members of the Chemical Warfare Service for their assistance in the experimental work: A. W. Kenney, C. L. Dougherty, W. M. Craig and D. O. E. Peterson.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

CONDUCTIVITY AND FREQUENCY.

BY E. D. EASTMAN.

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There is reason to suppose that the general form of the conductivity-frequency curve for solutions of electrolytes may correspond in type to that shown in Fig. 1. The features of this general curve are the rise, from *A* to *B*, to a maximum of conductivity as the frequency is increased from zero, and the subsequent decrease, from *B* to *C*, and asymptotic approach to zero conductivity at infinite frequency. The necessity of the approach to zero as the frequency is indefinitely increased is obvious, and the portion of the curve from *B* to *C* requires little comment other than to point out the possibility that certain resonance effects may make the curve less simple in this region than the one here shown, and that the decrease in conductivity undoubtedly begins only at frequencies far higher than those ordinarily used in conductivity measurements. It is in the portion *AB* of the curve that the interest of the present paper centers, and the basis of the assumption of increase in conductivity in this portion of the curve may be briefly discussed.

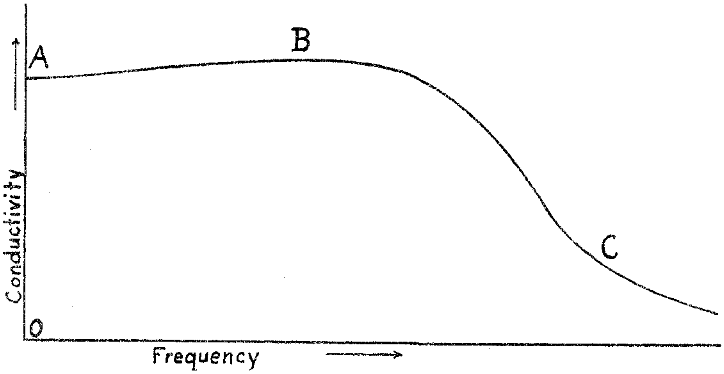

Fig. 1.—Theoretical form of conductivity-frequency curve.

If current theories are correct there are present in solutions of electrolytes numerous electric dipoles, or multipoles, consisting of molecules or ions of solute in various stages of dissociation and solvation. Under the influence of an alternating electric field these polar molecules should all be more or less free to take part in oscillatory rotation about their centers, and this rotation should contribute to the current carried by the solution and ordinarily attributed exclusively to the linear motion of free ions. Other effects due to the alternating field may be readily imagined, but these probably do not affect conductivities as ordinarily measured. For example, oscillations, in the direction of the electric field, of the charged parts of undissociated molecules may occur, or electrons may vibrate between atoms of the same molecule or of different molecules. But the forces opposing the external field in such vibrations are no doubt elastic in character, affecting the capacity rather than the conductance of the solution, and the effects may, therefore, be compensated by the use of capacities in the external circuit. These considerations do not apply, however, to the rotation of the molecules, the resistance to which is probably largely frictional and of the same nature as the resistance to the motion of the ions. The magnitude of this rotational effect, owing to the present imperfect state of knowledge of the structure of solutions, cannot be calculated. Approximations which may be made on the basis of various simple assumptions as to the possible number and electrical moments of the complexes involved, give 1% of the total current as the order of the effect for *N* potassium chloride solution at 1000 cycles per second.

On the experimental side there is in the literature no work which definitely precludes a difference of this magnitude. The best of the older researches comparing direct and alternating current conductivities is that of Sheldon.[1] The average of his final results for various salts at different concentrations shows good agreement between the two methods. But the possible constant errors in his methods are such that the agreement found might well be purely fortuitous. Again, the results which have been thus far obtained, in various laboratories, while far from complete or conclusive, seem to indicate that at frequencies of the order of one or two thousand cycles, changes of conductivity with frequency are in general quite small, *i. e.*, a portion of the curve in Fig. 1 is horizontal or slopes but slightly. It does not follow, however, from the approximate constancy of the values obtained by measurements at these frequencies, or by extrapolation from lower frequencies,[2] that the values corresponding to zero frequency are identical with them. At intermediate frequencies polarization appears as a disturbing factor, largely destroying the value of the results.

As it appears then that a variation in conductivity with frequency may theoretically be expected even at low frequencies, and as the magnitude

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[1] Sheldon, *Ann. Physik*, **34**, 122 (1888).

