

magnifying glass, after the pressure regulator was adjusted and showed an equilibrium condition. It was possible to keep the variation of the pressure constant within the maximum limits of 0.5 mm. of mercury.

A number of distillations of pure water were made in this apparatus in order to test the constancy of the boiling point and the efficiency of this method of regulating and maintaining a constant pressure. Equilibrium conditions with water were readily maintained.

The pressure was more readily controlled when the mixture was distilled at slower rates.

Summary

It was found that an aqueous solution of hydrogen bromide when boiled under a pressure of 760 mm. of mercury forms a distillate that contains an average value of 47.795% of hydrogen bromide, and boils at about 125°. The hydrogen bromide in the distillate obtained under a pressure of 760 mm. of mercury does not correspond to the formula $\text{HBr} \cdot 5\text{H}_2\text{O}$, containing 47.381% as reported by Calm.

The constant-boiling mixture is 5.9061 *N* (by weight); 1000 g. of water contains 915.27 g. of hydrogen bromide.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY]

THE BASIS FOR THE PHYSIOLOGICAL ACTIVITY OF CERTAIN -ONIUM COMPOUNDS.¹ THE MOBILITIES OF THE -ONIUM IONS. I. SULFONIUM IONS

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This is one of a series of papers to be presented on the physical-chemical properties of the -onium compounds. In the present article a description is given of the method and apparatus used, together with the results for the mobilities of the trimethyl- and triethylsulfonium ions.

From data already obtained and those to be described in forthcoming papers, it seems certain that the varied stimulating and paralytic effects on the propagation of the nerve impulse given by a series of -onium compounds is not due to properties that are ordinarily considered chemical. We have, therefore, begun in this Laboratory an extended investigation of the physical properties of a selected number of such compounds. Immediate plans include, in addition to a continuation of the mobility determination, a study of the effect of the ions on the potential of lipid-water

¹ This problem is being carried on in cooperation with Doctor Reid Hunt of the Harvard Medical School. The physiological data are the basis of a series of papers published elsewhere by him.

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interfaces, and the interfacial surface tension and energy. It is hoped that adsorption studies on certain membranes may be taken up, also, in the near future.

In Bredig's extended study of the conductance of salt solutions² he investigated the salts of several physiologically active-onium ions in which we are interested. From his data it is not possible to obtain better than approximate values for their mobilities. When one compares these values with the physiological activity of the ions, one finds that the probable values for the mobilities are in general in the same order as the intensity of the curare³ action. There is neither a striking nor clear-cut relationship, however, as is shown in Table I.

TABLE I
CURARE ACTION AND CONDUCTANCE

No.	Descending order of intensity of curare action ^{3a} Substance	Conductance $\nu = 1024$ $T = 25^\circ$	Remarks
1	(CH ₃) ₄ NCl	119.2	Very strong action
2	(CH ₃) ₃ SCl	122.7	Strong and equal action
3	(CH ₃) ₄ PCl	114.9	
4	(C ₂ H ₅) ₄ NCl	106.5	About 0.04 action of No. 1
5	(CH ₃) ₄ AsCl	112.9	No action at 75-150 times effective concentration of No. 1
6	(CH ₃) ₄ SbCl	106.5	

While it appears clear from this comparison that it is impossible to link the curare effect definitely with the ion mobilities, still there is much basis for believing that some sort of an electrical effect is involved. In addition to other reasons, the fact that these substances are active only when the -onium group exists as cation creates a strong presumption in favor of that idea. It seems desirable, then, to have precise data available on the mobilities of a selected number of the physiologically active ions. Some of the most important of these, Bredig did not study and those for which he did obtain results were not investigated in sufficiently dilute solutions to make possible a calculation of mobilities with high precision. On account, too, of the great advancement made in recent years in the treatment of the problem of determining conductance of dilute solutions notably by Washburn⁴ and by Kraus,⁴ it seems desirable also to make such measurements even for those substances with which Bredig worked.

Aside, however, from any question of bearing on the main problem of physiological activity, accurate data on the mobilities of alkyl and sub-

² Bredig, *Z. physik. Chem.*, **13**, 289 (1894).

³ This physiological effect, as well as the muscarine and nicotine effects have been discussed elsewhere. It was there pointed out that the curare effect is not an ideal one on which to test these substances.

