93. *The Conductivity of Potassium Chloride Solutions.*

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In the recent literature of conductivity measurements much emphasis has been placed on two possible sources of error, the presence of which, it has been claimed, may vitiate all the earlier results on which our knowledge of conductivities is based. The first of these concerns the method of earthing the bridge network : Jones and Josephs (*J. Amer. Chem. Soc.*, 1928, **50**, 1049) have proposed a new method, and regard all earlier procedures as erroneous. The second is one of cell design : Jones and Bollinger (*ibid.*, 1931, **53**, 411) and also Shedlovsky (*ibid.*, 1932, **54**, 1411) have shown that in cells of the well-known Hartley and Barrett type (J., 1913, **103**, 786), as well as in the pipette cells of Washburn (*J. Amer. Chem. Soc.*, 1916, **38**, 2431), parasitic currents may flow through capacity-resistance by-paths, causing errors in the measured resistance which will vary with the size of that resistance and with the frequency of the alternating current.

On the theoretical side these two potential sources of error are established, but their actual importance in any particular series of measurements is not easy to assess, and there are grounds for thinking that criticisms (Jones *et al.*; Shedlovsky; *locc. cit.*) of the earlier work of Kohlrausch and others are unduly pessimistic. The present work was undertaken partly to throw further light on this point, and partly to explain discrepancies that exist between the careful measurements of Shedlovsky (*loc. cit.*) on dilute potassium chloride solutions, and some earlier measurements of Grindley and Davies (*Trans. Faraday Soc.*, 1929, **25**, 133). These discrepancies are attributed by Shedlovsky, in part at least, to the use by Grindley and Davies of a Hartley and Barrett cell. Actually, Shedlovsky overlooked the fact that his results were based on the absolute measurements of Parker, whilst Grindley and Davies's figures were based on the Kohlrausch standard. This difference in cell constant basis accounts for the greater part of the discrepancy, but there is a small residual effect to be explained. To achieve these objects, measurements have been made in various cells and at various frequencies on dilute potassium chloride solutions at 18° and 25° partly with the Jones and Josephs earth and partly with the bridge not earthed.

EXPERIMENTAL.

The Bridge.—The measuring bridge was similar in type to that used in the earlier work (Grindley and Davies, *loc. cit.*). The resistance box was a calibrated " non-inductive " box by the Cambridge Instrument Co., and in parallel with this was a 0·0005 microfarad variable air condenser. In a few measurements this was insufficient to balance out capacity effects, and a 0·01 microfarad condenser was available for use in parallel with it. The detector was a single telephone ear-piece of 200 ohms resistance, connected to the two ends of the bridge wire. The bridge network was not earthed in any way for the measurements reported, but for a preliminary series of measurements a Jones and Josephs earth was built up, and resistance readings were made both with and without this arrangement. In every case the two readings agreed within the accuracy of measurement, which was better than 0·01% when the cell contained potassium chloride solutions and was about 0·1% when the cell contained conductivity water alone. The measuring bridge, as well as the thermostat and the two balances used in the work, was contained in a small room maintained at a constant temperature, about 1° lower than that of the thermostat, by thermostatically-controlled heating coils. The source of current was a valve oscillator of the type described by Woolcock and Murray-Rust (*Phil. Mag.*, 1928, **5**, 1130). This was housed in an earthed iron box some distance from the bridge, and delivered current of either 1000 or 3150 cycles. A switch was incorporated in the bridge whereby the leads from the oscillator could be interchanged (see Jones and Josephs, *loc. cit.*), but with the equipment used the resistance reading was always found to be independent of the setting of this switch, nor was it dependent upon whether the conduits carrying the leads from oscillator to bridge were or were not earthed. The procedure adopted with each resistance measurement was to set the box at a value close to the resistance of the cell and determine the two null points for the lower frequency, as described in the previous paper. This was then repeated for two more settings of the resistance box, the cell being shaken between each of the six readings. The same procedure was then repeated at the higher frequency. Normally the readings at a given frequency agreed with one another to within 0·01%.

The Cells.—Two cells were used in this work. The one used for all the measurements reported in detail was a Hartley and Barrett borosilicate cell with lightly blacked electrodes about 6 sq. cm. in cross-section and 0·7 cm. apart. The second was a similar cell with greyed electrodes. The cells when in use were supported in a thermostat filled with odourless paraffin (" chloridol "), and connection to the bridge was made through two test-tubes filled with mercury and immersed in the bath. The resistances of the leads to the cell electrodes were measured directly, and allowed for in the calculations. The runs were generally made alternately at 18° and 25°, and the thermostat was freshly set for each run by means of two standard thermometers calibrated at the National Physical Laboratory. Fluctuations in the thermostat temperature during a run never exceeded 0·005° and were normally much less.

