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THE DIELECTRIC CONSTANT OF AQUEOUS SOLUTIONS.

By Elmer A. Harrington.

THE principle of the method for the determination of dielectric constants consists in comparing, by the application of the telephone in the Wheatstone bridge, the capacity of a dielectric trough with that of a glass condenser of variable capacity. This apparatus was first used for these purposes by Nernst,[1] who found that liquids of conductivities as large as 2.10^{-10} could be measured quite accurately. With much larger conductivities the disturbances due to polarization, as well as the difficulties of a comparatively complete compensation of conductivity, become very great.

Since the effect of a polarization capacity, like that of a resistance connected in parallel with a condenser, decreases as the frequency increases, we have here, as a means of avoiding these difficulties, the application of an alternating current of high frequency,[2] which one easily obtains from the oscillatory discharge of a condenser through a self-induction.

The Apparatus.

The arrangement of the apparatus is shown in the accompanying figure (Fig. 1). It consists essentially of two systems, the first of which is really a sending system, while the second may be thought of as a receiving system.

I is a large induction coil, the oscillations being produced by a Wehnelt interrupter. The spark-gap *S* charges the two equal and symmetrically-placed condensers C_1 and C_2. P_1 and P_2 are comparatively loosely coupled self-inductions made up of a few turns of large wire about coaxial cylinders. P_2 excites the Wheatstone bridge, which consists of two self-

[1] Nernst, Zeit. f. phys. Chem., 14, p. 622, 1894.

[2] Nernst, Wied. Ann., 60, 600, 1897.

inductions p_1 and p_2, and of two variable condensers of capacity c_1 and c_2.

Since the frequency of the current is of the order of 1.10^6 per second it is necessary to use a wave detector *W.D.* and a battery *B* with the telephone *T* to show a balance in the bridge. A detector was first applied in this connection by Nernst.[1] *K* is a blocking condenser (3.2 microfarads), placed in the detector circuit as indicated.

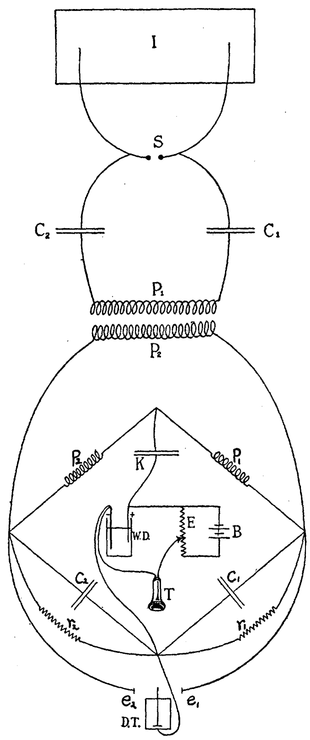

Fig. 1.

The dielectric trough *D.T.*, or condenser consists of a metal disc fixed at a certain distance from the bottom of the vessel, contains the liquid under investigation and may be connected in parallel first with c_1, and then with c_2, by means of the contacts e_1 and e_2.

The Transmitting Circuit.

An interrupter of the Wehnelt type was used in the primary circuit as it produced the most regular and uniform strengths of oscillations in the transmitting circuit.

An adjustable spark-gap *S* bought from the Clapp-Eastham Co., of Cambridge, was found to be most efficient and regular.

The condensers C_1 and C_2 are made up in such a manner as to minimize all brush discharges. The capacity of each condenser is 0.012 microfarad, and since they are connected in series, the capacity of the system is 0.006 microfarad.

The self-inductions P_1 and P_2 consist of 16 turns of large copper wire about coaxial cylinders of 19 cm. length and of 9 cm. and 13 cm. diameter respectively. Using the Fleming-Anderson bridge method of measuring self-inductions,[2] the following values were obtained:

$$P_1 = 1.5\cdot 10^4 \text{ cm.},\qquad P_2 = 2.6\cdot 10^4 \text{ cm.}$$

The maximum mutual induction between these two coils was found to be $M = 1.15\cdot 10^4$ cm. The coefficient of coupling is, therefore,

$$k = \frac{M}{\sqrt{P_1P_2}} = 0.58.$$

[1] Nernst, Ann. d. phys., 15, 836, 1904.

