ON THE DIELECTRIC CONSTANT OF DILUTE ELECTROLYTIC SOLUTIONS.

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IN 1892 E. Cohn¹ published the results of a series of determinations of the refractive index of water and dilute solutions of sodium chloride for electromagnetic waves of frequency about 10^8 per second. With an exciter of the well-known Hertz type he set up a system of stationary waves along two parallel wires suspended partly in air and partly in a long tank containing water or a salt solution. A comparison of the wave-lengths in the two sections of the wires, determined by a modification of Ruben's bolometer method, gave the results tabulated below where λ is the conductivity of the water or solution, l_a the half wave-length in air, l_w the half wave-length in water or the solution, and n the index of refraction. The temperature was always between 16.8° and 17.2° .

Substance.	$\lambda \times 10^6$	l_a	l_w	n	n^2
Water.	7.9	292.4	34.1	8.57	73.5
NaCl solution.	140.0	292.4	33.8	8.65	74.8
“	484.0	292.4	33.0	8.86	78.5

When the conductivity was greater than 532×10^6 he was unable to determine the position of the nodes in the solution owing to the increased damping of the oscillations.

A much more extensive and thorough investigation of the same subject, by a similar method, was published by P. Drude² in 1896. He used an oscillator of the Blondlot type and determined the position of the nodes along two parallel wires by the aid of Zehnder's vacuum tube. Great care was taken to develop a method of observation as free as possible from consistent errors and to apply suit-

¹ E. Cohn, Wied. Ann., 45, p. 370, 1892.

² P. Drude, Wied. Ann., 59, p. 17, 1896.

able corrections for such errors as could not be eliminated. Containing vessels, for the liquids experimented upon, of various dimensions and materials were tried and their effect on the results determined. After a comprehensive series of observations he was led to the conclusion that, up to a conductivity $\lambda = 5.3 \times 10^{-3}$, the square of the index of refraction of a solution varies less than one per cent. from the value for pure water. Solutions of copper sulphate and sodium chloride were used and the frequency of the electromagnetic waves was about 4×10^8 per second. For higher conductivities he found that n^2 decreased when the concentration was increased and reached a value about 10 per cent. less than that for pure water when λ equalled 40×10^{-3} .

In 1899 W. D. Coolidge,¹ using Drude's method, found the wave-length in water and in a copper sulphate solution of 6.5 times as great conductivity to be the same within 0.2 mm. at a temperature 19.2°. His mean result for the half wave-length in water was 66.184 cm., and in the CuSO_4 solution 66.202 cm.

Ernest Lecher,² in a footnote to an article on the "Measurement of Dielectric Constants by Means of Hertz Oscillations," states that the capacity of a condenser, measured by his method with Ruhmkorff oscillations, was just the same whether a vessel between its plates contained distilled water or a ten per cent. solution of sulphuric acid. The condenser plates were 28 cm. apart and the vessel containing the liquid was 27 cm. long.

E. B. Rosa³ in 1891 measured the force between a fixed and a movable electrode by means of a torsion balance and found that it decreased when hydrant water or minute quantities of acid or copper sulphate were added to the distilled water surrounding the electrodes. The difference of potential required for these measurements was furnished by a gravity battery and was mechanically reversed about fifty times per second. He thinks that the observed decrease in force was due to polarization of the electrodes.

The investigations of Drude and Coolidge indicate that the index of refraction of a dilute electrolytic solution, for electromagnetic

¹ W. D. Coolidge, Wied. Ann., 69, p. 134, 1899.

² Ernest Lecher, Wied. Ann., 42, p. 152, 1891; Phil. Mag. (5), 31, p. 181, 1891.

³ E. B. Rosa, Phil. Mag. (5), 31, p. 188, 1891.

waves, is independent of the concentration and the results of Cohn do not appear of sufficient weight to controvert this conclusion. Hence, assuming Maxwell's relation $k = n^2$, we might expect the dielectric constant of such a solution to be the same as that of pure water. But since this relation has been shown to fail in many instances, this deduction cannot be rigorously maintained without corroborative evidence from direct determinations of the dielectric constants of solutions. Published results of such determinations are meagre and inadequate, but they indicate that the change in dielectric constant with concentration is very small in comparison with the corresponding change in conductivity.