^{3a} See Hunt and Renshaw, *J. Pharmacol. Exptl. Therap.*, **25**, 334 (1925).

⁴ Washburn, *THIS JOURNAL*, **38**, 244 (1916). Kraus and Parker, *ibid.*, **44**, 2429 (1922). See also Wieland, *ibid.*, **40**, 161 (1918). Parker, *ibid.*, **45**, 2017 (1923).

stituted alkyl-onium ions will be of considerable interest in connection with the question of possible influence of the hydroxyl group, carbon-carbon double bond and the ester groups on solvation.

Preparation of Materials

Trimethylsulfonium Iodide.—The trimethylsulfonium iodide employed in this investigation was prepared by the interaction of dimethyl sulfide and methyl iodide in alcoholic solution. The product was twice recrystallized from alcohol. The analysis for iodine gave 62.16 and 62.25% as compared with the calculated value, 62.25%.

Triethylsulfonium Bromide.⁵—This was prepared by heating molecular quantities of diethyl sulfide and ethyl bromide at 38° for 125 hours. The product was purified by three consecutive precipitations from an anhydrous alcohol solution by dry ether. The analysis for bromine gave 40.18 and 40.31% as compared with the calculated value 40.14%.

Water.—The water employed in this investigation was purified by a method developed in this Laboratory.^{6a} Ordinary water was distilled from an alkaline solution of potassium permanganate. The first fraction of the distillate was discarded. The rest of the distillate was collected and maintained at a temperature below the boiling point in a copper still, where it was digested with a little potassium permanganate. During this time a slow current of air free from carbon dioxide was bubbled through the water, removing most of the dissolved gases. The water was then further purified by fractional condensation. The first and third fractions were discarded; the second fraction was collected directly into the conductivity cell. A slow current of air free from carbon dioxide was allowed to pass through the entire apparatus during the distillation, and thus contamination from the outside air was prevented.

Purification of Air.—Air free from carbon dioxide was necessary for the purification of the conductivity water as well as for stirring the solution in the conductivity cell during the resistance measurements. Air from the outside, sucked in by a water pump, was forced through an absorption train similar to that used by Weiland.⁶ It consisted of five absorption tubes, the first of which was filled with sulfuric acid, the next three with concd. potassium hydroxide solution, and the last with distilled water.

Measuring Apparatus

Bridge.—A drum-wound, slide-wire bridge with extension coils was used in measuring the resistance of the solutions. The bridge wire was calibrated by the method of Barus and Strauhal and by means of the corrections obtained it was possible to check resistance readings to 0.02%. Air condensers were used to balance out the effect of inductance and capacity in the circuit. The apparatus was carefully shielded, all connections were soldered and grounded and the assembled apparatus was kept in a metallic shield. The leads in either arm of the set-up were of equal resistance, so that no corrections for lead resistances were applied when readings were taken in the middle of the bridge. Otherwise, however, the resistance of the leads was subtracted from the total resistance. The leads were connected to the cell in the thermostat as recommended by Washburn.⁷

Resistances.—The resistance boxes consisted of Curtis-wound coils ranging from

⁵ The authors wish to express their thanks to Mr. H. T. Hotchkiss for the preparation of this material.

^{6a} Bencowitz and Hotchkiss, *J. Phys. Chem.*, **29**, 705 (1925).

⁶ Weiland, *This Journal*, **40**, 161 (1918).

⁷ Washburn, *ibid.*, **38**, 2440 (1916).

10 to 10,000 ohms' capacity. They were calibrated simultaneously with direct current as described by Parker and Parker.⁸ The 100-ohm position on the dial was checked directly against the 100-ohm standard. The 200-ohm position was measured against the standard plus the first in the second box. The same procedure was repeated with the other resistances. The 1000-ohm position on the dial was checked against a 1000-ohm standard as well as against the 900-ohm position on the second box plus the 100-ohm standard. The two resistance boxes were then interchanged and the 100-ohm standard again checked on either side; thus two independent values were obtained. The average of these measurements was taken to be the resistance of the corresponding setting of the dial.