[2] Fleming, Wave Telegraphy, p. 143.

The mutual induction can be decreased by sliding P_1 along the common axis, but the best results are obtained when the ends of the helices are just even; the minimum in the telephone is then sharper and any noise that may be heard in the telephone more nearly disappears.

The Wheatstone Bridge.

Self-Inductions.—The self-inductions p_1 and p_2 are made equal because this theoretically simplest case is found to be the most advantageous one experimentally. Each consists of 50 turns of insulated wire about a wooden cylinder 9 cm. in diameter, forming a coil 10 cm. long. The inductances, according to the Fleming method, are

$$p_1 = p_2 = 2.27 \cdot 10^5 \text{ cm.}$$

The coils are placed with their axes vertical and about 46 cm. apart. No mutual induction between the two coils could be detected.

Measuring Condensers.—The variable condensers c_1 and c_2 (Fig. 5), are similar to those used by Turner,[1] but important modifications have been introduced. Each is made up of three accurately planed brass plates, of which the two outer ones are metallically connected by means of a brass strip. Thus the outer plates play the part of the front plate in the old model, while the inner plate forms with these a double condenser, and at the same time it is protected from the influence of surrounding conductors. The inner plate is connected with one end of the coil P_2, so that its potential is much higher than that of the outer plates, whose potential is always nearly that of the earth.

The dimensions of the brass plates are: length, 19.95 cm.; height 7.23 cm.; thickness, 0.47 cm. The distance between the plates is 0.349 cm., and it is kept constant by four little glass rods of that length. Each plate is held in position by four brass screws (two above and two below), which pass through the plate glass beds (0.8 cm. thick) on which the plates are mounted.

In order to insure good insulation the brass plates do not actually touch the glass bed, but are separated from it by four pieces of glass about 0.1 cm. thick and 0.4 cm. square. The glass rods pass loosely through holes in glass strips 0.2 cm. thick and 0.7 cm. wide, and of the same length as the brass plates, cemented edge-on to the glass beds midway between the brass plates. The glass plates slide along on these glass strips. In this way edge corrections are reduced to a minimum, as only that part of the space between the brass plates is used where the lines of force are fairly straight. Insulation is further improved by

[1] Turner, Zeit. f. phys. Chem., 35, 385, 1900.

raising the glass bed 5 cm. from the table by means of three pieces of plate glass cemented edge-on to the bottom of the bed.

The use of glass for the bed of the condenser is a decided improvement in the apparatus, as glass does not twist and warp as hard rubber does; and the methods described above, of obtaining the best possible insulation are rendered more simple by using nothing but glass and brass in constructing the apparatus.

The glass plates are of optical glass 25 cm. long, 6 cm. wide and 0.3250 cm. thick. Each glass plate is movable between the middle and one of the outer brass plates, and its displacement can be read off the glass scale on the bed by means of the vernier on the glass plate. When the brass plates are exactly parallel, and the glass plates are of uniform thickness, the displacements of the glass plates are proportional to the change of capacity. The displacements are evidently additive, as the double condenser really consists of two condensers connected in parallel; and the capacity of one of them is not affected at al by a change of the other. From the dimensions of these condensers we may calculate approximately their capacity. The minimum capacity is about 100 cm., while the average capacity may be taken as 260 cm.

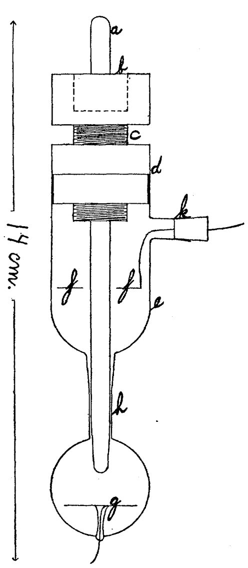

Fig. 2.

These condensers are placed on the table in an end-on position with their ends about 35 cm. apart. At this distance the effect of one condenser on the capacity of the other may be left out of account.