After a preliminary experimental and theoretical study of several of the best known direct methods, it was decided that small variations in dielectric constant could be most accurately determined by measuring the force between two electrodes immersed in the solution and maintained in the same relative position. The principal sources of error in such a method may be expected to arise from the polarization of the electrodes, from changes in their relative position, due to convection currents in the liquid or to inaccuracies in adjustment, and from errors in determining their difference in potential. The extent to which these difficulties have been overcome will appear in the following discussion. The first apparatus that gave intelligible results consisted of two electrometers, constructed on the attracted disk type, connected in parallel between the earth and one terminal of the spark-gap of a Hertzian plate-oscillator, having a frequency of about 4×10^7 vibrations per second.

The movable electrode or needle of one of the electrometers was shaped like the longitudinal section of a dumb-bell and suspended at its center of gravity by a fine platinum rhodium wire. The aluminum disks, of which it was made, were 3.8 cm. in diameter and 0.27 mm. thick, and their centers were 5 cm. apart in a horizontal line. The plane of the needle was vertical, and, in the zero position, parallel to and midway between the planes of the two fixed electrodes. These electrodes were slightly greater in area than the disks, and were placed adjacent to opposite ends of the needle, so that when charged they tended to rotate it in the same direction. An inverted glass bell-jar was clamped against the lower surface of the bed-plate

of the instrument and filled nearly to the level of the electrodes with strong sulphuric acid to absorb the moisture from the inclosed air. A small glass rod was suspended from the center of the needle by a platinum wire, and served to damp its vibrations. The other electrometer was constructed in essentially the same way, except that the electrodes were copper cylinders, about 2.9 mm. in diameter, with their axes lying in a horizontal plane and the acid and damper were dispensed with. A funnel passing through a hole in the bed-plate permitted the introduction of the liquid experimented upon, and a stop-cock in the bottom of the bell-jar facilitated its removal.

Both suspensions were provided with concave mirrors so adjusted that, when the needles were in the zero position, the two images of an illuminated wire, placed above the center of a scale some distance in front of the electrometers, were superposed on the middle division of the scale. When the oscillator was put in action both images were deflected from the center in the same direction and after their position became sufficiently steady they were caused to return to the center by suitably turning the torsion heads at the top of the suspensions. The action of the oscillator was then interrupted and the angles of torsion calculated from the resulting scale deflection of the images. When a sufficient number of similar independent observations had been made the solution in the second electrometer was changed and the operation repeated.

Owing to variations in the intensity of the oscillating current and to irregularities in the intervals between the wave trains sent through the electrometers it was at first found quite impossible to bring the two images together on the central division of the scale. The former difficulty was due to the varying condition of the surfaces of the spark balls of the oscillator and was to a great extent eliminated by rotating these balls at a high speed in opposite directions in a plane parallel to the spark gap. This operation apparently produced an effect similar to that of a strong air blast though the gap or of a strong magnetic field perpendicular to it and in the present instance was much more convenient than either of these devices. The latter difficulty was due to irregularities in the action of the interrupter to the induction coil that energized the oscillator. After extensive experiments with various well-known

forms of break, the following construction was found to give by far the most satisfactory results. A german silver wire, 0.8 mm. in diameter and 88 cm. long, was stretched between the poles of a powerful horseshoe magnet, and a platinum mercury contact was attached to its center and very near the magnet. The primary current of the induction coil was passed through this wire in such a direction that it was raised by the magnetic field and the circuit was broken. The tension of the wire could be varied at will through a long range by a guitar string winch, and the relative time of closed and open circuit could be varied by raising or lowering the mercury cup by a screw adjustment. The mercury was covered with alcohol, and a Willyoung adjustable condenser was connected in parallel with the contact. When the instrument was in good condition and properly adjusted no spark was produced at the break, and the interruption could be maintained regular for an indefinite time. This form of break has been used by several investigators, but I am uncertain who first introduced it.