Measuring Cells.—A large quartz cell was employed with dilute solutions. This cell consisted of a 1-liter Vitreosil flask. The electrodes had an area of about 5 sq. cm. and were placed approximately 4 mm. apart. The electrodes were sealed into a quartz tube and were held rigidly by two heavy platinum wires welded on the small platinum tubes leading from the closed seal.⁹ This was found to give sufficient rigidity as shown by the constancy of the cell constants. The solution was stirred by a slow current of air free from carbon dioxide which was blown into the cell through a quartz tube. This tube as well as the electrode stem was sealed by means of de Khotinsky cement into a glass stopper which was carefully ground to the neck of the cell. The stopper had an additional tube through which the conductivity water was collected and the stock solution used in making up the solutions in the cell was introduced.

Two auxiliary cells of the Washburn pipet type¹⁰ were employed for the purpose of calibrating the quartz cell. One of these cells which is designated here as Cell I had electrodes of an area of about 1.5 sq. cm. which were approximately 6 cm. apart. The second cell had electrodes of about the same area but they were only 3 mm. apart. The latter cell is designated here as Cell II. The electrodes in all cells were platinized while those in the quartz cells were heated in the blow pipe until the platinum black turned gray.

The Thermostat.—The thermostat employed in these measurements was kept at a constant temperature within 0.002° by a vacuum tube device described by D. J. and J. J. Beaver.¹¹ A toluene-mercury thermo-regulator of a large volume was employed. This was constructed of glass tubing and bent in a vertical zigzag to fit the inside of the bath. The bath was filled with glycerol, inasmuch as at low resistances capacity effects apparently are introduced when a water-filled thermostat is used.

Balance.—The balance which was used for weighing out the salts, as well as the weight pipet in which the stock solution was weighed, was a standard analytical balance sensitive to within 0.1 mg. The weights employed were calibrated by Richards' method.¹²

Variation of Cell Resistance with Frequency and Potential.—Taylor and Acree¹³ in their investigation on conductance measurements found a variation of the cell resistance with the frequency of the current and also with the value of the impressed voltage. The work of Haworth¹⁴ pointed out that the change in resistance with the frequency is most pronounced

⁸ Parker and Parker, *THIS JOURNAL*, **46**, 312 (1924).

⁹ Thanks are due to the Cooper Hewitt Co. for their valuable assistance in making this difficult and important seal.

¹⁰ Washburn, Ref. 7, p. 2449.

¹¹ Beaver and Beaver, *Ind. Eng. Chem.*, **15**, 359 (1923).

¹² Richards, *THIS JOURNAL*, **22**, 144 (1900).

¹³ Taylor and Acree, *ibid.*, **38**, 2415 (1916).

¹⁴ Haworth, *Trans. Faraday Soc.*, **16**, 365 (1921).

at low resistances. These results were confirmed by other investigators.¹⁵ This variation can be eliminated by sufficient platinization of the electrodes, so much so, in fact, that the difference in resistance between 500 and 1700 cycles is reduced to 0.01%.^{15a}

The change of resistance with the voltage seems to be more obscure. Taylor and Acree suggested that it was due to contamination of the cell. The results of Kraus and Parker, however, indicate that the most thorough cleaning of the cell is not sufficient to eliminate this effect. Morgan and Lammert, on the other hand, seem to confirm the conclusion of Taylor and Acree. Whatever the cause of this effect may be, it has been shown that the change is very much less at higher voltages. The measurements in this investigation, therefore, were conducted with a current of 1000-cycle frequency and an impressed voltage of 6 v., and as an additional precaution no reading was taken with a resistance below 250 ohms.

Care of the Electrodes.—The electrodes were washed with hot cleaning solution and hot water. They were then rinsed with alcohol, in order to remove the absorbed acid, and finally steamed and washed with conductivity water. The directions recommended by Morgan and Lammert,^{15c} regarding short circuiting the electrodes while the cells were being cleaned and brought to proper temperature, were closely followed as an additional precaution. The electrodes of the quartz cell when not in use were kept in a specially constructed tube so that any displacement of the electrodes was prevented.

Cell Constants.—The data of Kohlrausch and Holborn¹⁶ which were universally used for the purpose of calibrating conductivity cells were shown to be in error.¹⁷ Recently, Parker and Parker¹⁸ repeated these measurements and obtained new values for the specific conductance of potassium chloride solutions. These values were adopted for the determination of the cell constants in this investigation.