Compensating Resistances. — The compensating resistances r_1 and r_2 are like those used by Turner,[1] in which the distance between the electrodes remains constant, and the resistance is changed by pushing a glass rod into the constriction in the vessel and thus decreasing the area of cross section of the resistance liquid. The details are easily understood from the figure below.

The glass rod (*a*) fits closely in a cork (*b*) in the hard rubber screw (*c*), and yet it is easily displaced; the nut (*d*), also of hard rubber, is fixed in the glass tube (*e*). The electrode (*f*), is a platinum ring with a platinum wire attached; the other electrode (*g*) is fused into the glass at the bottom.

In order to obtain a sufficiently large variation of the resistance, the glass rod must fit as accurately as possible into the narrow part (*h*) of

[1] Turner, Zeit. f. phys. Chem., 35, 385, 1900.

the glass tube. The diameter of the rod is 0.6 cm., while the inner diameter of the tube is about ½ mm. larger. In order to allow a very exact setting when using the smallest resistances, the mouth of the tube (*h*) in the upper part of the vessel is made slightly conical and the rod is given a similarly conical form. The side-neck (*k*) serves to lead in the wire of the electrode (*f*).

The vessel is mounted in a wooden frame in such a way that the lower electrode (*g*) is about 4 cm. above the table. The vessel is then placed about 20 cm. from the measuring condenser. Polarization may be neglected with these comparatively large electrodes. Magnanini solution[1] is used as the compensating liquid on account of its low temperature coefficient. Another advantage of this form of apparatus is that the outer variable capacity is reduced practically to zero.

Dielectric Trough.—The dielectric trough *D.T.* is a modification of that used by Turner (*loc. cit.*). The figure below shows a cross section of the trough. The sides and bottom are of brass, silver plated inside and nickel plated outside. The cover is of glass, and it fits so well into the top of the trough that the whole trough may be picked up by the cover. In this way all sidewise motion is completely overcome. The hole (*a*) in the center of the cover is enough larger than the brass rod which passes through it, so that the rod does not touch the glass cover, but is held in position by the hard rubber cylinder (*b*) which is cemented to the cover. In the cover there is a second hole, (*c*) through which the liquid to be investigated may be introduced.

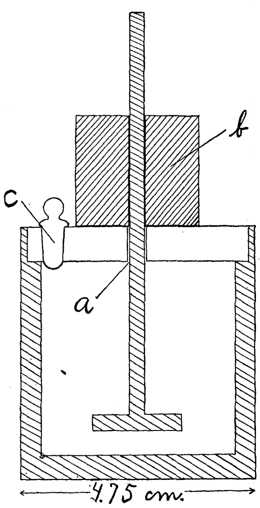

Fig. 3.

With a cover of glass, and a cylinder of hard rubber fastened on the top through which the rod passes easily but not too easily, the errors due to a sidewise movement of the rod in the cover of the trough, or of the cover itself on the top of the trough, are eliminated. The cover is not elastic and it is not affected by the vapor of the liquid in the trough.

The dielectric trough should be filled to two thirds or three fourths of its height. That is, the trough should be filled till no lines of force are drawn into the upper surface of the liquid. This will be the case when the surface of the liquid is in the direction of the lines of force. It is also evident that the trough must be filled to the same height in

[1] Magnanini, Zeit. f. Phys. Chem., 14, p. 622, 1894.

every case. In these experiments 30 c.c. of liquid were always introduced into the trough through the hole (*e*) by means of a pipette.

As it is difficult when using conducting solutions to keep the temperature of the trough sufficiently constant, it is found convenient to put the trough in a thick-walled brass cylinder, bored out so that the trough fits in snugly but easily (see Fig. 4). On account of the high conductivity of the brass there is practically no difference of temperature between the upper and lower parts, while the large mass of the cylinder gives a regular and slow exchange of heat with the surrounding air. In this way the temperature varies very slowly, and seldom changes more than 0.4°–0.5° during a series of readings. A hole is bored down into the brass and a thermometer placed in it gives the temperature to within 0.1°. The cylinder used is 6.4 cm. long and 7.8 cm. in diameter, the walls being 1.5 cm. thick.

