[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

ABSOLUTE MEASUREMENTS OF THE SURFACE CONDUCTIVITY NEAR THE BOUNDARY OF OPTICALLY POLISHED GLASS AND SOLUTIONS OF POTASSIUM CHLORIDE

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This communication is the result of measurements initiated at Bristol University with W. F. Darke in 1919[1] and continued by R. T. Dale, C. S. Salmon, W. J. Elford and ourselves, subject only to long delays in supply, measurement, remeasurement and replacements of optically polished slits of adhesed glass; it was necessary to carry out the final measurements with slits of poor quality delivered in a damaged condition.[2]

J. Stock[3] found that quartz powder, dropping through nitrobenzene, ether or toluene, imparted a distinct additional conductivity to the system; this he interpreted in accordance with the suggestions of Smoluchowski.[4] Since our work was begun, several investigators found an enhanced conductivity in the presence of powders and other finely divided materials of unknown surface area. Thus Miss Laing[5] found that soap curd conducted better than the mother liquor entrained among the curd fibers; similarly, Fairbrother[6] with quartz glass and carborundum, Stamm[7] with wood fibers, and in particular Briggs[8] with cellulose. All these rendered the existence of excess conductivity in the neighborhood of surfaces extremely likely, but quantitative evaluation would require measurement of the obstruction offered by the fibers as well as the extent and accessibility of the surfaces. Likewise, the origin of such enhanced conductivity, whether due to free mobile ions corresponding to uncovered or unbalanced charges on the interface or due to mere concentration or positive sorption of salt solution in the neighborhood of the interface, remained uncertain. However, another[9] experimental measurement of absolute surface con-

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[1] J. W. McBain and W. F. Darke, "General Colloid Discussion," *Trans. Faraday Soc.*, **16**, 150 (1921); *Kolloid-Z.*, **28**, 239 (1921).

[2] The last set of glass slits, costing £80, were delivered through the mail, loose in a wooden box without packing.

[3] J. Stock, *Anzeiger Akad. Wiss. Krakau*, Reihe A, 635 (1912); 131 (1913); 95 (1914).

[4] M. Smoluchowski, *Physik. Z.*, **6**, 529 (1905).

[5] M. E. Laing and J. W. McBain, *J. Chem. Soc.*, **117**, 1506 (1920).

[6] F. Fairbrother and H. Mastin, *ibid.*, **125**, 2319 (1924); F. Fairbrother, *ibid.*, **125**, 2495 (1924).

[7] A. J. Stamm, "Colloid Symposium Monograph," **4**, 253 (1926).

[8] D. R. Briggs, *J. Phys. Chem.*, **32**, 641 (1928).

[9] J. W. McBain and C. R. Peaker, *Proc. Roy. Soc. London*, **125A**, 394 (1929). A further communication (*J. Phys. Chem.*) will deal with results which we have obtained in a much simplified, easily made apparatus, permitting rapid comparisons of surface conductivity and quantitative determinations of its absolute amount.

ductivity leaves little room for doubt that the conductivity is due to the mobile ions corresponding to those attached to the interface. These experiments measured the conductivity in the neighborhood of the monomolecular film of fatty acid on water and showed that such a film is composed to the extent of about one-ninth of fatty ions, the remaining molecules being undissociated. Hence the conductivity is due to the free mobile hydrogen ions corresponding to the fatty ions in the thin film. Once any absolute measurements have been made, it is easy to standardize other experiments involving the same materials.

The experiments of Darke and the subsequent ones of Dale and Salmon were carried out with fine capillaries of fused silica. To magnify the conductivity, these were mounted in a large group in parallel, passing through a partition of shellac melted on and around them so that only their ends projected. Enhanced conductivity was observed, but such measurements could not be regarded as definitive, owing to the possibility of a leak or defective insulation between the tubes and the shellac. This was obviated by making two partitions of shellac with an accessible air gap between, the whole being enclosed in glass tubing. This arrangement yielded low values or excess conductivity and was discarded because of the impossibility of ensuring that the interior of the quartz surfaces had not become contaminated by the necessary manipulations. These results will be referred to in the discussion.

The next extensive series was made by Elford, using a pile of fifteen parallel quartz plates with optically polished surfaces. They were held in a rectangular cell made of optically polished glass, adhesed to form a unit. This was made by A. Hilger, Ltd. (London), and the dimensions (supplied at a much later date in place of those first communicated) were determined by them in a specially developed interferometer with a probable error of only 4000 Å. The results were definitely positive, but the method was ultimately abandoned on account of the difficulty of accurately evaluating dead spaces between the plates and cell, especially with the slight ledges necessary to hold the quartz plates in "position." The quartz plates were piled horizontally to minimize the chance that an optically polished edge might touch a true surface and introduce comparatively large resistance. The results are given later.

The next design made use of during the past six years (whenever available) consisted of a single rectangular slit with optically polished surfaces in a flat piece of glass one inch square. The first three slits, made by Mr. C. Ord of Adam Hilger, Ltd., were very satisfactory, and the dimensions of the slit were known to about one-eighth of the wave length of light. Unfortunately cracks gradually extended from one or more of the adhesed surfaces of the slits during the series of measurements made with them. An anonymous description of the mode of manufacture which appeared in *Nature*[10] may be quoted as follows: "The thickness of a piece of plain parallel quartz some $1^1/_4''$ × $1^1/_4''$ × $^1/_8''$ was being measured on a Michelson interferometer. The half coating of silver had been removed from one of the mirrors of the instrument, and the specimen was then 'contacted on' to this mirror so as to cover one-half of it. The whole was then half silvered, and the distance between the two surfaces was measured in air. What appeared to be a slight scratch in the center of the specimen was in reality a slit in the glass, of width only 16 wave lengths of light (λ 5461). This slit was made in the manner illustrated in the accompanying diagram (Fig. 1). It will be seen that the quartz plate was in reality built up of four pieces, all accurately finished with extreme accuracy. Starting with 1, 2 and 3 were contacted on and heated sufficiently to make these three join up into one piece, but, of course, not too much, or the optical perfection of the surfaces would be spoiled. The protruding edges of 2 and 3 where they meet 4 were then ground and polished so that they extended beyond 1 a distance equal only to 16 wave lengths. This distance was measured with the Michelson interferometer, and then 4 was contacted on and the heating process repeated."

