst, and according to Kohlrausch and Maltby. The new values obtained by Parker and Parker are different from those obtained by Kohlrausch by substantial amounts (within the limits of −0.027% for 0.1 N at 25° to −0.229% for 0.01 N at 0°). Parker and Parker recommend that their new value for the 0.1 demal solution at 0° should be used by others for the determination of cell con-

---

[3b] F. Kohlrausch and Margaret E. Maltby, *Wiss. Abh. phys. techn. Reichsanstalt*, **3**, 210 (1900).

[4] H. C. Parker and E. W. Parker, THIS JOURNAL, **46**, 312 (1924).

[5] "International Critical Tables," Vol. I 1926, p. 2.

stants, namely, that for a solution containing 7.47896 g. of potassium chloride per 1000 g. of water (weighed in air) the specific conductance at 0° should be taken as 0.007129_5 cm.^{-1} ohms^{-1}.

The Editors of the "International Critical Tables" reached the conclusion that the new values of Parker and Parker are more reliable than the older values of Kohlrausch and accordingly recomputed the data in the literature which are based on the older Kohlrausch standard solutions to the new basis. As a consequence nearly every figure in the ninety pages devoted to the conductance of solutions in the "International Critical Tables" is different from the figures in the original literature.

The great discrepancies between the results of Kohlrausch and of Parker and Parker make it desirable that the standard of reference for conductance measurements should be redetermined in a new and entirely independent investigation in which every effort should be made to avoid systematic errors. The first step in such an investigation was a study of the bridge[6] and its accessories[7] which revealed several important sources of error which have hitherto been overlooked or ignored. A new bridge designed so as to avoid these errors was built and demonstrated to be superior to the older types.

Another possibility of systematic errors was suggested by the work of Parker,[8] who has published experiments which appeared to show that cell constants are not really constant but apparently vary with the specific resistance of the solution being measured. A critical study of cell design described in the third paper[9] of this series demonstrated that capacitance between parts of the cell may cause a substantial error which is responsible for the Parker effect. It was demonstrated that the error is aggravated by sealing the cells together as was done by Parker and Parker in their absolute measurements. This study of cells made it clear that the Parker effect can be prevented by avoiding close proximity of parts of cells of opposite polarity.

It has been shown in the third and fourth papers of this series[10] that apparent variations of resistance with the applied frequency and voltage, which have been observed by many other experimenters as well as in this Laboratory, are due to polarization or to faulty design of the cells or of the bridge and can be eliminated by the designs which have been developed in this Laboratory. Therefore, it has been our regular practice to make all alternating current measurements with at least two different frequencies and to regard any discrepancy as a clear indication that a condition requiring correction is present.

(6) Grinnell Jones and R. C. Josephs, THIS JOURNAL, **50**, 1049 (1928).

(7) Grinnell Jones and G. M. Bollinger, *ibid.*, **51**, 2407 (1929).

(8) H. C. Parker, *ibid.*, **45**, 1366 (1923).

(9) Grinnell Jones and G. M. Bollinger, *ibid.*, **53**, 411 (1931).

(10) Grinnell Jones and G. M. Bollinger, *ibid.*, **53**, 1207 (1931).

Outline of the Method Used

The determination of the cell constants of our cells from measurements of their linear dimensions with a precision equal to that attainable in the resistance measurements is so difficult that it is desirable to avoid it if possible. It is impossible to obtain tubes for the cells which are perfectly uniform in their internal cross section and the determination of the effect on the cell constant of the irregularities is a difficult experimental and mathematical problem. The methods have been developed by Wolff, Shoemaker and Briggs[11] in connection with the preparation of wire equivalents of the standard mercury ohm. We have found it possible to avoid this task by using mercury as a reference substance. Since the international ohm is defined in terms of the resistance of a column of mercury, the specific conductance of mercury is known with high precision. We have prepared a series of primary cells (Z cells) which when filled with mercury have a resistance at 0° slightly less than 1 ohm. The exact resistance was measured with direct current on a Kelvin bridge by comparison with a standard 1-ohm coil whose exact value in terms of the International ohm has been determined for us by the Bureau of Standards. Then the cell constant of these cells can be computed by the relationship $(l/a)_Z = \kappa_{Hg}R_Z$. Then if the resistance of any other solution should be determined in these cells its specific conductance could be computed. However, in practice it is not quite so simple because a 1 N solution of potassium chloride at 0° would have a resistance of about 160,000 ohms and a 0.1 N solution of about 1,500,000 ohms. It would probably be impossible to measure such high resistances with sufficient precision with alternating current because the errors due to capacitance bypaths, which cannot be wholly eliminated, increase as the square of the resistance being measured. This difficulty was overcome, however, by using a solution of sulfuric acid in the primary cells (giving a resistance of about 20,000 ohms at 0°) and simultaneously in other cells (Y cells) having a cell constant about one-tenth that of the primary cells. The cell constant of the secondary cells may then be computed from the relationship $(l/a)_Y/(l/a)_Z = R_Y/R_Z$. The cell constant of the Y cell having thus been determined at 0° the slight correction to give the constants at 18 and 25° may be computed from the known coefficient of expansion of the glass.

These Y cells were then used to determine the specific conductance at 0, 18 and 25° of 1 D potassium chloride solutions made as defined by Parker and Parker. At the same time these solutions were placed in a pair of cells (N cells) having a cell constant of about one-tenth that of the Y cells so that the cell constants of these cells were determined by direct comparison with the Y cells. These N cells in turn served for the determination of the specific conductance of a number of 0.1 D potassium

---

(11) F. A. Wolff, M. P. Shoemaker, and C. A. Briggs, *Bull. Bur. Standards*, **12**, 375 (1916).

chloride solutions and also for the calibration of a pair of still smaller cells (Q cells) which in their turn were used to determine the specific conductance of a number of 0.01 *D* potassium chloride solutions. The resistance boxes used in the measurements were calibrated by comparison with Standard 10-, 100-, 1000- and 10,000-ohm coils provided with Bureau of Standards certificates.

The Specific Conductance of Mercury at 0°C.—The International Ohm is defined as follows. "The International Ohm is the resistance offered to an unvarying electric current by a column of mercury at the temperature of melting ice, 14.4521 grams in mass, of a constant cross-sectional area, and of the length of 106.300 centimeters."[12]

The "International Critical Tables," Vol. II, p. 458, gives 13.5955 g. per milliliter for the density of mercury. But 1 milliliter equals 1.000027 cc.; therefore, $d = 13.5955/1.000027 = 13.5951$ g./cc.