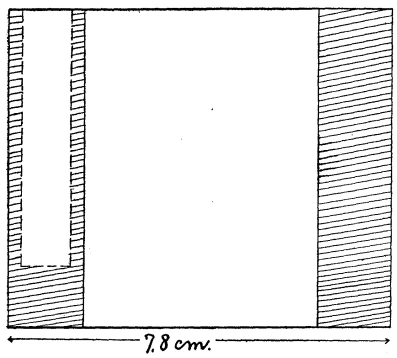

Fig. 4.

The dielectric trough and the brass cylinder are insulated from the table by being placed on a brass disc 5 cm. in diameter cemented to the top of a large piece of glass 7.5 cm. high. Good contact between the bottom of the trough and the disc is very important, because if air is between a condenser of small but finite capacity is introduced. The bottom of the trough and the top of the disc are therefore planed and scraped in order that the area of contact should be as large as possible.

The glass base can be slid from side to side along glass ways so that the rod of the dielectric trough touches the wire e_1 or e_2. In this way the trough can be connected in parallel with the measuring condensers c_1 or c_2, respectively, as the brass disc is always connected by wires to the outer brass plates of these condensers. By means of a glass rod frame e_1 and e_2 are kept in the same positions relatively to c_1 and c_2, and to themselves (it is 6 cm. from e_1 to e_2).

Wave Detector.—The detector used in these experiments is an electolytic detector. The accurate adjustment of the local voltage is made by the use of a potentiometer, *E*.[1]

Telephone.—A Fritz Köhler telephone of 80 ohms' resistance was selected as the most sensitive for this kind of work. With the electrolytic detector properly adjusted it is possible with this telephone to obtain a

[1] Pierce, Principles of Wireless Telegraphy, Fig. 233, p. 325.

very sharp minimum in which absolutely no noise is heard, even when the dielectric trough contains a liquid of as high conductivity as $1 \cdot 10^{-5}$. Under these conditions it is comparatively easy to set the glass plates of the measuring condensers to within 0.1 mm.

It must be emphasized that extreme sharpness in the telephone is the necessary condition not only for precision, but also for convenience. No determination is to be considered accurate in which the minimum is flat, because it evidently means that somewhere in the bridge something is out of order. Attention must be given to good contact; the existence of a small spark in any part of the bridge is a source of error, as the minimum in the telephone is destroyed and the observation is worthless.

All parts of the apparatus are well insulated and their positions are fixed on the table in order that no change of capacity or self-induction should be introduced. The apparatus is also arranged as symmetrically as possible.

The frequency of the current in the primary circuit and in the Wheatstone bridge may be calculated from the dimensions of the apparatus which have been given. For convenience we may record at this point some of the values in the calculations:

Self-induction in primary $= P_1 = 1.5 \cdot 10^4$ cm.
Capacity in primary $= C = 0.006\ MF = 6 \cdot 10^{-18}$ elec. mag. units.
Self-induction in bridge $= p_1 = 2.27 \cdot 10^5$ cm.
Capacity in bridge $= c_1 = 260$ cm. $= 2.9 \cdot 10^{-19}$ elec. mag. units.
Exciting self-induction $= P_2 = 2.6 \cdot 10^4$ cm.

If N = frequency in primary circuit, and n = frequency in bridge, then

$$N = \frac{1}{2\pi\sqrt{P_1 C}} = 5.4 \cdot 10^5/\text{sec.}$$

and

$$n = \frac{1}{2\pi\sqrt{(p_1 + 2P_2)c_1}} = 5.6 \cdot 10^5/\text{sec.}$$

It is evident that the frequency in the bridge changes with every change in the capacity c, which is produced by moving the glass plates in or out when taking readings; and the compensating resistances have a strong damping effect on the oscillations, whereby the frequency in the bridge is somewhat decreased; but these calculated values give an idea of the order of magnitude of the frequency of the currents used during an experiment.

Theory.