With these appliances the two images could be adjusted to the center of scale within an error of one mm., but they could be held there only a short time. Calling A the observed angle of torsion for the electrometer containing the solution and B that for the other electrometer the ratio A/B is proportional to the ratio of the forces acting on the needles when in the zero position and any change in this ratio when the solution is changed indicates a corresponding difference in the dielectric constants of the solutions. Distilled water of conductivity about 4×10^{-6} and ten copper sulphate solutions varying in concentration from 5×10^{-5} to 4×10^{-4} gram equivalents per liter were tested in this way. The values for A/B thus obtained were very irregular not only for the different solutions but to a slightly less extent for the same solution. The average values for the very dilute solutions showed a small irregular increase with the conductivity but when the concentration was greater than about 2×10^{-4} they were irregularly distributed about the mean value for distilled water. The temperature was so nearly constant during the series of observations that the irregularities could not be attributed to its variations and it seemed possible that they might be due to changes in the constant of the electrometer, caused by

completely emptying and refilling it between each set of observations, or to corrosion of the copper electrodes. These electrodes were consequently replaced by platinum ones of a similar construction and the solutions were made in the electrometer itself, by adding small quantities of a solution of copper sulphate to the water it contained, thus leaving the suspended system entirely undisturbed. After each addition of the salt sufficient time was allowed to elapse for the solution to become uniform before observations were undertaken. The results were similar to those before obtained and only slightly less irregular. They are graphically represented in Fig. 1

Fig. 1.

where the abscissas are proportional to the concentration N in gram equivalents per liter and the ordinates are proportional to the ratio A/B .

Although these results indicate a slight increase of dielectric constant with the concentration the method appears incapable of giving a trustworthy determination of the relation. This failure is believed to be due to several causes. In the first place the oscillator became less regular in its action as the conductivity of the solutions increased and frequently ceased to act altogether so that some of the observations may have been made with Ruhmkorff in place of Hertzian currents. In this case, on account of the small superficial area of the electrodes, an appreciable polarization may have been

produced. After some of the settings a slow drift of the image, from the electrometer containing the solution, was noticed that may have been due to the subsidence of such a polarization. At all events the direction of the drift was harmonious with such an explanation. Small convection currents in the air electrometer or slight brush discharges from the comparatively sharp edges of the needle may have introduced irregular errors. Furthermore the fixed and movable electrodes of this instrument were placed very near together in order to make its capacity nearly equal to that of the other electrometer and it is obvious that small errors in the position of the needle would produce relatively large errors in the observed force. Since the difficulty experienced in setting the needle in the zero position increased with the conductivity of the solution this source of error probably accounts for a large part of the observed irregularity. It is apparent that errors of setting would have had less effect on the result if electrometers of the quadrant type had been used in place of those of the attracted disk type. The latter type was adopted because I had been unable to devise a high frequency oscillator that would produce wave trains of sufficient energy to cause readable deflections with the quadrant form and with low frequencies polarization completely masked the results. A slight change in one of the oscillators already tried, without success, obviated this difficulty and after some further preliminary work the disposition of apparatus about to be described was adopted and found to give satisfactory results.

Fig. 2 is a diagram of the oscillating system and electrometer

Fig. 2.

connections. Two large Leyden jars L , L' were placed on glass insulating stands and their outside coatings connected to an adjustable spark gap S . The parallel parts of these connections were brass rods, about 12 mm. in diameter, 20 cm. long and 10 cm.

apart, fitted with right angle clamps at their free ends that supported shorter rods 6 mm. in diameter and terminating in brass balls 2.3 cm. in diameter. The inside coatings of the jars were connected with two parallel copper wires, about eight meters long and 20 cm. apart, that extended in an inclined plane from the oscillator to the ceiling of the room. One pair of quadrants, the needle and the brass case of each of the electrometers *A* and *B* were connected together and to a point *x* on one of the parallel wires about 2.5 meters from *L*. The remaining quadrants were insulated from the case and connected to the point *y* on the other wire equidistant from *L*'. A bridge *pp'* was arranged to slide freely on the wires and its motion was controlled by a flexible cord passing over pulleys in the ceiling of the room and extending to the left hand end of the observing scale. When it was in contact with *xy* the observed electrometer deflections were very small, but as it was drawn away they gradually increased and finally exceeded the length of the scale. The frequency of electrical oscillation of the system was about 10^6 vibrations per second and it was not appreciably affected by the changes in position of the bridge necessary to produce any desired deflection within the limits of the scale. When first set up the inside coatings of the jars were connected to the spark gap and the outside coatings to the parallel wires, but with this arrangement the energy of the oscillations was so small or the damping so great that no deflection could be obtained when the conductivity of the liquid in either electrometer was greater than that of pure water. With the reverse connection appreciable deflections were produced in liquids of conductivity as high as that of a decinormal solution of copper sulphate. The cause of this great difference in action is not apparent, but it may be due to differences in effective insulation.