Cell I described above was used as a reference cell. It was calibrated directly with a 0.1 *D* solution at 25° (0.1 *D* is a term suggested by Parker and Parker, meaning 0.1 mole per 1000 cc. of solution). This solution is as nearly dilute as a solution can be made and handled in the laboratory air without special precautions against contamination, and still be sufficiently dilute so that one accurate intercomparison with the reference cell, whose constant was determined directly with this solution, would be sufficient for the determination of the constant of another cell which requires a much more dilute solution.

¹⁵ (a) Kraus and Parker, *THIS JOURNAL*, **44**, 2429 (1922). (b) Parker, *ibid.*, **45**, 1369 (1923). (c) Morgan and Lammert, *ibid.*, **45**, 1692 (1923).

¹⁶ Kohlrausch and Holborn, "Leitvermögen der Electrolyte," Teubner, Leipzig, 1916, p. 76.

¹⁷ Ref. 15 a, p. 2442.

¹⁸ Parker and Parker, Ref. 8, determined this error to be -0.145% .

The solution was made up as follows. About 1000 g. (weight in air) of conductivity water, whose conductance had been previously determined, was weighed into a Pyrex Erlenmeyer flask. This flask had been carefully cleaned with cleaning mixture, hot water and steam and finally dried with purified air. The weight of potassium chloride required for the solution was calculated from this amount of water using the data given by Parker and Parker, that is, 7.47896 g. (weight in air) of potassium chloride to 1000 g. of water (weight in air). The value of the specific conductance of the solution thus made up is given as 0.0128524. The potassium chloride employed was twice recrystallized from conductivity water. It was then heated in a platinum crucible until a part of the salt melted. After the crucible had been allowed to cool in a desiccator, the fused portion of the salt was removed, the exact quantity required was weighed into a watch glass and finally added to the conductivity water. The solution was transferred to the cell by means of a siphon. The cell was filled thrice and the resistance measured against four known resistances four times at half-hour intervals. The cell was thoroughly cleaned as described above before each filling. The average deviation from the average was 0.01%. The constant of the cell was redetermined afterwards with an independent solution similarly prepared. The constants checked within 0.015%: determined June 7, 2.08133; October 24, 2.08106; average, 2.08119. A similar drift in the cell constant was noticed by Kraus. In this investigation, however, we used the average of the two determinations as the cell constant. The error introduced by this procedure was less than 0.01%.

The constant of Cell II was determined by intercomparison with Cell I, using solutions of different resistances. Our results confirm the work of Parker^{15b} in that the constant of the cell varies with the resistance, giving a minimum at low resistances. The variation, however, is very slight at higher resistances. The results obtained are given in Table II.

TABLE II
INTERCOMPARISON MEASUREMENTS OF CELL II

Resistance, ohms	33.097	86.956	132.642	132.714	176.442
Cell constant Ratio, I/II	0.810643	0.809709	0.805885	0.808351	0.809651
Cell constant from Cell I	.168710	.168513	.167771	.168231	.168503
Resistance, ohms	171.047	188.776	224.279	944.485	1276.355
Cell constant Ratio, I/II	0.805289	0.812195	0.812032	0.812757	0.812032
Cell constant from Cell I	.167589	.169031	.169000	.169050	.169002

In Row 1 are given the resistances of Cell II obtained at each of a series of concentrations of potassium chloride. The values obtained by dividing the resistance of Cell II by that in Cell I for the same concentrations are given in Row 2. The figures given in Row 3 are obtained by multiplying the ratio of the resistances by the cell constant of Cell I, 2.08119. The average of the last four constants in the table was adopted as the constant of Cell II.

The constant of the quartz cell was determined by intercomparison with Cells I and II through using solutions of different resistances. When the value of the resistance was plotted against the corresponding constants, a minimum was obtained. The resistance of this point in the curve corresponded to that of an approximately 0.001 *N* potassium chloride solution. The average of the constants obtained from resistances in proximity to this point was accepted as the constant of the quartz cell. Throughout the investigation, therefore, the cell constant of the cell was redetermined before and after each run by intercomparison with Cells I and II using an approximately 0.001 *N* potassium chloride solution. The constants for each run are shown in Table III.