The Conductivity Water.—The water was obtained from a still of the type described by Bourdillon (J., 1913, **103**, 791). Its conductivity varied between 0·2 and 0·8 gemmho.

The Potassium Chloride Solutions.—Four separate samples of " AnalaR " potassium chloride were used. The salt was recrystallised three or four times in glass vessels and finally from conductivity water in a platinum dish. The crystals obtained on cooling were drained as free as possible from mother-liquor, dried in a vacuum oven at 100° for 2 or 3 days, and finally heated to dull redness over an open flame. The product was neutral to indicators. The stock solutions were made by weighing about 1 g. of the salt into a small weighing bottle, which was then tipped into a suitable weight of conductivity water in a seasoned flask. The weights were corrected for buoyancy. No stock solution was used more than twice.

Measurements at 25°.—In each run the conductivity of the water was measured, and about four additions of stock solution were then made from a weight burette. The results are in Table I. Col. 1 shows the equivalent concentration, based on a molecular weight for potassium

TABLE I.

Measurements at 25°.

	$10^4/R$, corr.					
$C \times 10^4$.	at 1000.	at 3150.	true.	Λ.	Δ(2).	Δ(1).
1·9825	3·9294	—	3·9298	148·61	+0·02	+0·07
3·0907	6·1091	6·1112	6·1105	148·29	−0·03	+0·02
3·3390	6·5987	6·5998	6·5998	148·22	±0·00	+0·05
4·1381	8·1722	8·1730	8·1730	148·10	+0·07	+0·11
4·9013	9·6645	—	9·6655	147·88	+0·02	+0·05
5·2151	10·278	10·280	10·280	147·81	±0·00	+0·04
6·0093	11·824	11·827	11·827	147·58	−0·07	−0·04
8·1535	16·013	16·017	16·017	147·30	+0·02	+0·04
8·7463	17·161	17·165	17·165	147·16	−0·02	−0·01
9·8869	19·391	19·394	19·394	147·09	+0·07	+0·09
11·832	23·149	23·149	23·152	146·73	−0·02	−0·01
13·148	25·685	25·692	25·692	146·53	−0·05	−0·05
17·820	34·698	34·712	34·710	146·07	+0·02	±0·00
19·660	38·246	—	38·254	145·91	+0·05	+0·02
21·956	42·607	42·619	42·619	145·56	−0·07	−0·11
41·828	80·289	80·338	80·351	144·05	—	—
62·768	—	119·54	119·56	142·86	—	—

chloride of 74·553; Col. 2 shows the measured conductivity of the potassium chloride at a frequency of 1000, obtained by subtracting the conductivity of the solvent, corrected where necessary for interionic attraction effects (Davies, *Trans. Faraday Soc.*, 1929, **25**, 129), from that of the solution. Col. 3 shows the corresponding figure at a frequency of 3150. At the higher concentrations the measured conductivity at 3150 cycles is consistently greater than at 1000 cycles, and the difference is of the order of magnitude to be expected on account of polarisation effects; but at resistance values greater than 300 ohms (for which the cell was primarily designed) the difference never exceeds 0·04%, and the mean difference for 34 separate measurements is 0·014%. This mean difference does not greatly exceed the random errors of the measurements, but it is probably real and is to be attributed partly to traces of polarisation, and partly to any errors that may be inherent in the design of the bridge and cell. Since it is, so far as can be judged, independent of the size of the resistance measured, and present equally in cell-constant determinations and in subsequent measurements in the same cell, it cannot lead to errors as large as 0·01% in the subsequent conductivity measurements, and it seems reasonable to conclude that the data of Kohlrausch and others, who in the past have used " dipping electrodes," are also free from serious errors due to faulty cell design. Shedlovsky (*loc. cit.*) has reported somewhat greater errors when using dipping electrodes, but his electrode leads appear to have been separated by a distance many times less than in the ordinary Hartley–Barrett cell.

The finally accepted figures shown in Col. 4 of Table I were obtained by plotting, for all the solutions studied, the difference between the readings at 1000 and 3150 cycles against the resistance, and using the smooth curve to correct the readings at 1000 cycles for polarisation. The figures in Col. 4 of the table are the mean of the conductivity at 1000 cycles corrected in this way and the conductivity at 3150.