The specific conductance of mercury at 0° is

$$\kappa_{\mathrm{Hg}} = \frac{l}{aR} = \frac{l^2}{vR} = \frac{l^2 d}{wR} = \frac{106.300^2 \times 13.5951}{14.4521 \times 1.00000} = 10629.63 \text{ ohms}^{-1} \text{ cm.}^{-1}$$

The "International Critical Tables," Vol. VI, p. 136, gives 94.0766×10^{-6} as the specific resistance of mercury at 0° equivalent to 10629.64 for the specific conductance.

The Primary Cells

Five different primary cells were constructed. They are designated herein as Z_1, Z_2, Z_3, Z_4, Z_5. They were constructed of Jena normal 16 III red stripe glass. This variety of glass was selected because platinum electrodes can be readily and permanently sealed into it, because it is relatively insoluble, and because its coefficient of expansion is well known ($\alpha = 8.08 \times 10^{-6}$ per degree). The cells consisted of a capillary tube to each end of which was sealed a tapering bulb which enclosed the electrodes. The filling tubes which were sealed to the bulbs terminated in a grinding surrounded by a cup which served to hold the mercury for a mercury seal. The grindings were provided with an interchangeable cap and filling tube. The electrodes were circular platinum disks, 0.5 mm. thick and 1.0 cm. in diameter in the case of cells Z_1, Z_2 and Z_4 and 2.0 cm. in diameter in the case of Z_3 and Z_5. Two platinum wires each 0.5 mm. in diameter were welded to the back of each electrode, being separated by a distance of 1 mm. at the point of attachment to the electrode. The electrodes were held rigidly in place by the glass which covered nearly all of the back side. The two platinum wires were embedded separately in the glass supporting the electrodes and terminated inside separate contact tubes, which were filled with mercury when the cells were in use. One of these platinum wires served as the current lead and the other as the potential lead during the measurements with the Kelvin bridge.

The dimensions of the capillaries were so chosen that the resistance when filled with mercury at 0° would be slightly less than 1 ohm. The capillaries of Z_1 and Z_2 were about 70 cm. long; Z_3 and Z_5 were 61.6 cm. long; and Z_4 was 53 cm. long.

The cell was cleaned and dried and then evacuated by means of a good rotary oil pump. The ground joints between the cells and the connecting tubes were sealed with mercury on the outside. During this evacuation one end of the cell was connected to

---

(12) Circular, Bur. Standards, **60**, 29 (1916).

the pump and the other was closed by a filling tube which was drawn out to a fine capillary and then sealed. The cell was then filled completely with mercury by breaking the capillary tip of the filling tube while it was immersed in mercury.

The mercury used was agitated with dilute nitric acid by blowing air through it for a long time, then dried and repeatedly distilled under a vacuum according to the method of Hulett.[13] Several different samples were used but no difference in the observed resistance which could be attributed to differences in purity could be detected. All samples which were used are believed to have been sufficiently pure for the purpose.

Temperature Control.—The ice thermostat consisted of a large copper tank packed in dry powdered diatomaceous earth which proved to be an excellent heat insulator. The cells when filled with mercury were placed in the thermostat and surrounded by fine pieces of ice obtained from a local factory. Repeated tests with a Beckmann thermometer have shown that the melting point was 0.001 or 0.002° lower than that of the purest ice which we could make from conductivity water. The temperature coefficient of the resistance of mercury is only 0.0008862 per degree ("I. C. T.," Vol. VI, p. 136) and therefore a change of 0.002° would change the resistance by less than two parts in a million. The cells remained constant in resistance within two parts in a million for long periods and must therefore have attained the temperature of the ice. The resistance of the cells was observed at intervals for twenty-four hours or more with occasional repacking with fresh ice and drainage of the water until it was certain that they had attained the temperature of the ice.

The Kelvin Bridge.—The resistance of the mercury-filled and chilled primary cells was determined by means of a Kelvin bridge with direct current. The essential feature of the Kelvin bridge is that it provides means to eliminate from the results the resistance in the wires connecting the cell with the bridge. This is necessary for high precision when low resistances (1 ohm) are being measured. Our bridge was modeled after the one used by Wolff, Shoemaker and Briggs[14,15] of the Bureau of Standards. Our bridge was filled with oil and thermostated. The main ratio coils A and B were 100-ohm Leeds and Northrup standard coils, and were interchangeable. Two variable resistances to compensate for the leads are required. These consisted of a glass tube 3 mm. internal diameter sealed at the lower end with a piece of platinum wire passing through the seal and immersed in a larger tube filled with mercury. An amalgamated copper wire 1 mm. in diameter could be adjusted vertically within the inner tube, thus giving a variable and controllable resistance between the copper wire and the mercury in the outer tube. The whole was mounted in the thermostat.

The cells were measured against a standard Leeds and Northrup 1-ohm coil shunted by a calibrated resistance box which was adjustable in steps of 0.1 ohm. In the most unfavorable case the resistance in the shunt was a little more than 200 ohms and in such a case an error of 0.1 ohm in the value of the shunt, which seems improbable, would cause an error in the computed value of the cell of less than three parts in a million. Two different standard 1 ohm coils were used: No. 106,173 hereafter designated as Coil H and No. 146,935 hereafter designated as coil J. No. 106,173 has been calibrated three times by the Bureau of Standards with the results shown.

	Coil H	Coil J
Date of B. S. certificate	International ohms	
Jan. 6, 1926	0.999985	
May 18, 1928	0.999985	
Aug. 29, 1931	0.999982	0.999984

---

(13) G. A. Hulett, *Phys. Rev.*, **33**, 307 (1911).

(14) F. A. Wolff, M. P. Shoemaker, and C. A. Briggs, *Bull. Bur. Standards*, **12**, 444 (1916).

(15) Most of the work on the design and construction of our bridge was done by the late Dr. G. M. Bollinger, whose assistance is greatly appreciated.

The later figure was used since it was determined in the middle of the period when these measurements were made. The constancy of its value is gratifying. The galvanometer used was a Leeds & Northrup instrument type 2285 and was sufficiently sensitive so that when using 0.05 ampere in the bridge, adjustments could be made to within two parts in a million.

Table I gives the results for the resistance of the primary cells indicated in the heading when filled with mercury at 0°. The value given is the average obtained with the ratio coils, A and B, in their original position and reversed, which serves to eliminate any error due to a slight inequality in A and B. The value for the cell constant is obtained by multiplying the resistance by the specific resistance of mercury at 0°, 10629.63.

Each recorded result with the H coil represents a complete independent experiment with a new filling of the cell. All recorded data obtained with the J coil are independent of one another but each depends on the same filling of the cell as one of the results obtained with the H coil.