TABLE III
CONSTANTS OF QUARTZ CELL USED IN MEASURING THE CONDUCTANCE OF SULFONIUM SALTS

	Trimethylsulfonium iodide			Triethylsulfonium bromide		
	Before	After	Average	Before	After	Average
Run 1	0.0274697	0.0274675	0.0274686	0.0274699	0.0274679	0.0274689
Run 2	.0274789	.0274787	.0274788	.0275287	.0275279	.0275285
Run 3	.0275349	.0275318	.0275333	.0275498	.0274975	.0274981

Density.—In order to reduce the concentrations to a volume normal basis, it was necessary to determine the density of the salt solutions. An Ostwald pycnometer of about 15cc. capacity was employed for the measurement. The data obtained are given in Table IV. The curve shows that the points at lower concentrations do not coincide with the curve which is drawn straight down to the density of water at 25°. The apparent deviations, however, though larger than the experimental error of the density measurements are much less than the error with which the concentrations were determined. Furthermore, the corrections for the change in density on dilute solutions employed in this investigation are almost negligible. The densities finally used were read off the smooth curve.

TABLE IV
DENSITIES

	Trimethyl sulfonium iodide		Triethyl sulfonium bromide			
Concn.	0.0033663	0.00802203	0.0664169	0.00987564	0.065734	0.0753519
d_4^{25}	.997345	.997723	1.00290	.997465	.999964	1.000523

Experimental Procedure and Results

Manipulation.—The method of carrying out a series of conductance measurements was as follows. The quartz cell was cleaned with hot cleaning solution, after which hot water was allowed to run through for half an hour. It was then steamed with frequent rinsing and finally it was attached to the still. To prevent contamination from the external atmosphere a slight pressure of purified air was applied, when the cell was being

filled. In collecting the water, the cell was thoroughly rinsed with water nearly at its boiling point, finally it was repeatedly rinsed by filling and siphoning off the water. Throughout these operations, measurements of the resistance of the water were taken. When the latter was of the desired quality, the cell was filled, removed from the still and placed in the thermostat where it was allowed to stand for several hours until temperature equilibrium was reached. This was determined by several resistance measurements. The specific conductivity of the water was determined and the first solution was made up by introducing a weighed quantity of a stock solution which had been previously prepared. This solution was made up by weighing out carefully a calculated amount of the salt and introducing it into a weighed quantity of conductivity water. The strength of this solution was approximately 0.1 *N*. It was stored in a quartz flask and was introduced into the quartz cell by means of a weight pipet shown in Fig. 1.

Weight Pipet.—All parts of this pipet were constructed of Pyrex glass.

Its capacity was about 5 cc. Due to the fact that the neck of the conductivity cell was long and narrow it was necessary to bring the end of the pipet almost to the very surface of the water in the cell to prevent spattering. Tube A, therefore, was made of such length that when the pipet was placed in the cell through a special opening in the stopper its end was about 3 cm. above the surface of the water in the cell. The cap B was ground on to tube A, to prevent evaporation when the weight of the pipet was determined. The flow of solution from Bulb D into the cell was controlled by the stopper C. As soon as the latter was slightly raised, the solution ran into Bulb E and then into the cell. The solution flowing from Bulb D fell in drops from the tip of the inner tube F. These drops were counted and the approximate weight of the solution introduced was thus determined before the pipet was removed from the cell and weighed. When the flow of the solution was arrested by forcing the stopper all the way down, some of the solution was retained at the end of Tube A, due to capillary action. This solution was blown out by air free from carbon dioxide applied to Tube G. Thus, any loss of solution while the pipet was withdrawn from the cell through the rather long neck was prevented.

The stock solution was kept in the pipet for only 20–30 minutes, so that the contamination due to the solubility of Pyrex glass was negligible. The weight of the pipet was reproducible to less than 0.2 mg., and the smallest amount of solution weighed was 0.8000 g. In all, about 15 g. the solution was added to the cell in each run. The addition of this amount of liquid did not change the height of the solution in the cell sufficiently to change the cell constant appreciably. The solution in the cell was stirred by means of air free from carbon dioxide previously saturated with water and brought to the temperature of the bath. The resistance at each concentration was measured thrice at 15-minute intervals, each

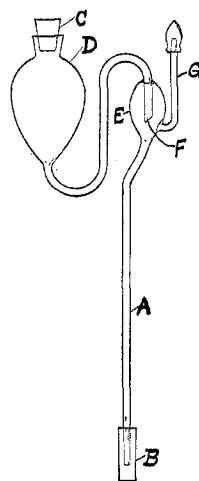


Fig. 1.

measurement being taken with four known resistances. When the run was completed the cell was removed from the thermostat, the outside was washed with ether and with alcohol, dried and the cell then weighed. The weight of the empty cell was determined several times during the investigation. This weight was constant to within 0.01%, as is seen from the following series: July 14, 325.956 g.; August 31, 326.003 g.; September 25, 326.010 g.; November 30, 325.987 g. The concentrations were reduced to volume normality by means of the densities read from the smooth curve.