The two electrometers *A* and *B* were made as near alike as possible and each was filled with water, or a solution, so that their electrostatic capacities were nearly equal. The connecting wires for corresponding parts were of equal length and diameter and were so arranged that the two branches of the circuit had nearly the same self-induction. Each electrometer was supported by a brass bed plate, 15 cm. in diameter and 5 mm. thick, rigidly attached, by means of three leveling screws, to a substantial wooden frame that

was held in position on a brick pier by a heavy weight. A brass tube 2 cm. in diameter and 30 cm. long was supported over a hole in the center of the plate by a flange and shoulder, and carried at its upper end a torsion head from which the needle was suspended by a platinum rhodium wire about 20 cm. long and 0.05 mm. in diameter. A small rectangular window near the base of this tube was closed by plate glass and served to admit light to a small concave mirror on the suspended system. The fixed electrodes were in the form of shortened quadrants of a cylindrical surface 9 cm. in diameter and 3 cm. high and were supported by brass shanks 15 mm. in diameter that passed up through hard rubber plugs screwed into holes in the bed plate. The insulating spaces between their adjacent edges were about 4 mm. wide. The needle was bent to coincide with two opposite quadrants of a concentric cylindrical surface 7 cm. in diameter and 2 cm. high and the shank by which it was supported carried a small binding screw at its upper extremity by which it was clamped to the lower end of a short brass wire soldered to the suspending wire. Both cylindrical surfaces were normal to the bed plate and their axes coincided with the suspension. The needle and electrodes were cut from sheet German silver 0.2 mm. thick and were thoroughly plated with platinum and platinized before being bent into shape. They were so constructed that all soldered connections came above the surface of the liquid in the electrometer. A glass bell-jar, about 11 cm. in diameter and 700 cc. capacity, with a stopcock in its closed end was clamped in an inverted position against the under surface of the bed plate and surrounded by a cylindrical copper vessel that served to shield the electrodes from external electrostatic influences and to convey a current of water from the city mains for the purpose of regulating the temperature when necessary. Generally, however, the temperature of the room was more constant than that of the water and the latter device was seldom used. The temperature was indicated by a mercury thermometer supported by the bed plate with its bulb very near the fixed electrodes and as far as possible from the needle.

The suspensions of the two electrometers were 30.5 cm. apart and the line joining them was parallel to and 177.8 cm. in front of an observing scale, 150 cm. long, supported by a wooden stand on

a brick pier and so placed laterally that a normal erected to its central division would pass midway between the electrometers. Directly above this normal a fine steel wire was stretched vertically across a small window in the supporting stand and illuminated by an incandescent electric lamp and a condensing lens. The concave mirrors on the suspensions were so adjusted that the two images of this wire were superposed on the central scale division when the electrometer needles were symmetrically situated with respect to the fixed electrodes. The images were very sharp and slightly less in width than the division marks of the scale, so that readings could be easily made to fractions of 1 mm. when desirable. The motion of each torsion head was controlled by an endless belt of fine steel wire that engaged a wooden lever arm attached to the head and, after passing over a system of fixed pulleys, circulated several times about a small wooden reel attached to the scale support. The belts were kept taut by brass spiral springs and worked so smoothly when the reels were turned that no tremor of the images were observed during the motion. The stretched wire interrupter described above, the condenser, and the switch for the primary circuit of the induction coil were placed within easy reach of the observer at the scale. The electrometers and scale were enclosed in a tent of dark cloth supported by a wooden frame attached to the floor of the room and mechanically insulated from the brick piers.

The relative conductivity of the solutions used was determined by Kohlrausch's telephone method with the aid of two pairs of small platinum test electrodes similar to the "Tauchelektroden" for poorly conducting liquids, described by Kohlrausch and Holborn.¹ These electrodes were supported by the bed plates of the electrometers, in a position diametrically opposite to the thermometers, and were insulated from them by glass tubes covered with paraffin. They were kept in a fixed position throughout the investigation and could be insulated or connected to either arm of the resistance bridge by suitably placing copper connectors in a mercury commutator constructed from a large block of paraffin.