The average deviation of a single measurement from the mean for the cell is about three parts per million.

TABLE I

DETERMINATION OF THE CELL CONSTANTS OF THE PRIMARY CELLS AT 0°

Resistance in International ohms of cells when filled with mercury

Standard coil	Z_1	Z_2	Z_3	Z_4	Z_5
H	0.995109	0.995104	0.997540	0.999068	0.999054
	.995115	.995095	.997540	.999077	.999057
		.995098	.997548	.999077	.999063
				.999076	
				.999080	
J	.995112	.995094		.999075	.999054
				.999077	.999060
				.999079	.999065
Average R	.995112	.995098	.997542	.999076	.999059
Av. cell constant	10577.67	10577.52	10603.51	10619.81	10619.63

After the work on the determination of the cell constants by means of mercury was well advanced we were fortunate in having Dr. Frank Wenner of the Bureau of Standards visit our laboratory. He suggested that in spite of the gratifying consistency of our results there might be a small constant error. Dr. Wenner pointed out that in our Z cells the spatial distribution of the lines of flow of the current in the bulbs at the ends of the cells would be slightly different when the cell is filled with mercury and when it is filled with sulfuric acid. When the cell is filled with acid the electrode can be regarded as essentially an equipotential surface because the specific resistance of the acid is about 200,000 times as great as that of the platinum. On the other hand, when the cell is filled with mercury, which has a specific resistance about eight times that of the platinum, the platinum cannot be regarded as a strictly equipotential surface and in consequence the lines of flow of the current in the end bulbs will be displaced toward the center of the electrode slightly more than they will when the cell is filled with the acid. It is to be expected that this effect, if large enough to be significant, will be greater in cells Z_3 and Z_5 which had electrodes 2 cm. in diameter than in cells Z_1, Z_2 and Z_4 whose electrodes were 1 cm. in diameter. In order to determine whether or not this slight displacement of the lines of flow in the bulbs would have a significant effect on the cell constant of our primary cells we built a new primary cell Z_6, designed by Dr. Wenner. In this cell the capillary tube has a fork about 3 cm. from each end with a bulb carrying an electrode and filling tube on each side of the fork. The potential leads are thus brought into contact with the main current through a fine mercury thread. This design ensures that the resistance measured on the Kelvin bridge will be due solely to the mercury in the capillary tube between the forks where the capillary tube branches, since the resistance of the mercury in the connecting tubes outside these forks, in the bulbs, and the resistance of the platinum electrodes is all included in the lead wires and is eliminated in the measurements with the Kelvin bridge.

The results obtained for the cell constant of Z_6 by measurements with mercury are given in Table II below.

TABLE II

DETERMINATION OF CELL CONSTANT OF PRIMARY CELL Z_6 AT 0°

Date	Cell	Standard coil	Shunt S, ohms	R, ohms	Cell constant, l/a
11/10/31	Z_6	H	1902	0.999456	10623.85
11/10/31	Z_6	J	1891	.999455	10623.84
12/18/31	Z_6	H	1872	.999448	10623.76
12/18/31	Z_6	J	1857	.999446	10623.74
1/11/32	Z_6	H	1900	.999458	10623.87
7/15/32	Z_6	H	1920	.999461	10623.91
7/15/32	Z_6	J	1920	.999463	10623.93
				Average	10623.84

The cells Z_4 and Z_5 and Z_6 were then simultaneously filled with sulfuric acid (approximately 6 N) and their resistance measured with alternating current in the manner described in more detail below. Assuming that the effect suggested by Wenner would be absent in Z_6 on account of its design, an evaluation of the magnitude of the effect in Z_4 (or Z_5) is given by comparing the ratio of Z_4 (or Z_5) to Z_6 when filled with mercury and when filled with acid. The measurements with Z_6 when filled with acid were necessarily carried out in a different manner than usual since the resistance desired was not the total resistance of the cell between the two opposite electrodes but the resistance between the points of contact with the potential leads used in the measurements with the Kelvin bridge. The desired resistance was obtained, however, in a manner similar to that used by Shedlovsky,[16] by using each of the potential leads in turn as the midpoint of the bridge and reversing the leads from the ends of the cell to the bridge. The mean of the two resistance measurements obtained in this way gives the true resistance between the potential leads. The fact that the contact of the potential leads with the main current is not a true point makes no difference because the spatial distribution of the lines of flow of the current will be the same when the cell is filled with mercury as it is when filled with acid. The results of these comparisons are shown in Table III.

TABLE III

MEASUREMENT OF THE WENNER EFFECT IN CELLS Z_4 AND Z_5

	Z_6	Z_4	Z_5	Z_4/Z_6	Z_5/Z_6
First acid filling	12871.05	12864.7	12863.79	0.99951	0.99943_6
Second acid filling	12870.4	12863.6	12863.17	.99947	$.99943_8$
Third acid filling	12871.4	12864.87	12864.2	.99949	$.99944_1$
Average				.99949	.99944
Ratio of resistances when filled with mercury				.99962	.99960
Correction for Wenner effect in Z_4				− .00013	
Correction for Wenner effect in Z_5					− .00016

It seems clear the that Wenner effect is measurable in our cells and that the corrections indicated in the table above should be applied. The Wenner effect, as was to be expected, turned out to be slightly larger for Z_5, which has electrodes 2 cm. in diameter and a correspondingly larger bulb, than for Z_4 which has electrodes 1 cm. in diameter. Similar measurements could not be carried out on cells Z_1, Z_2 and Z_3 because these cells had been accidentally broken before Z_6 was made. However, the correction for Z_3 would be the same as for Z_5 because the latter was made by repairing a break in the capillary of the former with no change in the position of the electrodes or shape of the bulb. Similarly the same correction is applied to Z_1 and Z_2 as to Z_4 because the electrodes all had the same diameter, and the bulbs, although not identical in shape, were similar. The corrected values for the cell constants of the primary cells which are used in all subsequent calculations are shown in Table IV.

TABLE IV

CELL CONSTANTS OF PRIMARY CELLS AT 0°

Z_1	10576.3	Z_3	10601.8	Z_5	10617.9
Z_2	10576.1	Z_4	10618.4	Z_6	10623.8

The Secondary Cells

Two secondary cells having cell constants approximately one-tenth of the primary were constructed and designated Y_1 and Y_2. The filling tubes and contact tubes osite polarity were well separated in order to avoid capacitance between parts of in accordance with the principles of design discussed in the third paper of this

---

hedlovsky, THIS JOURNAL, **52**, 1806 (1930).

series. Figure 14 of the paper referred to represents sufficiently well the secondary cells used in this investigation. The horizontal tube constituting the resistance element of the cell was, for Y_1, 0.14 cm. inside diameter and 18.6 cm. long, and for Y_2, 0.16 cm. inside diameter and 21 cm. long. The electrodes were circular platinum disks 2.0 cm. diameter and 0.03 cm. thick. They were very lightly platinized.