Conductance Data.—The results obtained in this investigation are given in Table V, where are shown the values of the specific conductance,

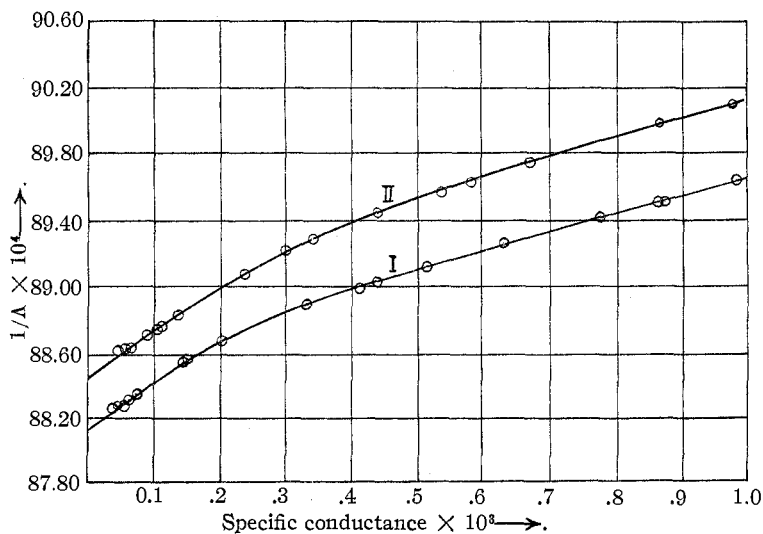


Fig. 2.—I, triethylsulfonium bromide. II, trimethylsulfonium iodide; subtract 10.00 from $1/\Lambda$.

equivalent conductance and the concentration. The latter is expressed in millimoles per liter. All weights given are reduced to a vacuum. The molecular weights were assumed to be 204.067 for trimethylsulfonium iodide and 199.130 for triethylsulfonium bromide. At the head of each sub-table are given the cell constant K , the specific conductance of the water used L_w , the total weight W , of the water employed in making up the solution in the cell, and the strength of the stock solution in g. per 1000 g. of solution (the weight of the salt is reduced to a vacuum while that of the solution is in air). These data are shown in Fig. 2 where $1/\Lambda_c$ is plotted against the specific conductance, L_s , of the solutions. In extrapolating to infinite dilution the first point of each run was neglected.

In Table VI are given the values at round concentration. These values were interpolated from a curve obtained by plotting $\Lambda_o - \Lambda_c$ against Δ_c .

TABLE V
CONDUCTANCE OF TRIETHYLSULFONIUM BROMIDE

RUN 1			
$K = 0.0274686$		$L_w = 0.09 \times 10^{-6}$	$W = 1044.98^a$
Concn. $\times 10^3$	Λ_c	Concn. $\times 10^3$	Λ_c
0.0348645	113.329	0.456211	112.217
.128252	112.943	.770230	112.740
.290410	112.540	.975377	112.552
RUN 2			
$K = 0.0274788$		$L_w = 0.085 \times 10^{-6}$	$W = 986.09$
.0403089	113.303	.387523	112.286
.0553541	113.231	.691425	111.850
.129463	112.943	.881516	111.565
RUN 3			
$K = 0.027528$		$L_w = 0.13 \times 10^{-6}$	$W = 1019.75$
.0472120	113.296	.365677	112.376
.0596537	113.230	.552745	112.047
.174708	112.786	.779222	111.727

Concentration of stock solution = 0.0664160 moles per 1000 g. of solution (weight in air).