TABLE II.

Measurements at 18°.

$C \times 10^4$.	$10^4/R$, corr.	Λ.	Δ(3).	$C \times 10^4$.	$10^4/R$, corr.	Λ.	Δ(3).
0·90987	1·5647	128·96	+0·05	9·4237	15·982	127·18	−0·08
1·4078	2·4192	128·74	+0·01	10·162	17·217	127·05	−0·12
2·2642	3·8789	128·47	−0·01	10·237	17·358	127·15	−0·01
3·0876	5·2830	128·31	+0·03	13·326	22·534	126·81	±0·00
3·5179	6·0121	128·16	−0·03	15·312	25·860	126·65	+0·04
3·6067	6·1660	128·20	+0·03	15·668	26·441	126·56	−0·01
4·9107	8·3809	127·98	+0·05	16·208	27·354	126·54	+0·01
5·3792	9·1690	127·82	−0·02	20·835	35·042	126·13	+0·02
5·8921	10·035	127·72	−0·04	22·404	37·642	126·00	+0·02
7·5131	12·775	127·51	±0·00	22·583	37·939	125·98	±0·00
8·4875	14·416	127·36	−0·02	49·815	82·653	124·42	—

Results at 18°.—The measurements at 18° were carried out in the same way and the results are in Table II, where Col. 1 shows the equivalent concentration, and Col. 2 the measured conductivity, calculated in the same way as for Col. 4 of Table I.

Measurements with Greyed Electrodes.—A number of runs at 18° and 25° were made in the cell with greyed electrodes. These need not be reported in detail; their main feature was that the readings at the two frequencies differed far more than when the cell with black electrodes was used. This difference was appreciable at all but the highest dilutions; it increased inversely as the square of the resistance and was evidently due to polarisation. It amounted to 0·1% when the resistance of the solution was 300 ohms, and its equivalent concentration was 0·001*N*. The measurements leave no room for doubt that the " greying " of electrodes is less effective in minimising the effects of polarisation than has been assumed in the past.

Discussion of Results.

Jones and Bradshaw (*J. Amer. Chem. Soc.*, 1933, **55**, 1780) recently made new absolute measurements on the conductivity of potassium chloride solutions, and concluded that the figure of Parker and Parker, which Shedlovsky used as his absolute standard, is 0·028% too low. Shedlovsky has accepted the new basis, which will raise all his figures for potassium chloride by 0·04 unit. All the figures hereafter quoted are adjusted in this way, and are therefore based on the Jones and Bradshaw standard.

If the new measurements at 25° are compatible with those of Shedlovsky, it should be possible to combine Shedlovsky's equation for the equivalent conductivity of potassium chloride

$$149{\cdot}86 = (\Lambda + 59{\cdot}79\sqrt{C})/(1 - 0{\cdot}2274\sqrt{C}) - 94{\cdot}9C\,. \quad . \quad . \quad . \quad (1)$$

with the measured conductivities shown in Table I, Col. 4, and obtain a satisfactory cell constant. This test was found to fail, the " cell constant " figures showing a definite trend with concentration in the more dilute solutions. Closer examination showed that the new measurements are quite compatible with Shedlovsky's observed conductivities, but that his equation does not agree satisfactorily with either set of observed figures at the lowest concentrations. This is illustrated in Table III, which reproduces, in Cols. 1 and 2, Shedlovsky's actual results up to 0·0033*N*; Col. 3 shows the difference between the observed conductivity and that calculated from Shedlovsky's equation. For every one of the six most dilute points the difference is positive, and it seems clear from the figures in this column that, although Shedlovsky's equation fits the data fairly closely right up to a concentration of 0·1*N*, it is nevertheless in error by more than the probable experimental error in the more dilute solutions, and leads to a Λ_0 value that is too low. An empirical equation that has been found to agree better with Shedlovsky's results up to 0·003*N* is

Table III.

$C \times 10^4$.	Λ.	$\Delta(1)$.	$\Delta(2)$.
0·32576	149·37	+0·05	−0·01
1·0445	148·95	+0·04	−0·01
2·6570	148·42	+0·06	+0·02
3·3277	148·23	+0·05	±0·00
3·5217	148·16	+0·03	−0·02
4·6948	147·93	+0·06	+0·02
6·0895	147·56	−0·04	−0·07
8·4200	147·27	+0·06	+0·03
9·2856	147·11	+0·02	±0·00
11·321	146·80	−0·01	−0·02
14·080	146·50	+0·03	+0·03
15·959	146·30	+0·04	+0·05
20·291	145·76	−0·05	−0·03
20·568	145·75	−0·05	−0·01
23·379	145·52	+0·01	+0·05
27·848	145·04	−0·13	−0·07
28·777	145·03	−0·06	+0·01
32·827	144·68	−0·11	−0·02
Average deviation :		0·05	0·02

$$\Lambda = 149{\cdot}92 - 93{\cdot}85\sqrt{C} + 50C \qquad \ldots\ldots \qquad (2)$$

The difference between the observed values and those calculated from this equation are shown in Col. 4 of Table III.