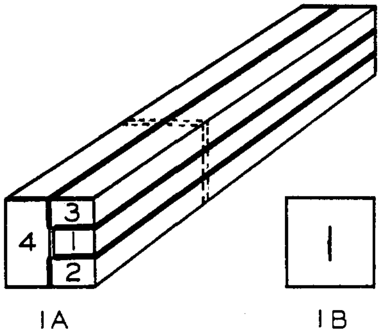


Fig. 1.—1A. Method of preparing slits by "adhesion" of optically polished glass surfaces. The dark lines show the surfaces which have been heated until they "adhered" or united. 1B. Cross section of glass showing slit.

These slits were actually made from four pieces of glass about 10 cm. long so that a number of cross sections could be cut, yielding slits of identical dimensions. At a later date no more of this batch could be supplied, and, although one of us went through the measurements of the glass pieces for the final batch at the factory, the slits actually supplied were of different dimensions which could, of course, no longer be determined interferometrically. The widths of the slits were therefore determined by means of a microscope fitted with a calibrated eyepiece scale, or with a calibrated micrometer eyepiece. Various objectives and eyepieces were used (both Leitz and Zeiss). Measurements were made at intervals of 0.5 to 1.0 mm. along the slit. The lengths of the slits were determined with a traveling microscope, reading to 0.001 mm., the scale of which had been calibrated. The thicknesses of the slits were determined (1) by examination at intervals along the edges of the block with a microscope fitted with a calibrated eyepiece scale, or with a calibrated micrometer eyepiece; (2) by examination at intervals around the edges of the block with a

[10] *Nature*, **112**, 223 (1923).

traveling microscope; (3) by means of a micrometer caliper, reading to 0.0001 in.

The dimensions obtained by these methods agreed fairly well with those given by Hilger for slits Nos. 1 and 2, but not for the later slits Nos. 4, 5, 6, 7 and 10, the results for the widths of the narrow slits (Nos. 4, 6, 10) being about 10% lower than those of Hilger and about 2% lower for the wider slits (Nos. 5, 7). These were just about the differences Hilger stated might exist due to sagging of the glass, hence the microscopic measurements have been taken as being correct for these slits, while Hilger's measurements have been used for slits Nos. 1 and 2. According to a statement by Hilger, the narrower slits (4, 6, 10) were all cut from the same block, and the wider slits (Nos. 5, 7) from another. It was decided, therefore, that the best procedure would be to average all the values obtained for the widths of the narrower slits (and similarly for the wider slits) and use this average value as the width of all the narrower slits (and similarly for the wider slits) instead of the average values obtained from the measurements of each slit alone. Table I records the dimensions of the slits which have been used in this investigation.

Table I

Dimensions of Slits

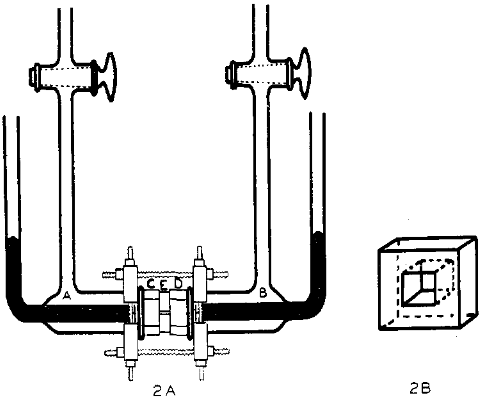
Slit No.	Width, mm.	Length, mm.	Thickness, mm.	Observer
S	0.00939	10.000	0.983	Hilger
1	.0344	10.03	...	Hilger
	.0337	10.10	0.999	King
2	.00634	10.06	...	Hilger
	.00667	10.11	1.001	King
4	.0125	10.01	1.066	Peaker
6	.0125	10.01	1.058	Peaker
10	.0125	10.01	5.014	Peaker
	(.014)	(10.00)	...	Hilger
5	.0567	10.02	1.033	Peaker
7	.0567	10.02	2.101	Peaker
	(.058)	(10.00)	...	Hilger

The accuracy of the final values obtained in this investigation depends greatly on the accuracy with which the dimensions of the slits are known. The possibility of error is greatest in the widths of the slits, since this is the smallest dimension; we estimate that it is probably known to within 2% for the narrower slits used and within 0.5% for the wider slits. The error in the lengths of the slits is probably not over 0.1% and in the thicknesses not over 0.3%.

Procedure for Cleaning Cells and Slits.—The electrode arms of the "main cell" were thoroughly cleaned with nitric acid (1:1), conductivity water, distilled alcohol and distilled ether. Mercury for the electrode arms was cleaned by allowing it to stand in contact with nitric acid (1:1) for a short time, washing with distilled water and filtering through pin-holes in filter paper until clean and dry.

The main cell was cleaned thoroughly with cold dichromate–sulfuric acid mixture and thoroughly rinsed with conductivity water, distilled alcohol and distilled ether. Then it was rinsed out with distilled alcohol and conductivity water. The optically polished "central cell," previously used by Elford to hold quartz plates, was subjected to similar treatment before use.

The glass blocks containing the slits were cleaned externally with dichromate mixture, rinsed with conductivity water, and rubbed lightly with a clean cloth dipped in distilled alcohol. (Treatment with dichromate mixture was omitted in the case of slits Nos. 1 and 2.) After assembling the cell, the slits were cleaned as follows. The cell was filled with fresh dichromate mixture and this drawn back and forth through the slit by applying suction. Then the cell was rinsed out thoroughly in turn with conductivity water, distilled alcohol, distilled ether, distilled alcohol and conductivity water, suction being used to draw the liquids through the slit. (Treatment with dichromate mixture was omitted in the case of slits Nos. 1 and 2.)



2A 2B

Fig. 2.—2A. The conductivity cells. 2B. Central cell: one is placed on each side of the slit.

The Conductivity Cells.—The type of cell used for measuring the conductivity of potassium chloride solutions in glass capillaries is shown in Fig. 2. It consists of three parts: (1) the two half cells (A, B) containing the electrodes designated as "main cell"; (2) two glass blocks (C, D) about 1 inch square with an opening through them about 1.3 cm. square designated as "central cell"; (3) a glass block (E) containing the optically worked capillary slit. (In some of the measurements made by one of us, the central cell was not used.) These various parts are then clamped into the positions shown in the diagram. The clamp was made of square ebonite frames, pulled toward each other by four brass screws at the outside corners, the ebonite being separated from the glass by thick rubber tubing.