The cell constants of the Y cells were then determined by comparison with the Z cells by filling one of the Z cells and a pair of Y cells simultaneously with the same solution of sulfuric acid approximately 6 N having a specific conductance at 0° of about 0.52.

The acid, having been well shaken to ensure uniformity, was placed in a 4-liter Non-Sol bottle provided with a special ground-glass stopper carrying a delivery tube extending nearly to the bottom of the bottle and another tube serving to admit compressed air to the bottle to force the solution into the cells. The air used for this purpose was passed through several towers filled with glass beads wet with some of the same acid in order to ensure that there would be no change in composition of the acid caused by evaporation of the water into the air used to replace the acid in the bottle.

The three cells chosen for the experiment were connected to each other and to the delivery tube from the bottle by means of Pyrex glass tubes provided with ground joints which fitted the grindings on the filling tubes of the cells, so that the acid could be circulated through the cells without coming in contact with anything except glass. After the cells had been thoroughly rinsed and filled with the same acid they were separated and closed by their ground glass caps. The acid used in the different experiments had approximately the same concentration, but no effort was made to make any definite exact composition. It is therefore not to be expected that resistances shown by any given cell in the different experiments will agree exactly. The consistency of the results is to be judged by the concordance of the values for the cell constants of the Y cells as determined in different experiments and by comparison with different Z cells.

When measuring the resistance of the Z cells when filled with mercury by the use of direct current it was possible to bring ice directly in contact with the cells. However, when the cells were filled with acid and measured with alternating current this simple method of cooling, although used by Kohlrausch and by Parker and Parker, was avoided because it has been shown in the first paper of this series that errors will be caused by parasitic currents outside the cell in the ice-bath. These errors are functions of the frequency and they increase rapidly with the resistance being measured. To avoid this error the cells after being filled with acid were thoroughly dried on the outside, then mounted in a suitable relative position in a sheet metal trough containing a molten mixture of soft paraffin, vaseline and transformer oil. After the mixture had solidified a paper cylinder was fitted around the filling and contact tubes at the end of each cell and the melted paraffin mixture poured into the cylinder and allowed to solidify. By this arrangement all parts of the cells except the tip of the contact tubes were surrounded by solid paraffin for a distance of 5 cm. in every direction. The whole block was then packed in ice and allowed to remain until the paraffin was hard enough to permit the removal of the metal trough. A flexible rubber tube was attached to the end of each contact tube to carry and insulate the copper wires which made electric contact with the cells. The block of cells mounted in solid paraffin was then packed in broken ice in the ice thermostat already described. Our experience soon showed that about twenty-four hours is required for the cells to reach the temperature of the ice-bath and therefore in all the later experiments we waited at least twenty-four hours before beginning the resistance measurements. In all cases resistance measurements were made at intervals for many hours to ensure that the temperature was constant. The water was drained from the thermostat and fresh ice added as necessary during this interval to keep the cells completely surrounded by ice.

Our later experience showed that it would have been easier, quicker and just as accurate to have determined the cell constant ratios between the Z and Y cells at 25° instead of at 0°, but at the time the cell constants of the Y cells were determined we did not have available an oil-filled thermostat of sufficient size for the purpose. Later a suitable thermostat was built for use in the determination of the specific conductance of our standard solutions at 18 and 25°, but it seemed unnecessary to repeat the comparison of the Z and Y cells since their relative values were already known with sufficient precision.

The bridge used in the early part of the work was the instrument built and described by Jones and Josephs. In the later part of the work a new instrument built by Leeds and Northrup in accordance with the principles of design laid down by Jones and Josephs was available. This bridge has been described in detail by P. H. Dike[17] of the Leeds and Northrup Company. Besides many improvements in mechanical details of construction which are relatively unimportant because they affect the appearance and manufacturing procedure more than the performance of the instrument, they have made one very important electrical improvement in their design. This improvement consists in a new method of winding the resistance coils in the form of a ribbon with a silk warp and a manganin woof. Dr. Dike's experiments indicate that these new coils have less inductance and capacitance than is attainable by any other known method of winding. We have found, in confirmation of Dike's experience, that these coils show less variation in resistance with time than our old resistance boxes. This is an important practical advantage because it means that the laborious calibration of the resistances need not be repeated at such frequent intervals as is necessary with the old boxes. Our experience with the new bridge has been entirely satisfactory. The resistances forming a part of the bridge were calibrated by comparison with Leeds and Northrup standard 100, 1000 and 10,000-ohm coils bearing a Bureau of Standards certificate using direct current since these standard coils are not designed for use with alternating current. By this method we are in effect depending on the Bureau of Standards for the intercomparison of the 1-ohm standard coils used in the measurement on the Z cells when filled with mercury and the 100, 1000, 10,000-ohm coils which serve as the resistance standard for the measurements of our solutions.

The oscillator used was built by the General Radio Company of Cambridge and was their type 608A. A two-stage audion-tube amplifier specially designed and built for us by the General Radio Company was used between the bridge and telephones.

All measurements were made with at least two different frequencies, commonly about 1000 and 2000 or 3000 cycles per second. In the great majority of cases no difference of as much as 0.001% could be observed when doubling the frequency. In some cases slight variations amounting to one or two thousandths of one per cent. were observed and in such cases the reading at the lower frequency was accepted as sufficiently accurate. In a few cases variations of several hundredths of a per cent. were obtained. Such variations were regarded as a sure indication that something was wrong with the bridge or cells and a search was made to ascertain the cause and remedy it. In the early part of the work there were a number of cases of variation of resistance with frequency which were due to a film of moisture on the outside of the cells. No results were accepted as reliable and published if the variation in apparent resistance when the frequency was changed from 1000 to 2000 cycles per second exceeded 0.002%. It is shown in the earlier papers of this series that errors due to polarization, capacitative shunts and improper grounding are all functions of the frequency. We regard this practice of checking all readings at a doubled frequency as extremely important because it gives a means of discovering abnormal conditions which may cause an error and which would escape discovery if the measurements were carried out at a single frequency only.