The condition for silence in the telephone is

$$p_1 : p_2 = c_2 : c_1.$$

When p_1 is made equal to p_2, and c_1 and c_2 are arranged as adjustable condensers, this method enables one to compare the capacity of the dielectric trough with another and thus determine the dielectric constant. The capacity of the dielectric trough is obtained first without and then with the dielectric between its plates. If c is the capacity of the dielectric trough when filled with air, and c' the corresponding value when the trough is filled with the substance in question, of which the dielectric constant is D, then we have

$$D = \frac{c'}{c}.$$

If the substance is a relatively good conductor the current in the condenser circuit not only charges the condenser but also flows through it, and this branch acts as if a non-inductive resistance were connected in parallel with the condenser. Equilibrium in the bridge can be obtained again if a corresponding resistance is connected in parallel with the measuring condensers. Let these variable non-inductive resistances be r_1 and r_2.

The conditions for equilibrium are

$$\frac{r_1}{\sqrt{1 + \omega^2 c_1^2 r_1^2}} : \frac{r_2}{\sqrt{1 + \omega^2 c_2^2 r_2^2}} = p_1 : p_2.$$

In order that there shall be no difference of phase:

$$r_1 : r_2 = p_1 : p_2.$$

From these two equations we get

$$c_1 r_1 = c_2 r_2$$

or

$$c_1 : c_2 = r_2 : r_1 = p_2 : p_1.$$

Thus the capacity does not depend on the frequency.

Practical Method.

In order to eliminate the outer capacity the ratio is taken of the difference of capacities at different distances of the disc from the bottom of the trough when the trough is filled (S) to that when it is empty (s). This ratio is, by definition, the dielectric constant,

$$D = \frac{S_1 - S_2}{s_1 - s_2}.$$

The chief source of error lies in the difficulty with which the correct displacement of the glass plates is obtained. The position of the plate corresponding to a minimum in the telephone is therefore determined by setting the plate ten times and taking the average of these readings. This is done when the dielectric trough is connected in parallel with c_1, and with c_2. The difference between the two average positions gives the displacement S (or s).

The dielectric constants given below are referred to air, the dielectric constant of which is taken as unity.

Results.

The object of these experiments is to find out the effect of change of concentration on the dielectric constant of aqueous solutions. The substances selected for investigation are non-electrolytes, and are either liquids, which can be easily purified by fractional distillation, or solids, which can be obtained in a very pure state. All readings were taken at 18.0° C.

As water has a very high dielectric constant it seemed advisable to use some liquid, which has a dielectric constant of about 10, as a standard with which to compare the water solutions. This method is not only more convenient but the percentage errors, due to the use of small displacements of the glass plates in the measuring condensers, are thereby diminished. The liquid chosen as the standard is ethyl bromide, because it is cheap, easily purified, not very volatile, does not absorb water readily, and has a dielectric constant of about 9.5.

The dielectric constant of ethyl bromide was found by comparing it directly with air. In this case S represents the displacement of the glass plates when the dielectric trough is filled with ethyl bromide, and s the corresponding displacement when the trough is filled with air. But in the later experiments, when ethyl bromide is used as the standard, s represents the displacement of the glass plates when the trough is filled with ethyl bromide, while S is the corresponding displacement when the trough is filled with the solution in question.

Ethyl Bromide.

The so-called "chemically pure" ethyl bromide, free from ether, was distilled twice in the ordinary way, and then distilled over phosphorus pentoxide. The middle part (probably nine-tenths) of the distillate, which boiled over at about 38.2°, was used in the following experiments.

Air.	Ethyl Bromide.
$s_1 = 1.205$	$S_1 = 3.791$
$s_2 = 1.206$	$S_2 = 3.799$
$s_3 = 1.207$	$S_3 = 3.799$
$s_4 = 1.205$	$S_4 = 3.796$
$s_5 = 1.211$	$S_5 = 3.807$

Air.	Ethyl Bromide.
s_6 = 1.211	S_6 = 3.811
s_7 = 1.214	S_7 = 3.812
s_8 = 1.210	S_8 = 3.806
s_9 = 1.207	S_9 = 3.802
s_{10} = 1.216	S_{10} = 3.814
s_{11} = 5.243	S_{11} = 41.865
s_{12} = 5.240	S_{12} = 41.851
s_{13} = 5.248	S_{13} = 41.939
s_{14} = 5.248	S_{14} = 41.925
s_{15} = 5.248	S_{15} = 41.951
s_{16} = 5.239	S_{16} = 41.856
s_{17} = 5.235	S_{17} = 41.828
s_{18} = 5.234	S_{18} = 41.782
s_{19} = 5.247	S_{19} = 41.882
s_{20} = 5.236	S_{20} = 41.847

$D = 9.443.$

Five months later another determination of the dielectric constant of ethyl bromide was made, and the following result was obtained:

$$D = 9.445.$$

The average value of D—9.444—was used in calculating the dielectric constants of the aqueous solutions.