In the earlier work a water thermostat was used; the later results were obtained with a thermostat filled with Transil Oil, as used by Grinnell Jones and R. C. Josephs.[11]

The conductivity measurements were made by the method of Kohlrausch, using the improved apparatus designed by Washburn[12] and supplied by Leeds and Northrup. (Some modifications were made in the apparatus used by one of us (C. R. P.) to conform with the recent work of Jones and Josephs.[11] Instead of the fixed ratio slide wire described by them, a Kohlrausch drum-type slide wire (Leeds and Northrup) was used; the grounding resistance was another slide wire of the same type. Since most of the readings were taken at the center of the wire, this arrangement is equivalent to that of Jones and Josephs.) The slide wire was carefully calibrated by the method of Strouhal and Barus,[13] and the necessary corrections were applied. The resistance box was of the five decade type, supplied by Leeds and Northrup; coils of 1000 ohms resistance and

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[11] G. Jones and R. C. Josephs, This Journal, **50,** 1049 (1928).

[12] E. W. Washburn and J. E. Bell, *ibid.*, **35,** 177 (1913).

[13] A. Findlay, "Practical Physical Chemistry," Longmans, Green and Co., London, 4th edition (1923), p. 154.

above were of the Curtis design. Variable air condensers were shunted across the resistance box. The balance point of the bridge was determined by the use of a set of tuned telephones (one of us (C. R. P.) used a one-stage vacuum tube amplifier in conjunction with the telephones). Alternating current was supplied to the bridge from a Vreeland oscillator at a frequency of 1000 cycles per second (or, by one of us (A. M. K.), from a high frequency generator, or vacuum tube generator).

Preparation of Potassium Chloride Solution.—Various types of stills were used for the preparation of conductivity water,[14] but the conductivity of the water obtained was rarely better than 0.7×10^{-6} mhos at 25° and averaged about 1.0×10^{-6} mhos at 25°. The water was collected and stored in flasks of Jena glass, which had been thoroughly cleaned with dichromate mixture and which were steamed out each time before use. Correction for the conductivity of the solvent has been made in the tables of data which follow.

The potassium chloride used was Kahlbaum's "for analysis, with guarantee." It was heated in a clean quartz or porcelain dish over a hot Bunsen flame until all crackling ceased and was allowed to cool in a desiccator over phosphorus pentoxide. It was kept in the desiccator at all times except for brief periods when solutions were being made up.

The solutions of potassium chloride were made up by the weight method, the details of which are described by Kraus and Parker.[15] The amount of potassium chloride required was weighed out onto a clean, dry watch glass and transferred to a clean flask (just previously steamed out and rinsed with conductivity water) through a clean funnel (just previously rinsed with conductivity water). The residue on the watch glass and funnel was then rinsed into the flask with conductivity water and the necessary amount of conductivity water added to the flask. The amount of solution was determined by substitution weighing, and from the data the exact concentration of the solution could be obtained. The solution was then well shaken and allowed to stand for several hours before use. In practically every case freshly made solutions were used.

Procedure in Making Determinations of the Specific Conductivity of Potassium Chloride Solutions in Slits.—After assembling and cleaning the conductivity cell as previously described, it was rinsed out three or four times with the most dilute solution to be used (0.001 *N* potassium chloride), suction being used to draw the solution through the capillary. The cell was then filled with this solution and placed in the thermostat. Usually about half an hour was allowed to elapse before beginning measurements. The resistance of the cell was measured at intervals until a series of constant resistances over a period of, say, one hour, were obtained. The solution was then drawn back and forth through the slit by suction several times and measurements continued until the resistance was again constant. This was repeated several times and the mean of all the constant values for the resistance of the cell taken.

The solution was then emptied out and the cell rinsed two or three times with fresh samples of solution; it was filled again and placed in the thermostat ready for a second series of measurements. Three such independent fillings, giving agreeing results, were considered sufficient; in later work two fillings giving agreeing results were accepted.

After finishing a series of experiments with one concentration, the cell was rinsed with the next most concentrated solution, suction being used as previously; then it was filled and the above procedure repeated. During the transition from 0.001 *N* to 1 *N* solution the cell was not taken apart.

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[14] C. A. Kraus and W. B. Dexter, THIS JOURNAL, **44**, 2468 (1922); G. D. Bengough, J. M. Stuart and A. R. Lee, *J. Chem. Soc.*, 2156 (1927).

[15] C. A. Kraus and H. C. Parker, THIS JOURNAL, **44**, 2422 (1922).

The following tables record the results which have been obtained in this investigation.[16] The first column gives the actual concentration of the solution used. The second column gives the resistances in ohms for each individual experiment. The values in the third column are the means of the values in Col. 2 for each concentration, corrected for the conductivity of the solvent and also corrected to round concentration (in making this slight correction, specific conductivity is assumed to be a linear function of concentration).

Table II

Resistances of Potassium Chloride Solutions in Main Cell and Central Cell and Slit S at 25.00 ± 0.02°

Concn., normality at 18° C.	0.01		0.1
Observed resistance, ohms	115,000	115,300	13,440
Corr. mean resist., ohms	115,150		13,440

Table III

Resistances of Potassium Chloride Solutions in Main Cell and Central Cell and Slit No. 1 at 25.00 ± 0.02°

Concn. (normality at 18°)	Observed resistance, ohms				Corr. mean resistance, ohms
0.000998	201,211	201,096	200,818		200,640
.001995	106,482	107,286	106,993	106,571	106,560
.010003	(23,743)	23,642.5	23,643	23,632.4	23,646
.10002	(2,613.5)	2,603.1	2,600.4	2,602.2	2,602.4
.9998	(301.13)	300.49	300.59	300.11	300.33

Table IV

Resistances of Potassium Chloride Solutions in Main Cell and Central Cell and Wide Slit No. 1 and Narrow Slit No. 2 at 25.00 ± 0.02°

Concn. (normality at 18°)	Observed resistance, ohms					Corr. mean resistance, ohms
0.000998	(898,711)	873,714	874,357	892,300		878,360
.001984	(553,996)	(539,721)	490,680	493,613		488,210
.010006	122,067	(118,860)	121,914	(124,574)	(127,692)	
	122,201	(120,300)	(127,148)	122,195	(121,369)	122,160
.1001	(14,791)	(14,616)	14,049	13,922		13,910
.9954	(1,673.2)	1,671.5	1,666.2			1,661.2

Table V

Resistances of Potassium Chloride Solutions in Main Cell and Narrow Slit No. 4 at 24.91–24.92°

Concn. (normality at 18°)	Observed resistance, ohms				Corr. mean resistance, ohms
0.001004	(552,310)	582,130	600,280	595,900	599,270
.001996	311,010	315,970			317,920
.001998	322,640				
.009995	75,408	74,950	74,662	74,612	74,863
.1000	7,435.0	7,443.2	7,448.5		7,442.9
.9975	854.97	859.77	858.35	856.62	855.26

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[16] The data for slits No. S, No. 1, and No. 1 and No. 2 together were obtained by Miss King; the remainder were obtained by Mr. Peaker.