---

(17) P. H. Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

The results for the comparison of the Y cells with the Z cells at 0° are shown in Table V. The accepted average values for the cell constants of the Y cells are apparently reliable to within a few thousandths of one per cent.

TABLE V

DETERMINATION OF CELL CONSTANT OF SECONDARY CELLS AT 0° BY COMPARISON WITH THE PRIMARY CELLS

		Cell Y_1		Cell Y_2	
Date	Primary cell	Y_1/Z	Cell constant, Y_1	Y_2/Z	Cell constant, Y_2
8/ 9/30	Z_1	0.108247	1144.85		
8/12/30	Z_1	.108239	1144.77		
		Average based on Z_1	1144.81		
10/30/30	Z_2	.108246	1144.82	0.104419	1104.35
11/ 5/30	Z_2	.108236	1144.72	.104422	1104.38
1/31/31	Z_2	.108242	1144.78	.104422	1104.38
11/ 5/31	Z_2	.108239	1144.75	.104419	1104.35
11/17/31	Z_2	.108241	1144.77	.104423	1104.39
		Average based on Z_2	1144.77	Average based on Z_2	1104.37
1/10/31	Z_3	.107979	1144.77	.104165	1104.34
		Value based on Z_3	1144.77	Value based on Z_3	1104.34
1/15/31	Z_4	.107813	1144.80		
1/19/31	Z_4	.107812	1144.79	.104015	1104.47
1/21/31	Z_4	.107811	1144.78	.104011	1104.43
		Average based on Z_4	1144.78	Average based on Z_4	1104.45
2/10/32	Z_5			.104015	1104.42
				Value based on Z_5	1104.42
		Grand average, Y_1 =	1144.78	Grand average, Y_2 =	1104.39

It is next convenient to compute the cell constant of these cells at 18 and 25°. The cell constant at any temperature, t, may be computed from the cell constant at 0° by the formula

$$\left(\frac{l}{a}\right)_t = \left(\frac{l}{a}\right)_0 (1 - \alpha t)$$

where α is the linear coefficient of expansion of the glass used. The linear coefficient of expansion of the Jena[18] normal 16 III glass used is 8.08×10^{-6} hence

$$\left(\frac{l}{a}\right)_{18} = \left(\frac{l}{a}\right)_0 (1 - 18 \times 8.08 \times 10^{-6}) = \left(\frac{l}{a}\right)_0 (1 - 0.000145)$$

and

$$\left(\frac{l}{a}\right)_{25} = \left(\frac{l}{a}\right)_0 (1 - 0.000202)$$

The accepted values for the cell constants of the Y cells are as follows.

---

(18) H. Thiene, "Glas," G. Fischer, Jena, Germany, 1931, p. 130.

TABLE VI

CELL CONSTANT OF SECONDARY CELLS

	Y_1	Y_2
0°	1144.78	1104.39
18°	1144.61	1104.23
25°	1144.55	1104.17

Having determined the cell constants of a pair of cells suitable for use with a 1 *D* potassium chloride solution the next step was to prepare such standard solutions and to measure their resistance in each cell at each of the three temperatures; and at the same time to determine the cell constants of another pair of cells (N cells) having a smaller cell constant which would be suitable for use with a 0.1 *D* potassium chloride solution.

The N cells were of course of the horizontal type recommended by Jones and Bollinger. Their electrodes were 2 cm. in diameter. The two Y cells and a pair of N cells were filled simultaneously with the same standard potassium chloride solution and then measured in quick succession while mounted in the same thermostat. The ratio of the cell constants is then equal to the ratio of the resistances. This ratio should be independent of the temperature since the cells are made of the same variety of glass and are filled with the same solution. These ratios were determined at 0, 18 and 25°, but no systematic variation with the temperature could be detected. Therefore, the cell constant ratios for a given pair of cells were averaged and the average multiplied by the appropriate value for the Y cell used to give the cell constant for the N cell at 0°. The results of the calibration of the N cells are shown in Table VII. The figures recorded on the same line under the different temperature headings were made on the same fillings of the cells, but figures on different lines represent independent experiments with different fillings. A blank means that the corresponding measurement was not made, or if made it showed a pronounced frequency effect or other evidence of unreliability. A

TABLE VII

CELL CONSTANTS OF N CELLS BY COMPARISON WITH Y CELLS

	N_2/Y_1			N_2/Y_2		
Sol.	0°	18°	25°	0°	18°	25°
5	0.136558	.....	.....	0.141552	.....	.....
6	.136561	.....	.....	.....	.....	.....
9-1	.....	0.136564	0.136537	.141563	0.141562	.....
9-2	.....	.....	.136562	.....	.....	0.141557
10-1	.136587	.136569	.....	.....	.141562	.141544
10-2	.136561	.....	.136572	.141553	.....	.141565
11-1	.....	.136584	.136562	.141539	.141555	.141550
11-2	.136566	.136561	.136561	.141531	.141549	.141540
12	.136554	.136564	.136549	.141543	.141545	.141550
13	.136568	.....	.....	.141559	.....	.....
14	.136571	.....	.....	.141545	.....	.....
Av.	.136566	.136568	.136557	.141548	.141555	.141551
Grand average		.136564			.141551	

Cell constant of N_2 from Y_1 at 0°
$0.136564 \times 1144.78 = 156.336$

Cell constant of N_2 from Y_2 at 0°
$0.141551 \times 1104.39 = 156.328$

Accepted average values for N_2
0°, 156.332 18°, 156.309 25°, 156.300

TABLE VII (*Concluded*)

	N_4/Y_1			N_4/Y_2		
Sol.	0°	18°	25°	0°	18°	25°
14–1	0.091047	0.091045	0.091033	0.094363	0.094359	0.094361
14–2	.091010	.091016	.....	.094345	.094342	.....
15–1	.091031	.....	.091033	.094355	.094356	.094354
15–2	.....	.....	.....	.094349	.094351	.....
16–1	.....	.....	.....	.094356	.094347	.094356
16–2	.....	.....	.....	.094350	.094348	.094335
17–1	.....	.....	.....	.....	.....	.094363
Av.	.091029	.091030	.091033	.094353	.094350	.094354
Grand average		.0910307			.0943523	

Cell constant of N_4 from Y_1 at 0°
0.0910307 × 1144.78 = 104.210

Cell constant of N_4 from Y_2 at 0°
0.0943523 × 1104.39 = 104.202

Accepted average value for N_4
0°, 104.204 18°, 104.189 25°, 104.183

detailed explanation of each case must be omitted to save space. The average values of the N cells computed from the different Y cells agree within 0.01% in all cases.