WATER.

Ordinary distilled water was redistilled twice—over alkaline and acid permanganate solution. This pure water was then compared with the standard, ethyl bromide.

Ethyl Bromide.	Water.	Ethyl Bromide.	Water.
s_1 = 7.875	S_1 = 59.418	s_{16} = 3.988	S_{16} = 26.921
s_2 = 7.888	S_2 = 59.495	s_{17} = 4.007	S_{17} = 27.119
s_3 = 7.623	S_3 = 57.216	s_{18} = 3.971	S_{18} = 26.904
s_4 = 7.689	S_4 = 57.678	s_{19} = 3.972	S_{19} = 26.947
s_5 = 7.880	S_5 = 59.370	s_{20} = 3.970	S_{20} = 26.786
s_6 = 7.782	S_6 = 58.610	s_{21} = 3.978	S_{21} = 26.726
s_7 = 7.685	S_7 = 57.770	s_{22} = 4.001	S_{22} = 27.118
s_8 = 7.378	S_8 = 55.132	s_{23} = 4.016	S_{23} = 27.136
s_9 = 7.607	S_9 = 56.979	s_{24} = 3.996	S_{24} = 27.106
s_{10} = 7.900	S_{10} = 59.595	s_{25} = 4.032	S_{25} = 27.288
s_{11} = 7.725	S_{11} = 58.191	s_{26} = 4.040	S_{26} = 27.224
s_{12} = 7.597	S_{12} = 57.064	s_{27} = 4.088	S_{27} = 27.895
s_{13} = 7.888	S_{13} = 59.547	s_{28} = 4.027	S_{28} = 27.145
s_{14} = 7.704	S_{14} = 57.989	s_{29} = 3.986	S_{29} = 26.988
s_{15} = 7.620	S_{15} = 57.253	s_{30} = 3.981	S_{30} = 26.903

$D = 78.73.$

Tap water was investigated, and the dielectric constant was found to be 78.5, a value which may be considered the same as that of pure water.

This dielectric constant is entirely independent of the conductivity. But the sharpness of the minimum in the telephone is greatly reduced by an increase of conductivity, and a corresponding reduction in the accuracy of the result is thereby produced.

Moreover, the conductivity of the pure water is considerably increased by pipetting the water into the dielectric trough, so that the conductivity of the water during an experiment is probably about $2 \cdot 10^{-6}$ absolute units.

Tables like the preceding were obtained for the following solutions, but they are too long for reproduction here. The method of calculating the results is exactly the same.

Sugar Solution.

Large crystals of Kahlbaum's purest saccharose were dissolved in pure water and the molar concentration was varied between 0.1 and 1.4. The dielectric constant was found at the different concentrations as follows:

Concentration.	Dielectric Constant.
0.1	77.64
0.2	76.73
0.4	75.53
0.5	75.05
0.6	74.46
0.7	73.84
0.9	72.52
1.0	71.84
1.2	70.36
1.4	68.67

From these results it is evident that an increase of the concentration of the sugar solution causes a decrease of the dielectric constant. This is as it should be, as the dielectric constant of sugar is not very high.

Urea Solution.

Kahlbaum's best "Harnstoff" was taken without any further purification and dissolved in pure water to give solutions of concentrations which varied from 0.5 molar to 3.0 molar.

Concentration.	Dielectric Constant.
0.5	80.22
1.0	81.51
1.5	82.81
2.0	83.98
2.5	85.16
3.0	86.17

From these data we see that an increase in the concentration of the urea solution gives an increase in the dielectric constant. Such a result is contrary to all expectation, and, so far as I know, it is unique.