After carefully cleaning the electrodes and bell-jars the electrometers were assembled and filled with distilled water until its sur-

¹ Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," edition of 1898, p. 18.

face was about one cm. above the top edges of the electrodes and 3 cm. below the bed plate. Determinations of the conductivity of the water showed that it increased about 30 per cent. per day and this was judged to be due to imperfect removal of the salts of the plating bath from the surface of the platinized electrodes by the extended washing in hot and cold water to which they had been subjected. Consequently the electrometers were allowed to remain undisturbed about one week and were then refilled with fresh distilled water. This operation was repeated at nearly equal intervals for three months and measurements then show that the rate of increase in conductivity had been greatly reduced. Nearly equal volumes of all the solutions investigated were used so that the free surface always occupied the same position and produced the same effect on the measurements.

The method of operation in taking the observations was as follows: The image of the illuminated wire due to one of the electrometers (say *B*) was set at a convenient position on the scale. The interrupter was started and when its pitch became regular the bridge *pp'* was moved along the parallel wires till the image *B* came to the central scale division (75th in this instance), keeping *B* stationary by slight back and forward motions of the bridge, corresponding to the irregularities in the intensity of the oscillating current, the image from electrometer *A* was brought into coincidence with it by turning the proper torsion head. This adjustment could be easily made to a small fraction of a millimeter and maintained constant for an indefinite time by slight motions of the bridge. The primary circuit of the induction coil was then broken and after the images had come to rest their position on the scale was recorded. Observations of the temperature and conductivity of the solutions in the electrometers were made and recorded. From six to ten sets of observations were taken in this manner, starting each time with the image from *B* in a different position, in order to obviate prejudice in making the settings. About 2 cc. of a centinormal solution of copper sulphate were then added to the water in electrometer *A* and the apparatus allowed to remain undisturbed for about twenty-four hours in order that the salt might become uniformly distributed. On succeeding days similar series of observations were made and the concentration

of the solution was increased by successive additions of from 2 cc. to 4 cc. of centinormal or decinormal solutions of copper sulphate until six different solutions had been tested. The solution in *A* was then kept constant and eight different copper sulphate solutions were formed in *B* and tested in a similar manner. After this series of observations *B* was emptied, thoroughly rinsed out and refilled with fresh distilled water. Similar sets of observations were made on this water and on five different potassium chloride solutions formed as described above. It will be noticed that in the first series of observations the solutions in *A* were compared with water in *B*, while in the last two series the comparison was between various solutions in *B* and a constant solution in *A*. This procedure was adopted since it was found that the conductivity of the dilute solution in *A* was much more constant than that of the water.

When the two images were superposed on the 75th scale division the needles of the electrometers were symmetrically situated with respect to the fixed electrodes and the electrostatic forces acting on them were balanced by the torsion of the suspending wires. Since the displacements were always small the torsional couples produced by the wires were proportional to the angles through which they were twisted and when the current was turned off the images were deflected along the scale a distance depending on the magnitude of the torsion. The formulæ ordinarily used in reducing scale readings to angular measure are obviously inapplicable when the apparatus is arranged as above described since the normals to the minors are not perpendicular to the scale when the images are superposed on the 75th division. It is, however, easy to show that the angle of torsion δ_a corresponding to a deflection of the image from electrometer *A* amounting to x_a scale divisions is given by the expression

$$\delta_a = \frac{1}{2} \tan^{-1} \frac{S}{1 + T \frac{x_a}{A^2}} \cdot \frac{x_a}{A^2}$$

where *S* is the normal distance between the scale and the line joining the electrometer suspensions, *A* the distance from the minor to the 75th scale division, *T* one half the distance between the suspen-

sions, and x_a is measured on the opposite side of the normal to the 75th division to that on which the electrometer is situated. Similarly for a deflection x_b on the same side of this normal as electrometer B .

$$\delta_\beta = \frac{1}{2} \tan^{-1} \frac{S}{1 - T \frac{x_b}{A^2}} \cdot \frac{x_b}{A^2}.$$

Expanding these expressions in ascending powers of x/A^2

$$\begin{aligned}\delta_a &= \frac{S}{2A^2} x_a - \frac{ST}{2A^4} x_a^2 - \frac{S(S^2 - 3T^2)}{6A^6} x_a^3 + \dots \\ \delta_\beta &= \frac{S}{2A^2} x_b + \frac{ST}{2A^4} x_b^2 - \frac{S(S^2 - 3T^2)}{6A^6} x_b^3 + \dots\end{aligned}$$