The average values for the various N cells based on Y_2 are slightly lower than the average values based on Y_1 for all three N cells but the deviations are less than 0.008%. The mean value based on both Y cells is accepted. The cell constants at 18 and 25° were computed from the linear coefficient of expansion of the glass in the manner described above.

In an exactly similar manner the cell constants of a pair of still smaller cells (Q cells) suitable for use with 0.01 *D* potassium chloride solutions were determined by comparison with the N cells when both cells were filled with 0.1 *D* potassium chloride solutions. The results are shown in Table VIII.

TABLE VIII

CELL CONSTANTS OF Q CELLS BY COMPARISON WITH N CELLS

Q_1

	Q_1/N_2			Q_1/N_4		
Sol.	0°	18°	25°	0°	18°	25°
20–1	0.074728	0.074736	0.074744	.....	.....	.....
20–2	.074738	.074740	.074744	.....	.....	.....
21–1	.074734	.074736	.074741	0.112133	0.112133	0.112123
21–2	.074736	.074739	.074737	.112121	.112117	.112118
22–1	.074742	.074739	.074740	.....	.112115	.112115
22–2	.074734	.074741	.074740	.112127	.112120	.112120
23–1	.074741	.074738	.074742	.112130	.112120	.112123
23–2	.074730	.074742	.074733	.112123	.112119	.112118
24–1	.074733	.074738	.074743	.112120	.112118	.112130
24–2	.074733	.074745	.074740	.112112	.112117	.112117
Av.	.074735	.074740	.074741	.112124	.112120	.112120
Grand average		.0747387			.1121213	

Cell constant for Q_1 based on N_2 at 0°
0.0747387 × 156.332 = 11.6841

Cell constant for Q_1 based on N_4 at 0°
0.1121213 × 104.204 = 11.6835

Accepted average values for Q_1: 0°, 11.6838 18°, 11.6821 25°, 11.6814

TABLE VIII (*Concluded*)

Q_2

	Q_2/N_2			Q_2/N_4		
Sol.	0°	18°	25°	0°	18°	25°
20-1	0.073026	0.073025	0.073027	.....	.....	.....
20-2	.073012	.073027	.073029	.....	.....	.....
21-1	.073024	.073020	.073029	0.109569	0.109558	0.109554
21-2	.073028	.073020	.073024	.109558	.109538	.109548
22-1	.073034	.073025	.073029	.....	.109543	.109548
22-2	.073017	.073028	.073021	.109551	.109550	.109542
23-1	.073031	.073027	.073028	.109565	.109552	.109552
23-2	.073024	.073031	.073025	.109563	.109553	.109555
24-1	.073020	.073022	.073027	.109549	.109545	.109556
24-2	.073025	.073030	.073025	.109549	.109544	.109545
Av.	.073024	.073025	.073026	.109558	.109548	.109550
Grand average		$.073025_3$			$.109551_6$	

Cell constant of Q_2 based on N_2 at 0°
$0.0730253 \times 156.332 = 11.4162$

Cell constant of Q_2 based on N_4 at 0°
$0.1095516 \times 104.204 = 11.4157$

Accepted average values for Q_2: 0°, 11.4159 18°, 11.4143 25°, 11.4136

Definition of the Standard Reference Solutions.—The really important consideration in the selection and definition of the standard reference solution is that it shall be prepared and described so that it can be reproduced as exactly as possible at any future time and in any laboratory.

For the convenience of users it is desirable to have several reference solutions differing considerably in specific conductance whose absolute values are known with greater precision than is commonly attained in routine work on conductance.

Potassium chloride was selected for this work because it is easily purified, is non-hygroscopic, sufficiently soluble, stable both in solid form and in solution, and non-poisonous. Moreover its selection is in accord with the best previous usage. The other salts recommended by Kohlrausch should be abandoned.

Kohlrausch defined his standard solutions of potassium chloride in terms of gram molecules per liter at 18° and Parker defined his standard solutions in terms of gram molecules per cubic decimeter at 0°. This method of definition is, however, objectionable for several reasons. The values commonly accepted for the atomic weights may be changed from time to time. Kohlrausch, Holborn and Diesselhorst used 74.59 as the molecular weight of potassium chloride; Kohlrausch and Maltby used 74.599; and Parker and Parker used 74.553, which does not agree exactly with the value 74.56 in the then current edition of the International Atomic Weight Table nor with the value 74.557 in the 1932 tables.[19] Moreover, this value is subject to change in the future. Therefore if the solution is defined in terms of gram molecules anyone who in the future wishes to

---

[19] THIS JOURNAL, **45**, 869 (1923); **54**, 1277 (1932).

prepare such a solution cannot safely rely on the Atomic Weight Tables then current but must look up the value for the molecular weight accepted at the time the specific conductance was determined. Since the user must in any case weigh the salt, the definition should be stated directly in grams.

A definition in terms of volume (liters or cubic decimeters) is objectionable because in practice it is less precise than a definition in terms of weight, owing to the numerous and well-known errors in volumetric procedure.

Both Kohlrausch and Parker in effect recognize the force of the objections to their primary definition by giving alternative definitions in terms of grams of salt per kilogram of solution or of water. Alternative definitions are, however, a source of confusion and should be avoided.

Both Kohlrausch and Parker, however, specify weights in air instead of *in vacuo* and hence introduce some uncertainty because the buoyancy of the air is variable from time to time in the same laboratory and still more so from one laboratory to another. The net vacuum correction for 1 D potassium chloride solution in our laboratory, which is near sea level, amounts usually to about 0.054% but it may vary more than 5% of its value with changes in weather and may be more than 10% less in laboratories at a high elevation above sea level. Therefore the standard solution should be defined in terms of weights corrected to vacuum.

We regard it as better practice to weigh the solution instead of the water because it permits the use of some of the water to rinse the container in which the salt was weighed and because losses of water by evaporation during the preparation of the solution cause no error.

Therefore the standard should be defined in terms of weight of potassium chloride per kilogram of solution corrected to vacuum. Each time a standard solution is prepared the appropriate vacuum correction should be applied depending on the density of the air at the time and place.

Since at the beginning of the work we assumed Parker's[20] results to be more reliable than the older work of Kohlrausch and since Parker's results had been accepted by the "International Critical Tables,"[21] we decided to retain his standard concentrations but to revise the definitions so as to avoid the indefiniteness inherent in weights uncorrected for air buoyancy. Our new definitions are equivalent to those of Parker within the degree of precision which the variability of the air buoyancy permits. Table IX shows a comparison of our new definitions with the older definitions. The last column shows the ratio of the Kohlrausch definitions to our new definitions.