CONDUCTANCE OF TRIMETHYLSULFONIUM IODIDE

RUN 1			
$K = 0.0275283$		$L_w = 10 \times 10^{-6}$	$W = 1017.11$
Concn. $\times 10^3$	Λ_c	Concn. $\times 10^3$	Λ_c
.0374284	127.259	.234825	126.247
.0500161	127.194	.423639	125.675
.0861536	126.985	.778770	124.860
RUN 2			
$K = 0.0275283$		$L_w = 0.95 \times 10^{-6}$	$W = 1013.50$
.0379072	127.241	.267142	126.135
.0705717	127.065	.459131	125.580
.106184	126.865	.691286	125.014
RUN 3			
$K = 0.0274981$		$L_w = 0.09 \times 10^{-6}$	$W = 1039.78$
.0446282	127.233	.345386	125.880
.0808910	127.017	.530761	125.405
.185391	126.471	.928658	124.563

Concentration of stock solution = 0.0753519 moles per 1000 g. of solution (weight in air).

^a In a vacuum.

At the lowest concentration, however, the values were calculated from the corresponding mass-action constant obtained from a $K-C$ curve.

TABLE VI
TRIMETHYLSULFONIUM IODIDE AT ROUND CONCENTRATIONS

Concentration $C \times 10^3$	Specific conductivity $L \times 10^4$	$\alpha = \frac{\Lambda_c}{\Lambda_\infty}$	$K = \frac{\alpha^2 C}{1 - \alpha}$	Equivalent conductivity Λ_c
0.0	0.0	127.49
.01	.0127434	0.9996	0.0211	127.434
.02	.0254748	.9990	.0211	127.374

TABLE VI (Concluded)

Concentration $C \times 10^3$	Specific conductivity $L \times 10^4$	$\alpha = \frac{\Delta_c}{\Delta_\infty}$	$K = \frac{\alpha^2 C}{1 - \alpha}$	Equivalent conductivity Δ_c
0.03	0.0381946	0.9986	0.0211	127.313
.04	.0509021	.9981	.0211	127.253
.05	.0635967	.9976	.0211	127.194
.06	.0762810	.9972	.0211	127.134
.07	.0889520	.9967	.0212	127.076
.08	.101612	.9962	.0212	127.015
.09	.114284	.9959	.0212	126.954
.10	.126900	.9953	.0213	126.900
.20	.252800	.99370	.02102	126.400
.30	.378118	.99860	.02571	126.040
.40	.502955	.98626	.02801	125.740
.50	.627451	.98427	.03033	125.490
.60	.751483	.98238	.03290	125.250
.70	.875238	.98069	.03489	125.034
.80	.998585	.97905	.03662	124.824
.90	1.12254	.97756	.03835	124.633
1.00	1.24500	.97618	.03998	124.454

TRIETHYLSULFONIUM BROMIDE AT ROUND CONCENTRATIONS

0.0	0.0	113.49
.01	.0113447	0.9996	0.0252	113.447
.02	.0226831	.9993	.0252	113.402
.03	.0340067	.9988	.0252	113.357
.04	.0453247	.9984	.0252	113.312
.05	.0566340	.9980	.0252	113.268
.06	.0679339	.9976	.0252	113.223
.07	.0792128	.9971	.0253	113.160
.08	.0905124	.9969	.0254	113.141
.09	.101783	.9965	.0255	113.094
.10	.113054	.9962	.0257	113.054
.20	.225462	.99329	.02947	112.732
.30	.337536	.99135	.03414	112.512
.40	.449247	.99060	.03759	112.312
.50	.560688	.98805	.04106	112.142
.60	.671950	.98677	.04414	111.990
.70	.782890	.98546	.04676	111.842
.80	.893538	.98412	.04885	111.692
.90	1.00396	.98288	.05086	111.552
1.00	1.11422	.98176	.05284	111.422

Discussion

The experimental values of $1/\Delta_c$ are plotted against C in Fig. 2. In the range of dilute solution, the slopes of both curves are practically parallel, indicating that the sulfonium salts as uni-univalent salts of strong acids and bases have the same degree of ionization in sufficiently dilute solutions.

The equivalent conductances at infinite dilution obtained from these curves are 127.49 for triethylsulfonium iodide and 113.49 for triethylsulfonium bromide. Assuming the limiting values for Δ_∞ of the iodide ion

at 18° to be 66.25 and that of the bromide ion 67.31 and the respective temperature coefficients, $\frac{1}{\Lambda} \left(\frac{d\Lambda}{dt} \right)_{18^\circ}$, as 0.2013 and 0.0215¹⁹ then the corresponding values at 25° are 76.12 and 77.44. The limiting value for Λ_∞ of the trimethylsulfonium and triethylsulfonium ions, therefore, are 51.36 and 36.05, respectively.