From the dimensions of the apparatus it follows that $S = 177.8$ cm., $T = 15.25$ cm. and $A = 178.5$ cm. Substituting these values

$$\begin{aligned}\delta_a \times 10^4 &= 27.9 x_a - .0134 x_a^2 - .000283 x_a^3 \\ \delta_\beta \times 10^4 &= 27.9 x_b + .0134 x_b^2 - .000283 x_b^3.\end{aligned}$$

A table of the values of $\frac{1}{2}\delta_a \times 10^4$ and $\frac{1}{2}\delta_\beta \times 10^4$ was calculated from these formulæ for values of x_a and x_b varying by one or two centimeters from zero to 60 cm. and the results were plotted to form curves with ordinates proportional to the angles and abscissas proportional to the deflections. The reduction of the observations was made with the aid of these curves and a series of calculations for points well distributed along the curves showed that the results obtained by this method never differed by so much as one tenth of one per cent. from the results calculated directly from the formulæ.

Since the two electrometers were symmetrically connected to the same points of the parallel wires they were acted upon by equal differences of potential when the oscillator was in action. Hence, if δ_a and δ_β represent the observed angles of torsion when the dielectric constants of the contained liquids are κ_a and κ_β respectively it is obvious that

$$\frac{\delta_a}{\delta_\beta} = \frac{C_a \kappa_a}{C_\beta \kappa_\beta} \quad (1)$$

where C_a and C_β are constants depending on the dimensions of the electrometers and the elastic properties of the suspending wires. Similarly for angles δ_a' and δ_β' corresponding to liquids of dielectric constant κ_a' and κ_β' ,

$$\frac{\delta_a'}{\delta_\beta'} = \frac{C_a \kappa_a'}{C_\beta \kappa_\beta'}. \quad (2)$$

Hence dividing (2) by (1)

$$\frac{\delta_a'}{\delta_\beta'} \cdot \frac{\delta_\beta}{\delta_a} = \frac{\kappa_a'}{\kappa_a} \cdot \frac{\kappa_\beta}{\kappa_\beta'} \quad (3)$$

from which either ratio κ_a'/κ_a or $\kappa_\beta/\kappa_\beta'$ can be determined when the other is known.

Owing to slight differences in the temperature of the liquids experimented upon it become necessary to reduce the observations to some standard temperature and the necessary corrections were calculated in the following manner. Write

$$\kappa_a = \kappa (1 + \beta_a t_a)$$

where κ_a is the value of κ when the liquid is at temperature t_a and

$$\beta_a = \frac{1}{\kappa} \frac{\partial \kappa}{\partial t}.$$

Similar expressions for the other κ 's may be written

$$\begin{aligned} \kappa_a' &= \kappa' (1 + \beta_a' t_a') \\ \kappa_\beta &= \kappa_0 (1 + \beta_\beta t_\beta) \\ \kappa_\beta' &= \kappa_0' (1 + \beta_\beta' t_\beta'). \end{aligned}$$

Since the temperature differences were small and the liquids used were all water or moderately dilute solutions, the temperature coefficients β_a , β_a' , etc., were assumed to be the same and equal to that for pure water at the mean temperature of the observations. Granting this assumption

$$\frac{\kappa_a}{\kappa_\beta} = \frac{\kappa}{\kappa_0} \left\{ 1 + \beta(t_a - t_\beta) \right\}$$

and

$$\frac{\kappa_a'}{\kappa_\beta'} = \frac{\kappa'}{\kappa_0'} \{ 1 + \beta(t_a' - t_\beta') \}.$$

Hence (3) becomes

$$\frac{\delta_a'}{\delta_\beta'} \cdot \frac{\delta_\beta}{\delta_a} = \frac{\kappa'}{\kappa} \cdot \frac{\kappa_0}{\kappa_0'} \cdot \frac{1 + \beta(t_a' - t_\beta')}{1 + \beta(t_a - t_\beta)}. \quad (4)$$

When B was used as the comparison electrometer the liquid in it was left undisturbed and if we neglect the possibility of small changes in its dielectric constant due to a slight increase in conductivity we have as a first approximation $\kappa_0 = \kappa'_0$ and

$$\frac{\kappa'}{\kappa} = \frac{\delta'_a}{\delta'_\beta} \cdot \frac{\delta_\beta}{\delta_a} \cdot \frac{1 + \beta(t_a - t_\beta)}{1 + \beta(t'_a - t'_\beta)} \quad (5)$$

where κ' is the dielectric constant of the solution experimented upon and κ that of the water from which it was made. β was taken equal to $-.004$ which is very nearly the mean of the best published determinations of this constant for temperature changes similar to those observed. When the functions of the two electrometers are reversed and A is used as comparison electrometer the reduction formula is the same as (5) with the α 's and β 's interchanged.