Table VI

Resistances of Potassium Chloride Solutions in Main Cell and Wide Slit No. 7 and Narrow Slit No. 4 at 24.91–24.92°

Concn. (normality at 18°)	Observed resistance, ohms					Corr. mean resistance, ohms
0.000992	509,750	873,720	816,600	803,340	839,840	820,640
.000997	751,050					754,900
.002002	417,600	420,700	424,290			423,220
.010026	92,965	92,402	91,174			92,534
.09999	10,050	10,041	10,031			10,041
.9975	1,160.1	1,159.3	1,157.0			1,155.9

Table VII

Resistances of Potassium Chloride Solutions in Main Cell and Wide Slit No. 7 at 24.91–24.92°

Concn. (normality at 18°)	Observed resistance, ohms					Corr. mean resistance, ohms
0.000997	242,670	242,000	(225,630)	245,660	247,220	245,360
.002001	127,900	127,580	127,900			128,230
.009998	27,363	27,694	27,579			27,557
.1000	3,060.1	3,040.0				3,050.2
.9965	354.69	354.90	354.33			353.40

Table VIII

Resistances of Potassium Chloride Solutions in Main Cell and Central Cell and Narrow Slit No. 4 at 25.01–25.02°

Concn. (normality at 18°)	Observed resistance, ohms		Corr. mean resistance, ohms
0.001006	584,940		591,430
.010012	64,560	66,351	65,570
.9821	851.36	857.50	839.15

Table IX

Resistances of Potassium Chloride Solutions in Main Cell and Central Cell and Narrow Slit No. 10 at 25.01–25.02°

Concn. (normality at 18°)	Observed resistance, ohms			Corr. mean resistance, ohms
0.01000	300,000	313,910	310,680	312,500
1.0020	4,244.0	4,237.2		4,249.1

Table X

Resistances of Potassium Chloride Solutions in Main Cell and Central Cell and Wide Slit No. 5 at 25.01°

Concn. (normality at 18°)	Observed resistance, ohms			Corr. mean resistance, ohms
0.001001	140,850	142,370		141,830
.010004	15,998			16,015
.1006	1,760.8	1,760.8		1,771.4
.9651	(220.77)	211.53	211.50	204.45
.9902	207.12			

TABLE XI

RESISTANCES OF POTASSIUM CHLORIDE SOLUTIONS IN MAIN CELL AND CENTRAL CELL AND NARROW SLIT No. 6 AT 25.00–25.01°

Concn. (normality at 18°)	Observed resistance, ohms			Corr. mean resistance, ohms
0.000992	532,110			529,710
.010004	65,372	65,450		66,214
.010014	66,683	66,979		
.1006	7,464.2	7,461.0	7,435.2	7,498.3
.9821	978.00	976.40		957.40
.9990	956.82	955.28		

Time Effect.—In the case of the dilute solutions, drawing the solution in the cell back and forth through the slit after equilibrium had been established (as shown by constant resistances over a period of time) generally caused the resistance to rise somewhat, and then it fell off with time until a value comparable with the previous value had been reached, after which the resistance remained fairly constant. This is what one would expect if the excess conductivity is ascribed to the mobile ions existing free in the solution. For the more concentrated solutions (0.1–1.0 *N*), drawing the solution through the slit caused slight, irregular variations. In the preliminary work of Dale, Darke and Salmon it was found that a new capillary on its first filling showed diminished conductivity (due to sorption) which was replaced by enhanced conductivity (ordinary bulk conductivity plus conductivity of mobile ions) upon drawing further solution through the capillary.

Precision of the Recorded Data.—For 0.01 to 1.0 *N* solutions the values averaged to give the recorded value for each experiment in the preceding tables do not differ by more than 0.1–0.2% from this value. The mean obtained for each concentration (Col. 3 of tables) is probably correct to 0.1–0.2%. For dilute solutions (0.001–0.002 *N*) the values averaged to give the recorded value for each experiment are within 0.5% of the mean. The mean values for each concentration are probably correct to about 1%.

Specific Conductivities of Potassium Chloride Solutions in Bulk.—Table XII gives the values of the specific conductivities of the potassium chloride solutions used in this investigation, as obtained from the literature.

TABLE XII

SPECIFIC CONDUCTIVITIES OF POTASSIUM CHLORIDE SOLUTIONS IN BULK

Concn. (normality at 18°)	0.001	0.002	0.01	0.1	1.0
Sp. cond. at 25°, mhos	0.0001466	0.0002907	0.0014104	0.012877	0.11169
Investigator	Kohlrausch	Kohlrausch	Parker and Parker	Parker and Parker	Parker and Parker

In Table XIII are given the calculated resistances of the various potassium chloride solutions in the slits which were used in this work. These values were obtained from the dimensions given in Table I and the specific conductivities in Table XII.

TABLE XIII

CALCULATED RESISTANCES OF POTASSIUM CHLORIDE SOLUTIONS IN SLITS (ASSUMING NO SURFACE CONDUCTIVITY)

No. of slit	0.001 *N*	0.002 *N*	0.01 *N*	0.1 *N*	1.0 *N*
S			74,223	8,129.4	
1	197,500	99,595	20,528	2,248.4	259.23
2	1,070,600	539,880	111,280	12,188	1,405.2
4	581,150	293,070	60,406	6,616.0	726.80
6	576,790	290,870	59,953	6,566.4	757.08
10			284,120	31,119	3,587.8
5	124,030	62,546	12,892	1,412.3	162.79
7	252,260	127,210	26,220	2,871.9	331.11

In order to decide whether there is any change in the specific conductivity of potassium chloride solutions in capillaries compared with that measured in bulk, it is necessary to determine from the observed resistances of main cell, central cell and slit the resistance of the slit alone. Comparison of the resistances so obtained with those given in Table XIII will then show whether or not there is any change in the conductivity when measured in capillaries.