Work of Previous Investigators.—Bredig²⁰ measured the conductance of the chlorides of these ions. The lowest concentration he worked with, however, was about 0.001 *N*. Conductance values of such concentrated solutions cannot be employed for extrapolating the limiting value, Λ_∞ , at infinite dilution, directly. There is an indirect method, however, by means of which this value can be obtained from Bredig's work with a fair degree of accuracy.

Assuming that in sufficiently dilute solutions all uni-univalent salts of strong acids and bases have the same ionization constants, K_E as expressed by the equation, $\Lambda_c C / [\Lambda_\infty (\Lambda_\infty - \Lambda_c)] = K_E$, is independent of the nature of the salt and, therefore, can be taken from Table VI. Solving this expression we find $\Lambda_\infty = \Lambda_c (1 + \Lambda_c C / \Lambda_\infty K_E)$, or with sufficient degree of accuracy, $\Lambda_\infty = \Lambda_c (1 + C / K_E)$, an expression by means of which the value Λ_∞ for any salt can be computed from a single value of Λ_c for that salt. (This method was developed by Washburn, and the validity of the assumption on which it is based was well demonstrated.)²¹ The chlorides of the sulfonium salts and the corresponding bromides and iodides are probably sufficiently similar to allow us to assume that even at concentrations as high as 0.001 *N* they have identical ionization constants. We can calculate, then, the limiting value of Λ_∞ of the chlorides using Bredig's data for $\Lambda_{0.001N}$ and K_E for the same concentration from Table VI. (Bredig's data were reduced to the proper units and corrected for atomic weights and cell constants. The latter correction was applied by subtracting 0.145%.) The value thus obtained for the limiting values of Λ_∞ of trimethylsulfonium chloride is 125.61 and that of triethylsulfonium chloride, 111.29. The limiting values of the respective ions, therefore, are 50.51 and 36.19.²² These values are in sufficiently good agreement with our values.

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¹⁹ These values were adopted by Washburn for the International Critical Tables.

²⁰ Ref. 2, p. 211.

²¹ Washburn, *THIS JOURNAL*, 40, 153 (1918).

²² The limiting value for the chloride ion at 25° was assumed to be 75.10, calculated from 62.24 at 18° and the temperature coefficient, $\frac{1}{\Lambda} \left(\frac{d\Lambda}{dt} \right)_{18^\circ} = 0.0216$.

Summary

1. The apparatus employed and precautions observed in carrying out conductivity measurements with trimethylsulfonium iodide and triethylsulfonium bromide between concentrations of 0.04 and 1.2 millimoles per liter are described. The measurements were carried out in a quartz cell. The solutions were made up by weight to an error of less than 0.05%. Water was used having a specific conductance of the order of 0.1×10^{-6} .

2. Values at round concentrations have been interpolated from the results upon trimethylsulfonium iodide and triethylsulfonium bromide.

3. Extrapolation of the results, on the assumption that the mass action is approached as a limiting form at infinite dilution, gives a value of Λ_{∞} for trimethylsulfonium iodide, 127.49, and for triethylsulfonium bromide, 113.49.

4. Assuming that the value of Λ_{∞} at 25° of the iodide ion is 76.12 and that of the bromide ion 77.44, then values of 51.36 and 36.05 for the Λ_{∞} of the trimethyl- and triethylsulfonium ions respectively, are obtained.

5. This is the first paper of a series of investigations on the mobility of the -onium ions. The investigation as well as other researches, such as the effect of -onium ions on the potential of lipid-water interfaces, have been undertaken in this Laboratory with the hope of obtaining an explanation of the mechanism of physiological activity.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

AZIDO-CARBONDISULFIDE. II. REACTION OF AZIDO-CARBONDISULFIDE AND OF FREE THIOCYANOGEN WITH HYDROGEN TRINITRIDE (HYDRONITRIC ACID) IN CERTAIN NON-AQUEOUS SOLVENTS¹

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In connection with an extended series of investigations in the field of the halogenoids and the halogenoid hydracids, certain reactions of these compounds toward each other, or toward other substances, including the halogens and the halogen hydracids, have been studied. The various reactions to be considered may for convenience be classified under seven headings, as follows. Interaction of (1) a halogenoid and a halogen,

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