[2] Taylor and Acree (THIS JOURNAL, **38**, 2396 (1916)) suggest this method. If only an electrode effect is involved, and no real change of conductance with frequency, the method is perhaps justified, though "extrapolation to infinite frequency" is misleading.

of this variation cannot be judged from existing data nor readily studied by the usual methods, the experiments below were undertaken. Their primary object was not the study of the effect in itself, though this is of some interest, but rather to find whether the expected differences are large enough at ordinary frequencies to affect calculations seriously, such as degree of dissociation, based on conductivity measurements, or to afford a method of study of the "structure" of solutions of electrolytes. The scheme first adopted was the measurement by a direct current method and comparison with alternating current values of some of the conductivities most accurately determined by Kohlrausch. This was done with *N* potassium chloride and with maximum conducting sulfuric acid. Later a method by which alternating and direct current measurements could be directly compared in the same cell was tried with *N* potassium chloride solution and with 10 *N* lithium chloride solution.

The Direct Current Conductivity of Normal Potassium Chloride Solution and of Maximum Conducting Sulfuric Acid by a Potentiometric Method.

Potassium chloride was selected for study because of the reproducibility of its solutions, and because of the accurate determination by Kohlrausch of its conductivity, and its consequent use as a standard in conductivity work. It is not, however, of the type which would be expected to show the largest effect of the kind considered. Of the other substances recommended by Kohlrausch as standards, sulfuric acid seemed most likely to exhibit a large effect, and was chosen for this reason.

The method of measurement follows. The solution to be studied is placed in a cell of the type shown in Fig. 2. This is connected, in series, with a standard resistance and with a source of steady current, by means of non-polarizable electrodes dipping into the reservoirs *A*, *A*. The potential at similar electrodes in *B*, *B*, and at the terminals of the standard resistance, is then measured by a potentiometer. The "cell constant" is determined in the same way, the electrolyte being replaced by mercury.

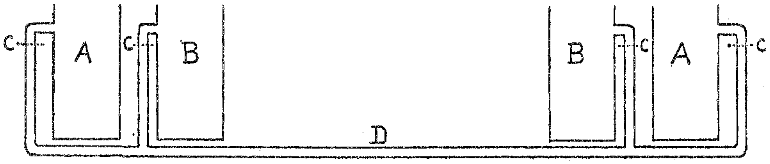

Fig. 2.—Direct current conductivity cell.

The electrodes were of very large reacting surface. Calomel and mercurous sulfate electrodes were used for the potassium chloride and sulfuric acid solutions, respectively, the electrolyte in the cell differing from that in the electrodes only in that it contained no dissolved calomel or mercurous sulfate. Both sets of electrodes were very constant. The correction to the potentiometer reading, which had to be made because the electrodes were not quite equivalent to each other, was of the order of a few hundredths of one per cent. of the reading.

All details affecting the accuracy of the results were carefully studied. The resistance used were compared with coils recently certified by the Bureau of Standards. The currents employed were systematically varied, giving readings in widely different ranges of the accurate potentiometers which were used. Heating effects, and the effects of impurities in all materials were shown experimentally to have been eliminated. Temperatures were constant to 0.01° and correct to 0.02°. The weights used in preparing the solutions were compared with a standard gram.

The mean of 8 series of observations upon 3 independently prepared solutions gave 5038.3 ohms as the resistance of the cell containing *N* potassium chloride solution (71.422 g. of potassium chloride per 1000 g. solution) at 25°, the average of the deviations of individual values from the mean being 0.014%. For the sulfuric acid solutions the corresponding values are 682.63 ohms and 0.±018%, and for mercury 0.054138 ohm and ±0.032%. From the definition of the international ohm, the specific conductance of mercury at 0° is 1.0630×10^4 reciprocal ohms. The temperature coefficient of resistance of mercury between 0° and 100° has been accurately determined by Jaeger and Steinwehr.[1] From their work the specific conductance at 25° is 1.03930×10^4 reciprocal ohms. The specific conductance of *N* potassium chloride solution is then calculated to be 0.11168 and of the sulfuric acid 0.8242 reciprocal ohm. The corresponding Kohlrausch values are 0.11180 and 0.8257 reciprocal ohm, which are 0.11% and 0.18%, respectively, higher than the results above. These differences are in the direction expected, and their magnitude exceeds the experimental error, ±0.05%, which can be assigned to the present work.

Newbery,[2] in a paper which was unknown to the writer until after the completion of this portion of the work gives a direct current measurement for potassium chloride which is 0.7% higher than the one here obtained, and is apparently in error by nearly this amount. Because the accuracy of Kohlrausch's work (though it is believed to be excellent) is not definitely known, a more direct comparison seemed desirable and was made in the experiments described below.

Direct and Alternating Current Conductivities by a Modified Bridge Method.

The principle of a method by which alternating current may be used in a cell of the type described in the preceding was suggested to the

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[1] Jaeger and Steinwehr, *Ann. Physik*, 45, 1089 (1914).