METHYL ALCOHOL.

Absolute methyl alcohol, free from acetone (from Eimer and Amend), was distilled over lime; and the middle part of the distillate (at least 90 per cent.), which boiled over at about 64.4°, was used in the following experiments. The amount of water with which the methyl alcohol was mixed was varied in six steps from 0 per cent. to 100 per cent.

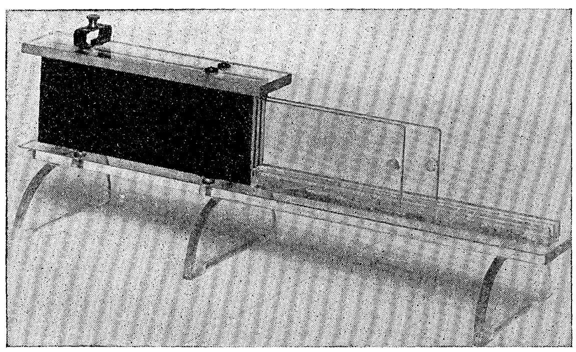

Fig. 5.

Concentration.	Dielectric Constant.
100.0	33.78
84.0	40.96
75.9	45.31
48.0	57.44
33.1	64.47
17.4	71.11

It is evident from these results that a nearly linear relation exists between the amount of water added to the methyl alcohol and the increase in the dielectric constant thereby produced.

CONCLUSIONS.

The Nernst method for the determination of the dielectric constant of liquids has been carefully examined; and the apparatus, particularly the measuring condensers and the dielectric trough, has been perfected so that it is now possible to measure accurately the dielectric constant of liquids whose conductivity is as high as $1 \cdot 10^{-5}$ absolute units. This is probably the highest conductivity for which consistent values of the dielectric constant have ever been obtained.

With this improved apparatus the effect on the dielectric constant of

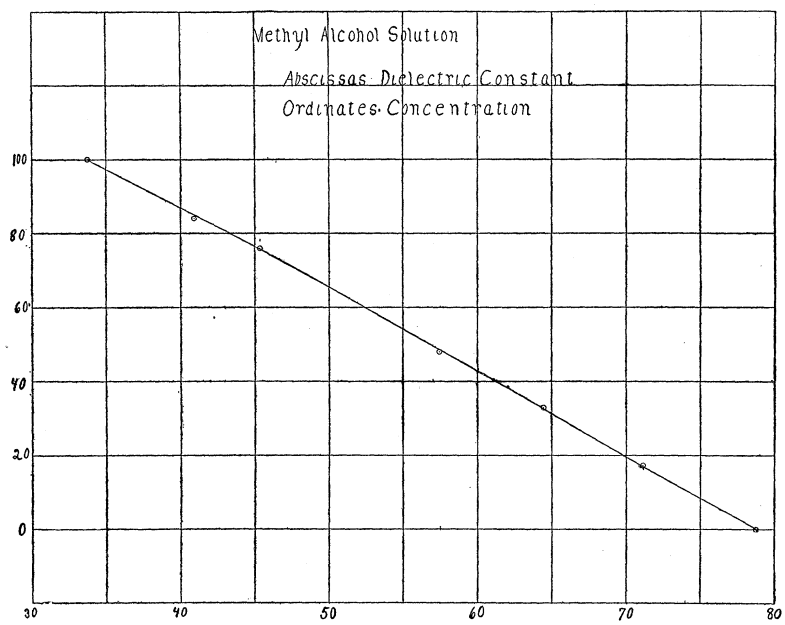
Methyl Alcohol Solution
Abscissas. Dielectric Constant
Ordinates. Concentration
100
80
60
40
20
0
30
40
50
60
70
80

Fig. 6.