For the preparation of our solutions we have thought it best to use conductivity water which was prepared in contact with laboratory air, having a specific conductivity of 1.0×10^{-6} more or less at 25° instead of attempt-

---

(20) H. C. Parker and E. W. Parker, THIS JOURNAL, **46**, 333 (1924).

(21) "International Critical Tables," Vol. VI, p. 230.

TABLE IX

COMPARISON OF DEFINITIONS OF STANDARD SOLUTIONS

Concn.	Parker g. KCl per 1000 g. H_2O in air	Jones and Bradshaw g. KCl per 1000 g. soln. in vac.	Kohlrausch g. KCl per 1000 g. H_2O in air	Kohlrausch g. KCl per 1000 g. soln. corr. to vac.	Ratio Kohlrausch to J. & B. definition
1*D*	76.6276	71.1352	76.9153	71.3828	1.00348
0.1*D*	7.47896	7.41913	7.49313	7.44037	1.00286
0.01*D*	0.746253	0.745263	0.74756	0.746554	1.00173

ing to prepare and use "ultra-pure" water. It is easy to obtain water having a conductivity substantially below 1.0×10^{-6} by sweeping out the container with air freed from carbon dioxide and ammonia and by bubbling the purified air through the water. But unless the solutions are prepared in a manner which excludes contact with the ordinary air of the laboratory at any stage they will gain in conductivity by absorbing carbon dioxide. It is of course possible to prepare the solutions with complete exclusion of the laboratory air but it requires elaborate special equipment and skill in manipulation, especially if it is desired to have the composition close to the definition of the standard.

The specific conductance of the water used was measured in advance and subtracted from the measured specific conductance of the solution. The measurements were made at 25° and the conductivity at 0 and 18° computed from that at 25° by multiplying by the factors 0.49 and 0.84.

Several different samples of potassium chloride were used. The purest material available by purchase was recrystallized several times with centrifugal drainage. Qualitative chemical tests for magnesium, and sulfate (the most likely impurities) gave negative results and the flame test indicated that no sodium was present. The salt was fused in a platinum crucible, poured into a platinum dish and transferred to a closed bottle while still hot. A saturated solution gave no test for alkali with phenolphthalein. The salt showed no tendency to gain in weight by absorption of moisture when allowed to stand on the balance.

The weights used were of course carefully intercompared and corrections applied. A standardization by comparison with a true gram is not necessary since both the salt and the solution are weighed.

For the measurements at 0° the cells were packed in solid paraffin and surrounded with ice as already described and a correction applied because the ice had a melting point of −0.001° (or −0.002° in a few cases). For the measurements at 18 and 25° a special oil-filled thermostat was used. When working properly no fluctuations of as much as 0.001 of a degree could be detected on a sensitive thermometer nor were there fluctuations in the resistance of our cells which could be ascribed to the effect of variations in temperature of the bath.

The temperature scale was determined by means of two mercury thermometers which were built especially for the purpose by J. H. Green of Brooklyn, New York. One of them had a scale between 17.5 and 21.0° which was 4.5 cm. long per degree, and the other, a scale from 24.5 to 26° which was 6 cm. long per degree. Each had also a scale covering the ice point with a bulb between the two scales. Since we were not interested in following a fluctuating temperature, the maker was instructed to make the glass walls of the bulb exceptionally thick. These thermometers were therefore much less influenced by variations in depth of immersion or variations in barometric pressure than the common Beckmann. They were graduated in hundredths of a degree and were read by means of a cathetometer provided with a magnifying telescope and a cross hair controlled by a micrometer screw and scale, permitting definite readings to 0.001°. The thermometers had been calibrated by the Bureau of Standards with corrections given to thousandths of a degree. The ice point of the thermometers was of course checked at frequent intervals. The regulator of the thermostat was adjusted until the temperature of the bath was within 0.001° of 18 or 25° as given on our scale.

The usual procedure in making the measurements and calculations was as follows. The water to be used was freshly distilled and its conductance at 25° determined. The salt was then weighed out and the weight of solution to be made computed. The solution was made in a large Non-Sol bottle, the weight adjusted by the addition of water until it was within 0.002% of the desired value, the solution was carefully weighed and the barometric pressure and the temperature of the balance room recorded to permit the vacuum correction to be computed. The cells were filled in the manner already described and then mounted in the oil thermostat which had already been adjusted to 18.000° (or 25.000°). The resistances were then read using at least two frequencies and followed for a sufficient time to be sure that the cells had attained the temperature of the bath. The cells were then removed, packed in solid paraffin in the manner described above, placed in the ice thermostat and allowed to remain at least twenty-four hours. In the interval the oil thermostat was brought to 25.000° (or 18.000°) by changing the regulator. After making the resistance readings at 0° the cells were removed from the ice thermostat, the solid paraffin cut off and the cells were next placed in the oil thermostat for the resistance readings at 25° (or 18.000°). The cells were then emptied and refilled either with the same solution or with a fresh solution. No solution was used more than twice. No systematic variation between the results of the first and second filling could be detected. However, if any serious delay occurred owing to troubles with the apparatus or for personal reasons the latter parts of the normal cycle were omitted.

The cell constant of the cell used was divided by the measured resistance (with calibration corrections for the coils applied) giving the actual specific conductance of the solution as measured. The specific conductance of the water used was next subtracted and the result divided by the factor expressing the actual concentration of the solution used in terms of the standard concentration. The correction thus applied rarely amounted to more than 0.002% and was usually less than 0.001%. No temperature corrections were applied at 18° or 25° except in one case, because the temperature was brought as near to the standard temperature as we could determine the scale. Since our ice was found to melt at $-0.001°$ (or $-0.002°$ in a few cases) the specific conductance at 0° was corrected by adding $+1.7 \times 10^{-6}$ for the 1 *D* solutions, $+0.21 \times 10^{-6}$ for the 0.1 *D* solutions and $+0.024 \times 10^{-6}$ for the 0.01 *D* solutions.