After the first series of observations had been made and reduced it was found that the value of the ratio δ_a/δ_β depended on the manner in which the test electrodes were connected to the resistance bridge. This effect was undoubtedly due to currents induced in the connecting wires by the oscillating current in the electrometer circuit and the following observations show that it was constant so long as the connections were unchanged. Three sets of connections were used, P_1 , test electrodes in A and B connected to adjacent bridge arms; P_2 , electrodes in A and a rheostat similarly connected, and P_3 , electrodes in B and a rheostat similarly connected. When both electrometers were filled with water at temperature $25.^\circ 7$ the observations lead to the values of δ_a/δ_β given in Table I.

TABLE I.

Connection.	P_1	P_3
$\left. \begin{array}{c} \delta_a \\ \delta_\beta \end{array} \right\}$	1.045	1.031
	1.044	1.033
	1.047	1.037
	1.048	1.035
	1.045	1.033
Mean	1.046	1.034

The scale deflections from which these results were calculated range from $x_a = 29.1$ cm. to $x_a = 56.9$ cm. and from $x_b = 27.4$ cm.

to $x_b = 51.5$ cm. Unfortunately this set of observations did not involve the connection P_2 and the corresponding value of δ_a/δ_β could only be obtained by calculation from the mean value of δ_a'/δ_β' corresponding to a solution for which the ratio κ'/κ had been determined from the observations with connections P_1 and P_3 . The solution for which the errors of observation were smallest was adopted for this purpose and the result thus obtained was $\delta_a/\delta_\beta = 1.05$ for connection P_2 . Table II. exhibits the observations and calculated results for a solution of copper sulphate of conductivity 3.86 times that of the water from which it was made. The letters in the column headed C indicate the connection of the test electrodes that existed when the corresponding scale deflections x_a and x_b were observed and the given values of κ'/κ were calculated from δ_a'/δ_β' with the aid of the value of δ_a/δ_β for corresponding

TABLE II.

x_a	x_b	δ_a'/δ_β'	C	κ'/κ
56.3	51.2	1.037	P_2	.987
53.7	49.6	1.024	P_3	.990
51.6	46.6	1.050	P_2	1.000
47.2	43.6	1.033	P_3	.999
44.8	40.7	1.054	P_2	1.002
40.7	37.8	1.034	P_3	1.000
39.3	35.9	1.050	P_2	1.000
35.8	33.3	1.036	P_3	1.003
34.1	31.3	1.049	P_2	.999
39.5	36.8	1.033	P_3	.999

connections. The mean error of the individual values of κ'/κ , calculated from the average value in the usual manner, is .0052 and since this is somewhat greater than the average of the mean errors for the other sets of observations, the results given in the table convey a fair idea of the general accuracy of the observations and reductions.

During the last two series of observations, A was used as comparison electrometer, and contained a dilute solution of copper sulphate. The test electrodes were always insulated while the electrometer settings were made, and hence but one value of δ_a/δ_β was obtained when B was filled with distilled water. More or less ex-

tensive sets of observations on various solutions of copper sulphate and potassium chloride lead to the results given in Table III. The

TABLE III.

<i>D</i>	<i>S</i>	<i>t</i> ₁	<i>t</i> ₂	λ_1	λ_2	κ'/κ	<i>E</i>	<i>N</i>
2	CuSO ₄	26.0	26.0	1.11	1.69	.998	.0034	8
3	"	26.3	26.3	1.40	2.92	1.010	.0037	8
4	"	25.9	26.0	1.61	3.86	.998	.0052	10
5	"	25.2	25.3	1.74	4.68	1.003	.0028	10
6	"	24.3	24.3	1.73	4.64	1.002	.0053	6
8	"	23.9	23.9	2.00	5.63	1.009	.0021	9
9	CuSO ₄	23.8	23.8	1.04	2.95	1.000	.0024	10
10	"	22.9	22.9	1.04	3.62	1.004	.0023	10
11	"	23.1	23.1	1.12	4.29	1.006	.0028	8
12	"	23.0	23.1	1.16	7.07	1.003	.0052	8
13	"	22.1	22.5	1.15	10.62	1.002	.0046	7
15	"	23.6	24.0	1.27	18.45	.986	.0177	4
16	"	24.9	25.5	1.28	19.74	.994	.0059	7
17	"	25.2	25.9	1.30	32.45	1.007	.0180	6
19	KCl	25.3	25.3	1.10	3.87	.997	.0047	8
20	"	24.8	25.0	1.15	7.65	.986	.0023	6
22	"	25.1	25.7	1.25	11.68	.990	.0056	6
23	"	25.3	25.8	1.27	14.70	.989	.0046	6
24	"	25.5	25.9	1.31	20.79	.989	.0141	6