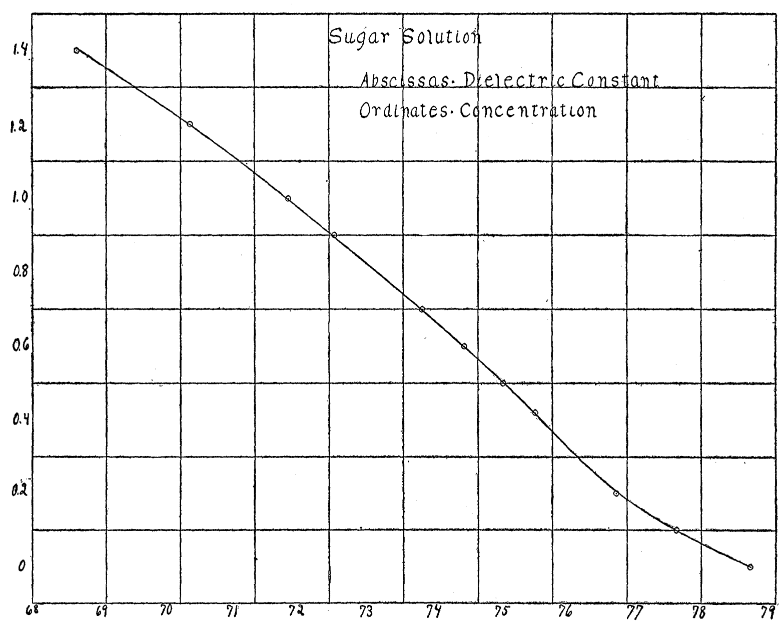
Sugar Solution
Abscissas. Dielectric Constant
Ordinates. Concentration
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
68
69
70
71
72
73
74
75
76
77
78
79

Fig. 7.

an increase of concentration of aqueous solutions of sugar, urea, and methyl alcohol respectively has been investigated; and the relation is bound to be nearly linear.

The author takes this opportunity to express his gratitude to Clark

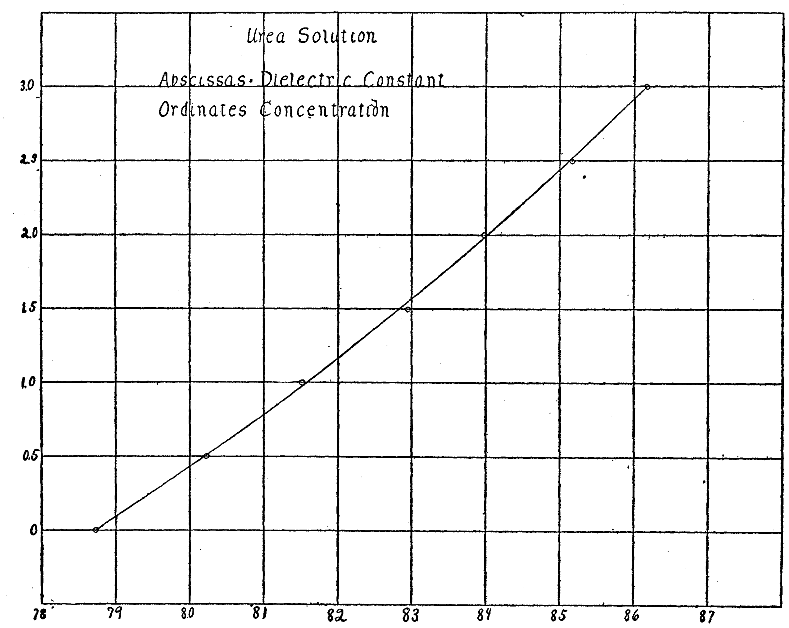

Fig. 8.

University for the apparatus placed at his disposal, and particularly to Professor Webster for many valuable suggestions in carrying out the research.

Clark University, Worcester, Mass.,
June 26, 1915.

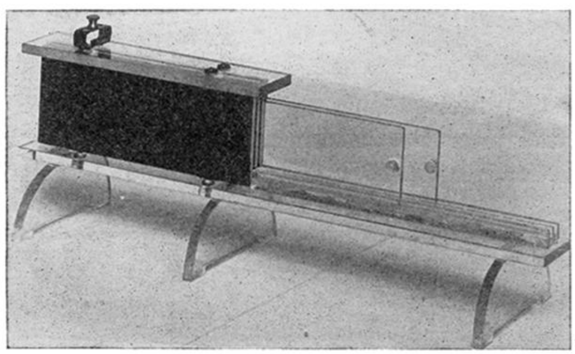

Fig. 5.