In the early stages of this investigation it was thought that by subtracting the resistance of the main cell and central cell, measured separately, from the resistance of main cell, central cell and slit, the result would be the true resistance of the solution in the slit; but when this was done, a decrease in the specific conductivity was obtained for the more concentrated solutions, and only for the dilute solutions was an increase observed. This decrease in conductivity observed in the concentrated solutions was evidently to be ascribed to a "pinch" effect,[17] operating in all concentrations and due to bending of the lines of current flow through the slit, and equivalent to a series resistance. In other words, the whole cross section of the main cell and central cell is not available for carrying current in the immediate neighborhood of the slit. A similar "pinch" effect operated in the experiments of Elford, referred to previously.

In order to eliminate the "pinch" effect, it was decided to use two slits together; in this way the resistance of one slit (say No. 1), obtained by

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[17] We satisfied ourselves with *ad hoc* measurements that the "pinch" effect not only exists but that its magnitude has been correctly deduced. For this purpose we used, for example, a fine platinum wire of the same diameter in place of the slit and found that the total resistance between the electrodes was about equal to the resistance between the central platinum wire and either of them. The resistance between the central wire and one of the electrodes was again doubled by putting a glass plate behind the platinum wire. In other experiments the half cell was closed with a paraffin block, into the surface of which a platinum wire had been crushed and then platinized, and a similar large "pinch" effect was found.

subtraction of the observed resistance of slit No. 2, main cell and central cell from that for both slits, main cell and central cell would be independent "pinch" effect. Since the slits used for this purpose were not of the same width (one being roughly five times the width of the other), the assumption is made in such a calculation that the "pinch" effect is the same for a slit, say, 0.05 mm. wide as for one only 0.01 mm. wide. In the early part of this investigation the truth of this assumption could not be checked because we had difficulty with cracking of the glass blocks containing the slits; later data, obtained on slits which were not cracked, showed that the assumption was not valid. If we consider the data for slits No. 5 and No. 6, this will be quite apparent.

For 1.0 N solution the resistance of main cell, central cell and slit No. 5 is 204.45 ohms (Table X). If we assume that for this concentration surface conductivity is negligible compared to bulk conductivity and consider that the resistance of the slit itself is 162.79 ohms, as calculated in Table XIII, then the "total effective resistance" of the main cell and central cell is 41.66 ohms. This is the sum of the "pinch" resistance and the true resistance of the main cell and central cell, measured separately. Since the measured resistance of the latter is 14.14 ohms, the former is 27.52 ohms.

Similarly, considering the data for main cell, central cell and narrow slit No. 6 for 1.0 N solution, we find the measured resistance of this combination to be 957.40 ohms (Table XI), while the resistance of the slit itself is 757.08 ohms (Table XIII). The "total effective resistance" of the main cell and central cell is then 200.32 ohms, and the "pinch" resistance is 186.18 ohms.

The ratio of the "total effective resistance" of the main cell and central cell in the two cases is 200.32/41.66 or 4.81; the ratio of the widths of the slits, which is the only dimension which need be considered, is 0.00567/0.00125 or 4.53. Thus, as a first approximation we may say that the "total effective resistance" of the main cell and central cell is inversely proportional to the width of the slit; the "pinch" resistance, on the other hand, appears to be an exponential function of the width.

Considerable difficulty was encountered in evaluating some of the results, owing to the fact that cracks developed, radiating from the slit, during the course of the experiments. Since the cell was not dismantled during the transition from 0.001 N to 1.0 N solution, it is difficult to say where the cracks first developed and to what extent. However, it seems very probable that the conductivity of such cracks is negligible compared to the conductivity of the solution in the slit itself. Under a microscope, using very high magnification, the crack appears only as a line, whose width cannot be estimated, while the slit covers about $^1/_6$ of the field (in the case of the narrow slit No. 4, for example).

It seems best, therefore, to include any effect of the crack in the term which is called the "total effective resistance" of the main cell and central cell, rather than attempt to make a special correction term for this effect. The following pages give typical methods of calculating the results.

1. Method of Calculating the Results for Slits Nos. 1, 5, 6 and 10 (Tables III, IX, X and XI).—For narrow slit No. 6 (Table XI) the resistance of main cell + central cell + slit No. 6 for 1 N solution, 957.40 ohms, less the calculated resistance of the slit for 1 N solution, 757.08 ohms, leaves the "total effective resistance" of main cell + central cell for 1 N solution equal to 200.32 ohms. Now the "total effective resistance" must be proportional only to the specific resistance of the solution for a given cell and slit. Hence the "total effective resistance" of the main cell + central cell for 0.001 N solution is $(200.32 \times 0.11169)/0.0001466 =$ 152,620 ohms. But the resistance of the main cell + central cell + slit No. 6 for 0.001 N potassium chloride was 529,710 ohms, leaving for the resistance of the slit alone 377,090 ohms. The resistance of the slit as calculated from its dimensions and specific conductivity (Table XIII) is 576,790 ohms. The percentage increase in specific conductivity for 0.001 N potassium chloride within the slit is then

$$\left(\frac{1/377{,}090 - 1/576{,}790}{1/576{,}790}\right) \times 100 = \left(\frac{576{,}790 - 377{,}090}{377{,}090}\right) \times 100 = 52.96\%$$

The specific conductivity of a 0.001 N solution in bulk is 0.0001466 mho at 25.00°. Hence the conductivity due to the surface would be 52.96% of 0.0001466 mho or 0.00007764 mho, if 1 cc. of 0.001 N potassium chloride solution were to be confined in a cell, the area of whose walls bore the same ratio to the volume as the area of the actual slit did to the volume of the slit.

It is essential to calculate the surface conductivity in absolute units. Volume conductivity is always expressed by specific conductivity, that is, the conductivity in reciprocal ohms of a cube of solution placed between parallel electrodes 1 cm. square and 1 cm. apart. Similarly, we must invent a specific surface conductivity in two dimensions instead of three (as regards the actual surface area), defining it as the conductivity in reciprocal ohms between two parallel electrodes 1 cm. long, placed 1 cm. apart on the surface. The surfaces in our slits conform to this requirement in that they are parallel to the lines of current flow. As long as the volume and area are varied in the same proportion, the ratio between volume and surface conductivity will remain constant. Hence from the determination given above, since the area of slit No. 6 was 1601.6 times its volume in cc., the specific conductivity of one square centimeter is $0.00007764/1601.6 = 4.85 \times 10^{-8}$ mhos.