[2] Newbery, *J. Chem. Soc.*, 113, 701 (1918). Newberry's method is similar in principle to that described above, except that the cell constant is obtained from its dimensions, instead of from its conductance when filled with mercury. The accuracy of his results is estimated by him as 0.1%.

writer by Dr. R. F. Newton. It may best be made clear by reference to Fig. 3. Here E and F are the points of connection to the source of current, a and b are resistances of known ratio, and R_1, R_2, R_3 are variable known resistances. The points A and D correspond to the reservoirs A, A, in Fig. 2, and the points B and C are the points of connection to the reservoirs B, B of Fig. 2. The resistance of the part BC is referred to as the resistance of the cell, as before, and called R. The procedure in measurement is to adjust the sum $R_1 + R_2 + R_3$ so that balance is obtained in the telephone T_1. Still maintaining $R_1 + R_2 + R_3$ constant, R_1 and R_2 are adjusted for silence in T_2, and lastly, maintaining $R_2 + R_3$ constant, adjustment of them is made for balance in T_3. When this has been done the value of R is known from the relation

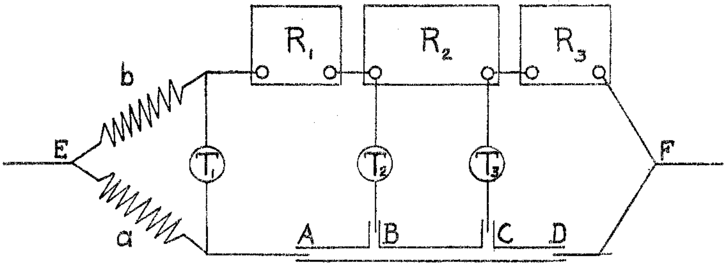

Fig. 3.—Modified bridge.

$$R = a/b\ R_2.$$

The same method is applicable with direct current, using suitable non-polarizable electrodes, and replacing the telephones by galvanometers. In practical operation a single telephone or galvanometer with appropriate switches may be used, and it may also be arranged to change, by the throw of a switch, from one type of current to the other, giving nearly simultaneous comparisons.

In the actual set-up, a and b were various combinations of a set of standardized Curtis coils. At times a calibrated rotary slide wire, with end coils, was substituted for these fixed ratio coils, the sliding contact in this case being at E in Fig. 3. The ratio a/b was widely varied in the different measurements. R_1 and R_3 were dial resistances and R_2 a dial box of Curtis coils. It was first arranged so that condensers could be thrown in parallel with either arm of the particular portion of the bridge being balanced, but it was later found that the adjustment of a condenser in any part of the system, *e. g.*, in parallel with R_3 or CD, sufficed to sharpen the minima in balancing the other portions. Alternating current of approximately 1000 cycles was obtained from a Siemens-Schuchert alternator, the external circuit being tuned with suitable capacities. The necessary shielding and grounding was provided. A hot wire milliammeter and a direct current milliammeter served to indicate the currents employed, though the alternating currents were too small to be accurately measured by the instrument used.

The alternating current in the cell was reduced to the lowest value consistent with sharp minima. It was on continously during the measurements, the heating effect being estimated by doubling the current in the cell. The correction, to be added to the resistance found for the lower current is then $^1/_3$ of the difference between the resistances at the higher and at the lower currents. This correction was negligible in several instances, was about 0.01% in many, and did not exceed 0.03% in any of the measurements.

The direct currents varied between 0.02 and 0.5 milliampere, and being on momentarily only were without appreciable heating effect. As the galvanometer circuit was always closed, deflections being noted when the main current was passed through the bridge, "parasitic" effects were eliminated. In balancing, the first deflection of the galvanometer was used, since the polarizing effect of the main current, in spite of the calomel electrodes, caused a change in the apparent resistance of the whole cell (through of course not in R). Though this reversal of direction of throw of the galvanometer appeared quickly, there was no difficulty experienced in making settings with the required accuracy.

The thermostat was an oil bath constant to 0.005°, the temperature of which was read on a Beckmann thermometer which had been compared with 3 standard Baudin thermometers.

The mean of the 15 alternating current observations which were made using N potassium chloride solution gives 5033.7 ohms as the cell resistance, the average deviation of individual results from the mean being 0.02%. Between each pair of alternating current measurements, a direct current measurement on the same solution was taken, the resulting value of the resistance being 5037.1 ohms, ±0.015%. The latter it is seen is in agreement with the result previously obtained.

Direct Comparison of Alternating and Direct Current Conductivities of Potassium Chloride and Lithium Chloride Solutions.