TABLE X

SPECIFIC CONDUCTANCE × 10^6 OF STANDARD POTASSIUM CHLORIDE SOLUTIONS (1 *D*) CONTAINING 71.1352 G. OF POTASSIUM CHLORIDE PER 1000 G. OF SOLUTION, BOTH WEIGHTS CORRECTED FOR AIR BUOYANCY, AND THE SPECIFIC CONDUCTANCE CORRECTED FOR THE CONDUCTANCE OF THE WATER USED

	0°C.		18°C.		25°C.	
Sol.	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2
2	65,179	....	....	....	.....	.....
3	65,176	65,173	....	....	.....	.....
5	65,170	65,169	....	....	.....	.....
9-1	65,186	65,170	97,826	97,829	111,340	111,332
9-2	65,184	65,188	97,828	97,845	111,336	111,336
10-1	65,184	....	97,839	97,838	.....	111,334
10-2	65,186	65,185	....	....	111,364	111,364
11-1	....	65,164	97,855	97,839	111,341	111,336
11-2	65,184	65,170	97,855	97,851	111,360	111,348
12	65,172	65,170	97,837	97,828	111,331	111,337
13	65,171	65,169	97,825	....	111,336	111,335
Average	65,179	65,173	97,838	97,838	111,344	111,340
Average	$65{,}17_6$		$97{,}83_8$		$111{,}34_2$	

TABLE XI

SPECIFIC CONDUCTANCE × 10^6 OF STANDARD POTASSIUM CHLORIDE SOLUTIONS (0.1 *D*) CONTAINING 7.41913 G. OF POTASSIUM CHLORIDE PER 1000 G. OF SOLUTION, BOTH WEIGHTS CORRECTED FOR AIR BUOYANCY, AND THE SPECIFIC CONDUCTANCE CORRECTED FOR THE CONDUCTANCE OF THE WATER USED

	0°C.		18°C.		25°C.	
Sol.	N_2	N_4	N_2	N_4	N_2	N_4
20	....	7138.8	11166.4	.....	12855.9	12855.4
21-1	7137.7	7138.6	11167.5	11168.5	12856.6	12855.7
21-2	7137.8	7137.6	11167.5	11166.5	12856.1	12855.4
22-1	7137.8	....	11166.9	11165.7	12856.8	12855.3
22-2	7137.3	7137.7	11166.6	11165.5	12855.6	12854.7
23	7137.5	7137.5	11167.1	11166.5	12856.8	12855.9
24-1	7138.3	7138.4	11167.2	11166.6	12857.0	12856.7
24-2	7138.2	7137.8	11167.0	11165.1	12856.4	12855.2
Average	7137.77	7138.06	11167.03	11166.34	12856.4_1	12855.5_3
Average	$7137._9$		$11166._7$		$12856._0$	

TABLE XII

SPECIFIC CONDUCTANCE × 10^6 OF STANDARD POTASSIUM CHLORIDE SOLUTIONS (0.01*D*) CONTAINING 0.745263 G. OF POTASSIUM CHLORIDE PER 1000 G. OF SOLUTION, BOTH WEIGHTS CORRECTED FOR BUOYANCY OF THE AIR, AND THE SPECIFIC CONDUCTANCE CORRECTED FOR THE CONDUCTANCE OF THE WATER USED

	0°C.		18°C.		25°C.	
Sol.	Q_1	Q_2	Q_1	Q_2	Q_1	Q_2
31-1	....	....	1220.72	1220.57	1408.80	1408.84
31-2	773.66	....	1220.59	1220.56	1408.84	1408.92
32-1	773.66	....	1220.48	1220.42	1408.84	1408.81
32-2	....	....	1220.45	1220.42	1408.66	1408.75
33-2	773.63	....	1220.60	1220.60	.....	.....
34-1	773.53	773.74	1220.66	1220.63	1408.72	1408.72
34-2	773.57	773.68	1220.48	1220.34	1408.72	1408.78
35-1	773.64	773.63	1220.56	1220.53	1408.67	1408.67
35-2	773.70	773.63	1220.42	1220.38	.....	.....
Average	773.64	773.64	1220.55	1220.49	1408.75	1408.79
Average	773.64		1220.52		1408.77	

The results obtained in this investigation are summarized and compared with those of Parker in Table XIII.

TABLE XIII

SPECIFIC CONDUCTANCE OF STANDARD POTASSIUM CHLORIDE SOLUTIONS IN OHMS^{-1} CM.$^{-1}$

	Grams KCl per 1000 g. of soln. in vac.	Specific conductance 0°C.	18°C.	25°C.
1 *D* new values	71.1352	0.065176	0.097838	0.111342
Parker's values		.065098	.097790	.111322
Difference		.000078	.000048	.00002
Difference, %		.12	.049	.019
0.1 *D* new values	7.41913	.0071379	.0111667	.0128560
Parker's values		.0071295	.0111636	.0128524
Difference		.0000084	.0000031	.0000036
Difference, %		.118	.028	.028
0.01 *D* new values	0.745263	.00077364	.00122052	.00140877
Parker's value		.00077284	.00122023	.00140789
Difference		.00000080	.00000029	.00000088
Difference, %		.104	.024	.062

Our results are higher than those of Parker for each of the three solutions and at each of the three temperatures. The deviations range from 0.019% to 0.12%, the average deviation being 0.062%. It is recommended that the new values be used for the determination of cell constants.

We have made a small beginning on the redetermination of the values of the Kohlrausch solutions, but the work has been unavoidably interrupted by the departure of the junior author from this Laboratory.

In view of the fact that our direct measurements do not include all of the Kohlrausch solutions at each of the three standard temperatures and are insufficient in number to be conclusive, we have decided not to publish them until they can be supplemented by additional data. Estimates can be made by applying a correction for the difference in concentration between our solutions and those used by Kohlrausch, but the difference between the concentrations is so great that the change in equivalent conductance cannot be ignored and any attempt to allow for this change introduces too much uncertainty. Kohlrausch apparently actually used the volumetric procedure in making his 1 *N* potassium chloride solution and diluted this solution volumetrically in making the more dilute standards. Parker has recomputed the equivalent gravimetric definitions of the standards (omitting the 0.02 *N* potassium chloride solution) and his revised definitions have been accepted by the "International Critical Tables."[22] Our direct measurements and estimates, however, indicate that Parker's corrections to Kohlrausch's values are too great in all cases. We regard it as inadvisable to use Parker's corrected values for the Kohlrausch solutions to recompute the conductance data in the literature.

Summary

1. A new method for the determination of the absolute specific conductance of solutions has been developed in which the cell constants are determined by resistance measurements when the cells are filled with mercury, instead of by measuring the linear dimensions of the cells.

2. The specific conductances of three standard potassium chloride solutions have been determined at 0, 18 and 25°. It is recommended that the new values be used for the determination of cell constants.

CAMBRIDGE, MASSACHUSETTS

RECEIVED SEPTEMBER 13, 1932
PUBLISHED MAY 6, 1933

---

[22] "International Critical Tables," Vol. VI, p. 230. Two misprints are present in this table due to displacement of the decimal point. The values for solution No. 1 and No. 3 at 0° *should be* one-tenth of the values given.