The value for the "total effective resistance" just calculated for the uncracked slit No. 6 had to be used for the results of Tables V, VII and

VIII. Slit No. 4 (Table VIII) evidently cracked before the measurement of 1.0 N potassium chloride, although the results for 0.001 N and 0.01 N agree with Table XI. For Table V the "total effective resistance" for 1.0 N potassium chloride is 242.58 ohms, obtained by multiplying the 200.32 ohms by that for the main cell (92.46) in Table V divided by that for the main cell + central cell (76.35) in Table VIII. Again for Table VII, the "total effective resistance" of the main cell for 1.0 N potassium chloride is $(242.58 \times 22.29)/200.32 = 26.38$ ohms; but slit No. 7 had become so badly cracked that the conductivity even of 1.0 N potassium chloride was slightly increased. Hence the volume conductivity of the crack had to be taken into account, and the surface conductivity of dilute solutions was apportioned between crack and slit in the ratio of their lengths.

For Table VI using wide and narrow slits, No. 7 and No. 4 together, the total effective resistance was taken as the mean of the two separately. Then the resistances within each slit were obtained by subtracting the values for the separate slits from the value of the two slits together. Therefore, the surface conductivities are both low on account of the neglected "pinch" resistance between the slits, the wide slit being most affected.

In Table II the original slit No. S was broken after measuring 0.1 N potassium chloride. Assuming the surface conductivity to be of negligible influence in 0.1 N in place of 1.0 N potassium chloride, the calculation gives 7.51×10^{-8} mhos per sq. cm. for the surface conductivity in 0.01 N potassium chloride. Based upon 1.0 N potassium chloride, this would have been a few per cent. higher, but it is in good agreement with the later work.

The earlier work of Dale with fused silica tubes and of Elford with plates of quartz is calculated in the same way. Dale's results (1921) are given for the last three cells he used. With 0.01 N the increased conductivity observed was 1.2 and 1.4%, corresponding to 16.1 and 17.2×10^{-8} mhos per sq. cm., respectively. That for 0.002 N was 2.7% or 3.6×10^{-8} mhos. The results with quartz plates for higher concentrations are omitted on account of the magnified experimental error. For 0.001 and 0.002 N potassium chloride the increased conductivity was 11.4 and 8.2%, and the specific surface conductivity was 3.9 and 5.6×10^{-8} mhos, respectively.

The data for slit No. 2 alone are omitted because of a wide crack which caused the 1.0 and 0.001 N potassium chloride solutions to exhibit an apparent increase of 42 and 93%, respectively. The difference, 51%, corresponds to a specific surface conductivity of 2.4×10^{-8} mhos.

Tables XIV and XV present the evaluation of the results by the methods just described, showing the percentage increase ascribable to surface conductivity and the magnitude of the surface conductivity in absolute units.

TABLE XIV

PERCENTAGE INCREASE IN SPECIFIC CONDUCTIVITY OF POTASSIUM CHLORIDE SOLUTIONS IN NARROW GLASS SLITS AND THE SPECIFIC SURFACE CONDUCTIVITY DEDUCED

Concn. (normality at 18°)	Total resist.	"Effective resistance"	Resist. of slit.		Increase, %	Sp. surface cond., mhos/cm.^{2} $\times 10^9$
			Obs.	Calcd.		
Narrow slit No. 6 (from Table XI)						
1.0	957.40	200.32	757.08	757.08	...	...
0.01	66,214	15,863	50,351	59,953	19.07	16.8
.001	529,710	152,620	377,090	576,790	52.96	4.85
Wide slit No. 5 (from Table X)						
1.0	204.45	41.66	162.79	162.79	...	...
0.1	1,771.4	361.3	1,410.1	1,412.3	0.16	5.66
.01	16,015	3,299	12,716	12,892	1.38	5.50
.001	141,830	31,740	110,090	124,030	12.66	5.23
Narrow slit No. 10 (from Table IX)						
1.0	4,249.1	661.3	3,587.8	3,587.8	...	...
0.01	312,500	52,370	260,130	284,120	9.22	5.13
Narrow slit No. 4 (from Table VIII)						
1.0	839.15	200.32	......	......	...	...
0.01	65,570	15,863	49,707	60,406	21.52	18.97
.001	591,430	152,620	438,810	581,150	41.56	3.81
Narrow slit No. 4 (from Table V)						
1.0	855.26	242.58	......	......	...	...
0.01	74,368	19,254	55,614	60,406	8.62	7.60
.002	317,920	94,713	223,207	293,070	31.29	5.68
.001	599,270	185,240	414,030	581,150	40.36	3.63
Wide slit No. 7 (from Table VII)						
1.0	353.40	26.38	......	......	...	...
0.1	3,050.2	228.8	2,821.4	2,871.9	0.34	13.43
.01	27,557	2,089	25,468	26,220	2.95	11.73
.002	128,230	10,135	118,095	127,210	7.72	6.33
.001	245,360	20,098	225,262	252,260	11.99	4.95
Narrow slit No. 4 (from Tables VI and VII)						
1.0	1,155.9	134.48	......	......	...	...
0.01	92,534	10,649	56,417	60,406	7.07	6.23
.002	423,220	51,670	253,450	293,070	15.63	2.84
.001	754,900	102,460	427,180	581,150	36.04	3.30
Wide slit No. 1 (from Table III)						
1.0	300.33	41.10	259.23	259.23	...	...
0.1	2,602.4	356.5	2,245.9	2,248.4	0.11	3.08
.01	23,646	3,255	19,391	20,528	5.86	1.80
.002	106,560	15,790	90,770	99,595	9.72	6.14
.001	200,640	31,310	169,330	197,500	16.64	5.30

TABLE XV

PERCENTAGE INCREASE IN SPECIFIC CONDUCTIVITY OF POTASSIUM CHLORIDE SOLUTIONS IN NARROW GLASS SLITS AND THE SPECIFIC SURFACE CONDUCTIVITY DEDUCED

Concn. (normality at 18°)	Total resist.	"Effective resist."	Resistance of				Increase, %	Sp. surface cond., mhos/cm.^{2} × 10^8
			Both slits (measured)	Slit No. 4 (Table XIV)	Slit No. 7 (by diff.)	Slit No. 7 (calcd.)		
Wide slit No. 7 (from No. 4 and No. 7 together, Table VI and slit No. 4, Table V)								
0.001	754,900	102,460	652,440	414,030	238,410	252,260	5.81	2.4[a]
				Slit No. 1	Slit No. 2	Slit No. 2		
Narrow slit No. 2 (from No. 1 and No. 2 together, Table IV, and slit No. 1, Table III)								
1.0	1,661.2	3.2	1,664.4	259.2	1,405.2	1,405.2	...	..
0.1	13,910	28	13,882	2,245.9	11,636	12,188	4.74	2.0
.01	122,160	253	121,190	19,391	102,520	111,280	8.55	4.0
.002	488,210	1,229	486,980	90,770	396,210	539,880	36.26	3.3
.001	878,360	2,438	875,920	169,330	706,590	1,070,600	51.52	2.4

[a] Plus conductivity offset by not allowing for "pinch" between slits.