The individual measurement above were in general more or less independent, involving numerous settings of different resistances, etc. To eliminate as many variable factors as possible a few measurements were made, in which all preliminary adjustments were determined before the final readings were taken. For example, with nearly correct settings of the resistances, the slide wire would be adjusted for balance, the settings of R_1, R_2 and R_3 accurately made as desribed above, and the slide wire setting again made, all with alternating current. Changing immediately to direct current, the new setting of the wire and minor adjustments, all in the unit dials, of the resistances could be quickly made.

The difference, direct minus alternating current resistance, found by this method in a series of 4 measurements with *N* potassium chloride solution varied between 0.004 and 0.058%, the average being 0.028%. In a set of 6 experiments with 10 *N* lithium chloride, in which the bath temperature was constant to 0.002° and heating effects were negligible, one negative deviation of 0.012% was obtained, the remainder falling between +0.014 and +0.039%, the average of all being +0.018%. Tests of the same method of comparison using metallic resistances of the same magnitude and approximately equivalent capacity in place of the electrolytic cell showed agreement by the two methods to 0.004%, the direct current resistance being apparently larger by this amount than the alternating.

Discussion.

The numerical results of the preceding absolute measurements are collected and compared with those of Kohlrausch in Table I.

TABLE I.

Conductivities at 25°.

Solution	Method	Conductivity
N KCl	D. C. Potentiometric	0.11168
N KCl	D. C. Modified Bridge	0.11170
N KCl	A. C. Modified Bridge	0.11177
N KCl	Value of Kohlrausch	0.11180
Max. Cond. H_2SO_4	D. C. Potentiometric	0.8242
Max. Cond. H_2SO_4	Value of Kohlrausch	0.8257

The agreement of the Kohlrausch values with all the others in the table is probably within the combined experimental error of the 2 sets of results. The divergence of 0.068% between the alternating and direct current values obtained in this work cannot, however, all be ascribed to the accidental error, ±0.02% in each measurement. After allowing for these chance errors the difference of about 0.03% which remains between the 2 values is of the same order as that found in the most direct comparisons which could be made, and is in the direction anticipated. The differences found in the direct comparisons are, therefore, believed to show the order of magnitude of a real effect, which is however too small to be of consequence in any ordinary measurements or calculations, and too small to be accurately determined with the facilities available in this work.

The failure of the difference experimentally found to equal in magnitude that given by the rough calculation referred to in the introduction cannot be definitely "localized" in the failure of any one of the assumptions involved regarding the number and moments of the polar aggregates pictured. The results, therefore, do not offer any evidence as to the state of electrolytes in solution. Considered in conjunction with the results of Sheldon, whose conclusion from a large number of less accurate experiments may be regarded as verified by the few more precise measurements described here, they indicate that the effect is too small at all concentrations to permit a study of this question, at least at low frequencies. The frequency at which the assumed maximum (*B* in Fig. 1) occurs is not known. If it can be located and if the effect there is appreciably larger than at 1000 cycles, a study of the change of the effect with concentration might contribute definite evidence concerning dissociation.

The accuracy of the absolute conductivities given above is of the order of 0.05%, which is probably about that of the measurements of Kohlrausch. That true conductivities of great accuracy are not often required is probably responsible for the fact that the experiments of Kohlrausch with potassium chloride, and other standard solutions, have not been repeated, introducing the more recent refinements of technique. The desirability of such a repetition has nevertheless been suggested by several authors. It seems in order to point out in this connection that if such a work is undertaken it should, for the sake of added definiteness, be paralleled with direct current measurements made with the high precision of which they are capable.

Summary.

In this paper it is suggested that the conductivity of solutions of electrolytes should be smaller at zero frequency than at any frequency in a certain range (of unknown limit) immediately above zero. Various measurements made to test this idea are described. It is concluded that the difference between direct current conductivities and those at 1000 cycles does not exceed 0.02–0.03% in the cases studied, but is in the expected direction. Incidentally, the conductivity of *N* potassium chloride at 25° given by Kohlrausch is confirmed, within 0.1%, by the measurements made here.

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NOTE.

The Use of Potassium Hydrogen Phthalate as a Standard in Alkalimetry.—In 2 recent papers Professor Hendrixson has shown the advantage of potassium hydrogen phthalate as a standard in alkalimetry.[1] Since this substance has been in use in my laboratory for 15 years (I advocated its use as a standard first in a paper read before the New York Section of the American Chemical Society, on January 8, 1904, and later in a published article in 1915,[2] it is gratifying even at this late date to have its merits recognized.

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[1] THIS JOURAL, **37**, 2352 (1915) and **42**, 724 (1920). In the former my original paper is referred to, but in the latter, undoubtedly by an oversight, this has not been done. Patten, Johnson and Mains (*ibid.*, **40**, 1156 (1918)) quote almost verbatim from my article without acknowledgment.

[2] *J. Ind. Eng. Chem.*, **7**, 29 (1915.)