independent series of observations are separated by horizontal spaces, and the days of July, 1901, on which the observations were made are indicated in column *D*. The salts in the solutions examined appear under *S*. *t*₁ is the temperature of the solution in the comparison electrometer, and *t*₂ that of the solution in the test electrometer. λ_1 is the conductivity of the former solution relatively to its value when the ratio δ_a/δ_β was determined, and λ_2 is the conductivity of the latter solution relatively to that of the water from which it was made. κ'/κ is the mean of *N* independent determinations of the ratio between the dielectric constants of the latter solution and distilled water, and *E* is the mean error of the individual values of κ'/κ . These results were derived from the observations by equation (5), on the assumption that the dielectric constant of the liquid in the comparison electrometer remained constant, except for temperature changes, during the several series of observations. Hence, if κ'/κ

had been found to vary with λ_2 corrections would have been necessary on account of the observed variation in λ_1 . But, since λ_2 varied much more rapidly than λ_1 and the variations of κ'/κ from unity were of the same order of magnitude as the errors of observation, this correction becomes unnecessary. The uniformly low values obtained in the third series are probably due to an error of about one per cent. in the determination of the ratio δ_a/δ_β when the test electrometer contained distilled water.

The conductivity of the distilled water from which the solutions were made, expressed as the reciprocal of the resistance in ohms of a column one centimeter long and one square centimeter in section, was about 7×10^{-6} . Consequently the maximum conductivity of the solutions tested was not over 2.5×10^{-4} which, for the copper sulphate solutions, corresponds to a concentration of about 0.003 gram equivalents per liter.

Considering the low conductivity of the solutions, the large area of the electrodes, and the high frequency of the oscillating current, the polarization might be expected to be vanishingly small and in fact the observations gave no evidence of such a disturbance. The electrometer needles were nearly dead beat and the images from the mirrors on the suspensions always came to rest in fifteen or twenty seconds without the least sign of drift due to subsiding polarization. During the adjustment of the images to the central scale division no gradual variation of the forces acting on the needles such as would be produced by accumulating polarization was observed. On account of irregularities in the action of the oscillator some of the settings occupied much more time than others and hence offered an opportunity for polarization to produce an increased effect, but the results calculated from these observations never differed from those occupying less time by more than the ordinary errors of observation.

When the images had come to rest after the current was turned off they remained perfectly steady so long as the apparatus was left undisturbed. Consequently the convection currents in the liquids must have been inappreciable.

In order to determine whether the deflections were influenced by changes in the torsional rigidity of the suspending wires due to the

heating effect of the currents they transmitted the period of torsional vibration of the needle of electrometer *A* was determined by comparison with the pendulum of the laboratory clock with the aid of a double chronographic record. The mean of a large series of observations gave 5,965 seconds when no current was passing through the suspension and 5,967 seconds when it was conducting a current larger than that used during any of the electrometer settings. Since the difference between these values lies within the probable errors of observation it is evident that the heating effect was negligible.

An inspection of the values of κ'/κ given in Table III., is sufficient to show that they do not differ from unity by greater amounts than might have been expected if distilled water had been used in the electrometers throughout all the observations in place of the solutions actually used. Hence it is highly probable that the dielectric constant of dilute electrolytic solutions, of conductivity less than 2.5×10^{-4} , is the same as that of pure water in electric fields varying at the rate of 10^6 oscillations per second.

It is obvious that the degree of electrolytic dissociation of such solutions is very large and the observed lack of change in dielectric constant may be due to this fact but the point cannot be definitely decided until determinations have been made with much more concentrated solutions. Some such observations have been made but they are not sufficiently accurate to lead to definite results and I shall therefore defer the discussion of them until I have had time to carry out a more thorough investigation of the subject with an apparatus modified to render it more adaptable to measurements with highly conducting liquids.

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