Results and Discussion

In Table XVI are collected the values obtained for the specific surface conductivities, including those of Dale (1921) with capillary tubes of fused silica and of Elford (1922) with optically polished plates of quartz. Since the surface conductivity remains of the same order of magnitude with different concentrations of the solution, whereas the specific conductivity (volume) increases nearly a thousand-fold between 0.001 and 1.0 *N*, it follows that accurate determinations of surface conductivity may only be made with dilute solutions, the experimental error for stronger solutions mounting almost in proportion to the concentration. Hence the results for 0.001 *N* potassium chloride are the most significant. Thus in some of the cells the surface conductivity is quite half of the conductivity of the solution in the capillary.

TABLE XVI

SPECIFIC SURFACE CONDUCTIVITY IN THE NEIGHBORHOOD OF OPTICALLY POLISHED GLASS SURFACES IN THE PRESENCE OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE, EXPRESSED IN MHOS × 10^8 PER SQ. CM.

Concn., *N*	Dale fused silica	Elford polished quartz	No. of glass slit and table reference										Mean
			No. 1 III	No. 2 III, IV	No. 4 VIII	No. 4 V	No. 4 VI, VII	No. 5 X	No. 6 XI	No. 7 VII	No. 7 V, VI	No. 10 IX	
0.1	..	...	3.0	(2.0)	..	...	...	6.0	..	13.0	...	...	(...)
.01	16.6	...	1.8	(3.8)	19.0	7.6	6.2	5.5	17.0	12.0	...	5.1	9.3
.002	..	5.6	6.1	(3.3)	..	5.9	2.8	...	..	6.3	...	...	5.3
.001	3.6	3.9	5.3	(2.4)	3.8	3.6	3.3	5.2	4.9	5.0	3.0	...	4.3

The results in Table XVI not only demonstrate the existence of surface conductivity but also yield approximate numerical values for the absolute specific surface conductances at optically polished glass surfaces. The surface conductances at smooth surfaces of fused silica or of optically polished quartz are the same as with polished glass. The surface conductivity of an insoluble film of fatty acid on water is of about the same magnitude.

Contrary to expectation on the basis of the dissociated double layer of Gouy, the surface conductivity seems to increase with increasing concentration of salt. Evidently the surface conductivity has a finite value even in the presence of 1.0 *N* salt, although it is less than 0.1% of the bulk conductivity even in the narrowest capillary spaces here used. Experiments on electroösmosis likewise show that, although fairly low concentrations of such salts as potassium chloride slow down the flow of liquid markedly, even large concentrations do not entirely stop it.

The negative ions which give the negative charge to the glass might be either OH^- or Cl^-, or even a mixture of the two.[18] Indeed it would be remarkable if there were not a small proportion of positive ions such as H^+ and K^+ also adsorbed on the glass. The corresponding free mobile ions in the solution would not be H^+ (or OH^-) because of the prolonged rinsing with further solution of potassium chloride, which would leave mostly K^+ (and for any positive ion adsorbed, a corresponding excess of Cl^-).

If the surface conductivity is entirely due to free mobile ions (K^+ and Cl^- whose mobility is in both cases 75 at 25°) then the specific surface conductivity, 4.3×10^{-8} mhos, equals 5.7×10^{-7} gram equivalents or 3.5×10^{14} actual ions. Now the distance between centers in a cubic face of potassium chloride crystal is 2.81×10^{-8} cm., when it follows that such a face comprises 12.7×10^{14} ions. Therefore, the surface conductivity in the presence of 0.001 *N* potassium chloride, if interpreted as free mobile ions, corresponds to one-third of the ions which could be accommodated in a monomolecular layer. That for higher concentrations approaches the value for a monomolecular layer.

One of us[19] has pointed out the erroneous voltages which necessarily

[18] H. J. Weiland, This Journal, **40**, 131 (1918), found that the addition of ground quartz raised the conductivity of 0.001 *N* potassium chloride by 0.02% and that of conductivity water (1×10^{-6}) by 10 or more per cent. The ratio between the area of quartz surface and the volume in cubic centimeters is about 80. He interpreted his figures to the effect that 8.8×10^{-12} equivalents of potassium chloride were adsorbed per sq. cm. of quartz surface. Elford in similar experiments with bundles of fine fibers of fused silica likewise found that the conductivity of 0.001 *N* potassium chloride was raised by 0.1% and that of conductivity water (1.8×10^{-6}) by 6.9%. Weiland called the effect on water "pollution." We interpret it as adsorption of OH^-, creating an excess conductivity through liberation of H^+. With potassium chloride, if only Cl^- is adsorbed, the conductivity is to that extent diminished; if, as the other extreme, only OH^- were adsorbed, the conductivity would be greatly increased. The balance observed would indicate that about five times as much Cl^- as OH^- is adsorbed. Our interpretation is reinforced by Weiland's figures, which, according to his interpretation, show an adsorption equal to only a few per cent. of that required to explain the actual surface conductivity here found. Several observers have noted that electrokinetic phenomena are rather fluctuating or ill defined with solutions of potassium chloride and glass.

[19] J. W. McBain, *J. Phys. Chem.*, **28**, 706 (1924). It is 56 volts for an interspace of 1×10^{-8} cm. between the two layers, and the same for 80×10^{-8} cm. if the di-

arise, from the formula for a condenser, if a complete monomolecular layer of ions all of one sign is compensated by an equal number of opposite sign. This might be reduced somewhat if the ions primarily adsorbed were not all of one sign, but the even more obvious alternative here is to ascribe some of the surface conductivity to mere concentration of the salt solution in the neighborhood of the surface. If this were the chief effect, the concentration of 0.001 N potassium chloride in the neighborhood of the glass surface would be raised to $^1/_2 \times 5.7$ N or $^1/_2 \times 0.57$ N, depending upon whether 10×10^{-8} or 100×10^{-8} cm. were taken as the effective range of molecular attraction. The concentration of hydrogen ions in equilibrium with a monomolecular layer of insoluble fatty acid appears to be about one-ninth of the total number of molecules in the oil film, no easy alternative being available. For comparison with the results of Table XVI it may be mentioned that 15.5×10^{-8} mhos would be the conductivity of free potassium ions taken equal in number to the atoms in a square centimeter of a surface of potassium chloride crystal.