When this same equation is applied to the new measurements, a satisfactory cell constant of 0·074986 ± 0·000005 is obtained. The extent of agreement is most clearly shown by using this cell constant value to calculate equivalent conductivities for the measurements of Table I. The values obtained are shown in Col. 5 of this table, and Col. 6 shows $\Delta(2)$, the difference between these values and those calculated from equation (2). The last column gives $\Delta(1)$, the difference between the measured values and those calculated from Shedlovsky's equation (1), and shows again the inadequacy of this equation at the lower concentrations.

Application of the cell constant derived in this way to the results at 18° gives the equivalent conductivities shown in Col. 3 of Table II, and Col. 4 shows the differences between these values and those calculated from the equation :

$$\Lambda = 129{\cdot}67 - 79{\cdot}55\sqrt{C} + 35C \qquad \ldots\ldots \qquad (3)$$

Here 129·67 is the equivalent conductivity at infinite dilution, and 79·55 is the slope predicted by Onsager's equation. The agreement is again satisfactory, the mean difference between observed and calculated values (0·02%) being no greater than the average error in the most accurate conductivity measurements. Kohlrausch and Maltby's classical measurements on potassium chloride at 18° have been represented by the equation $\Lambda = 129{\cdot}85 - 79{\cdot}8\sqrt{C}$ (see Frazer and Hartley, *Proc. Roy. Soc.*, 1925, **A, 109,** 355; Davies, *Trans. Faraday Soc.*, 1929, **25**, 129), but this is not comparable with the new measurements, since Kohlrausch and Maltby employed the value 74·60 for the molecular weight of potassium chloride. Making the necessary corrections, and modifying the authors' solvent correction to allow for interionic forces, Kohlrausch and Maltby's two series of measurements give the values shown in the first three columns of Table IV. The next two columns give the differences between these values and those calculated from equation (3). The average difference is $0{\cdot}06_5$%, and gives the difference between the new standard of Jones and Bradshaw and the

TABLE IV.

$C \times 10^4$.	Λ_1.	Λ_2.	$\Delta(3)_1$.	$\Delta(3)_2$.	$C \times 10^4$.	Λ_1.	Λ_2.	$\Delta(3)_1$.	$\Delta(3)_2$.
1·0377	128·93	128·90	+0·07	+0·04	10·185	127·23	127·21	+0·06	+0·04
2·0543	128·64	128·65	+0·10	+0·11	20·168	126·22	126·20	+0·05	+0·03
5·1186	127·99	127·98	+0·10	+0·09	50·261	124·33	124·29	+0·13	+0·09

older standard of Kohlrausch and Holborn for (approximately) 0·01*N*-potassium chloride on which Kohlrausch and Maltby's measurements depended.

Finally, the measurements of Grindley and Davies may be briefly considered. Before they can be compared with Shedlovsky's measurements, allowance has to be made for the different standards employed. When this is done on the basis of the figures just discussed, there remains a discrepancy which reaches a maximum value of 0·09% at 0·0015*N*, the Grindley and Davies value being the smaller. This is in the direction and of the order of magnitude to be expected on account of polarisation errors, since these authors employed greyed electrodes for their work.

SUMMARY.

1. The sources of error in conductivity measurements due to faulty cell design and inadequate earthing arrangements, recently discussed by Grinnell Jones and others, have been examined experimentally, and are not considered to have caused serious errors in the past.
2. On the other hand, serious polarisation errors are to be anticipated when a cell containing greyed electrodes is used outside a very restricted concentration range.
3. The equation proposed by Shedlovsky for dilute potassium chloride solutions is criticised. A modified equation, leading to a higher Λ_0 value, is proposed.
4. New measurements on potassium chloride at 25° are in agreement with Shedlovsky's figures, and, combined with new figures at 18°, lead to the conclusion that conductivities based on the Kohlrausch standard are 0·07% higher than those based on the new standard of Jones and Bradshaw.

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