To the many objections[19] revealing the fictitious nature of electrokinetic potential, ζ, may be added the assumption that the conductivity in the neighborhood of the surface is the same as the bulk conductivity, an assumption sufficiently disproved by the present work.

Another method of evading the fact that the surface conductivity corresponds to enough ions to cover quite one-third of a monomolecular layer is to assume that the mobility of a potassium ion in the neighborhood of the surface is different from that in the bulk of the solution. However, if the mobility is less, the concentration of ions must be more, and it is in proportion to the change in magnitude of the mobility that the number of ions deduced changes. It is very difficult to justify an *ad hoc* assumption that the actual mobility of the ions is much greater in the neighborhood of a solid surface of opposite charge. Adhesion tests in shear on such optically polished surfaces as are here studied show that the resistance encountered is of the order of one ton per square inch of polished surface,[20] negativing the idea of slip or facile flow.

One possibility remains, arising from the general formulations of Miss Laing[21] for movement in an electrical field, where it is shown that the movement with reference to the solvent is the same in electroösmosis as

electric constant of water be taken as usual at 80. The suggestion made by several adherents of the theory of complete dissociation, that the dielectric constant of water in the neighborhood of ions is to be imagined as 6, raises the latter voltage to $80/6 \times 56 = 747$ volts, as, for example, between a solution and its glass container, provided, of course, that the layer is complete.

[20] J. W. McBain and W. B. Lee, *Proc. Roy. Soc. London*, **113A,** 606 (1926); *J. Soc. Chem. Ind.*, **46,** 321T (1927); *Ind. Eng. Chem.*, **19,** 1005 (1927); *J. Phys. Chem.*, **31,** 1674 (1927).

[21] M. E. Laing, *ibid.*, **28,** 673 (1924).

in electrophoresis. If that is the case here and if the movement of solvent relative to the glass is about the same as the movement of the potassium ions through it, the total movement would about double the absolute velocity of the positive ions and would therefore halve the number deducible from the conductivity, giving only about $^1/_6$ of the number required to build a monomolecular layer. If the average distance of the mobile ions from the sessile charges on the glass is 80×10^{-8} cm., this would be equivalent to a condenser of about 9 volts, or, if the average separation of the mobile ions from the sessile ions is the same as the average distance between the ions throughout a normal solution of any salt such as potassium chloride, 10×10^{-8} cm., the voltage would be about one. However, if the mobile ions are not all of the same sign, which is almost inevitable, the voltage is very greatly reduced, although the Laing effect would be less than that just indicated for the extreme case. This conception assumes that the sessile ions are both positive and negative, the majority being negative.

Finally, it has been common knowledge for a generation or more that a glass surface, once exposed to an aqueous solution, is partially leached out so that it is superficially porous, and the less well-known facts may be recalled that the very best optically polished surfaces are full of infinitesimal cracks; therefore the actual surface of glass is much greater than appears from macroscopic examination. With surfaces such as here used, possibly true to 2–300 Å., these effects do not invalidate or possibly do not even appreciably change our results, although they are in the direction emphasizing the incompleteness of any layer of charges upon the glass, fused silica or polished quartz.

In our experiments with ordinary pyrex tubing[9] the value of the specific surface conductivity for 0.001 potassium chloride is 13×10^{-8} mhos as compared with the 4.3×10^{-8} mhos here found for optically polished glass.

Surface conductivity exists and has to be taken into account in any discussion of the electrical behavior or sorption equilibria of capillary spaces, or finely divided matter such as colloids or organisms containing an ionizing solvent.

Summary

For the first time absolute measurements of specific surface conductivity have been made. For aqueous 0.001 N potassium chloride at 25° the extra conductivity in the neighborhood of optically polished glass, fused silica and optically polished quartz amounts to a specific surface conductivity of 4.3×10^{-8} mhos. Thus in capillary spaces of less than 0.01 mm. half the conductivity may be surface conductivity, ascribable to free mobile ions corresponding to sessile ions of opposite charge upon the solid interface, which are probably not all of negative sign. These mobile

ions are not sufficiently numerous to form more than about one-eighth of a monomolecular layer. This is of the same order as that found in our measurements of specific surface conductivity of an insoluble fatty acid on conductivity water.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. VI. ETHYL IODIDE, ETHANOL, NORMAL-BUTANOL AND NORMAL-OCTANOL

BY C. P. SMYTH AND W. N. STOOPS

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The extreme complexity of the dielectric behavior of the alcohols as observed by various investigators over a limited range of temperature or of concentration, together with the importance of the electric moments of this group of substances, has made it desirable to measure several alcohols from the pure liquid to the most dilute solutions in non-polar solvents over the entire range of temperature within which they are liquid. The methods of measurement and calculation used in the present work have been described in the first two papers of the series on dielectric polarization.[1] In these earlier measurements, benzene and hexane were employed as non-polar solvents, the latter being particularly useful because of the wide range of temperature within which it is liquid. Since pure normal heptane can now be obtained much more readily than hexane of a comparable purity and, at the same time, is liquid over a wider temperature range, it has replaced hexane in the present determinations. Although it had been found that none of the isomers of heptane had detectable electric moments and the similarity of heptane to hexane[2] indicated that it would give identical results as a non-polar solvent, three solutions of ethyl bromide in heptane were measured for comparison with those in hexane previously studied. The results showed the expected agreement and are, therefore, omitted from this paper. However, measurements upon the similar substance, ethyl iodide, are reported and ethyl alcohol has been studied in both hexane and heptane with results that show similar behavior in the two solvents.

Method of Measurement

The densities were determined with the same type of pycnometer used in the earlier work and the dielectric constants were measured with the

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[1] Smyth, Morgan and Boyce, THIS JOURNAL, **50**, 1536 (1928); Smyth and Morgan, *ibid.*, **50**, 1547 (1928).

[2] Smyth and Stoops, *ibid.*, **50**, 1883 (1928).