PREPARATION & PROPERTIES
OF
PURE HYDROGEN PEROXIDE

THE PREPARATION AND PROPERTIES

OF

PURE HYDROGEN PEROXIDE.

A Thesis

by

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INTRODUCTION.

The research work described in this thesis involved three distinct experimental problems; the preparation of pure hydrogen peroxide, the measurement of the dielectric constant of ethereal solutions of hydrogen peroxide and an investigation of the accuracy of the resonance method when used for the measurement of the dielectric constant of slightly conducting solutions. The densities of the different ethereal solutions were required and also the dielectric constants of the three component system, ether, water and hydrogen peroxide were measured and compared with the dielectric constant of hydrogen peroxide in ether.

This whole investigation was a continuation of the study of hydrogen peroxide which has been carried out in this laboratory.[1] The method of preparation is essentially the same as that devised by Maass and Hatcher[2]. The crude commercial product was distilled from an alkaline solution to remove impurities and then concentrated. As will be seen, improvements were made in the method of concentration giving better yields of hydrogen peroxide. The anhydrous hydrogen peroxide was prepared by crystallization of the concentrated product.

The dielectric constant of hydrogen peroxide is important from the point of view of ionization. Cuthbertson and Maass[3] have measured this constant for hydrogen peroxide. The method used involved the same principle for the measurement of capacity as that described by Williams and Krchma.[4] Some innovations were made in the apparatus so as to avoid capacity of the leads and the complicated calculations of the same. In these measurements the question of the conductivity of the solution under measurement came into prominence. Since no definite experimental work has been done in this connection, it was considered advisable that some accurate measurements should be carried out. The results of these measurements are given in Section II. As will be seen, these results are of importance not only in connection with the measurements on ether solutions but still more so in connection with the validity of the measurements of Cuthbertson and Maass on water and hydrogen peroxide.

Hydrogen peroxide dissolves in ether to about sixty percent by weight (0.75 mol fraction). The dielectric constant of hydrogen peroxide may thus be estimated by extrapolating the dielectric constant of the various ether solutions to a hundred percent hydrogen peroxide. Since density affects the value of the dielectric constant, the densities of the solutions were necessary in order to make a proper extrapolation.

Unfortunately hydrogen peroxide - water mixtures are not nearly so soluble in ether, but an attempt was made to measure the dielectric constant of these solutions in a similar way. By a proper extrapolation, the dielectric constant of hydrogen peroxide - water mixtures was obtained.

SECTION I.

Prepatation of Pure Anhydrous Hydrogen Peroxide.

The crude hydrogen peroxide obtained from the manufacturer was a fairly pure product produced by the electrolysis of potassium persulphate. It usually contains 26 to 27 percent hydrogen peroxide by weight, contaminated with traces of impurities. In addition, the manufacturer always adds an inhibitor of some sort to prevent the peroxide from decomposing. It was therefore necessary to devise a sensitive test for these impurities.

Usually the crude peroxide contains a small percentage of sulphuric acid, but none of this impurity could be detected in the crude product which was used. The inhibitor in this case was salicylic acid and was very difficult to remove from the peroxide. A very sensitive test for salicylic acid is ferric chloride applicable if there are only very small amounts of inorganic salts present. Since the concentrated peroxide destroys the violet color produced by salicylic acid and ferric chloride, the peroxide first must be decomposed.

This is accomplished by making the solution very slightly alkaline with sodium hydroxide and allowing it to stand in a platinum evaporating dish in contact with a piece of platinum black. The peroxide decomposes in an hour or two, and the nearly neutral solution was tested for salicylic acid.

The acidity of the peroxide is due chiefly to the salicylic acid. The crude material is made slightly alkaline with standard sodium hydroxide, allowed to decompose, and then the excess alkali is titrated back with standard hydrochloric acid. In this way the acidity of the hydrogen peroxide is obtained, which is usually around 0.01 normal.

The strength of all aqueous hydrogen peroxide solutions was determined by means of standard potassium permanganate solution, which was standardized against re-crystallized oxalic acid.

In order to remove salicylic acid and any other non-volatile impurities the crude peroxide was vacuum distilled from slightly alkaline solution. The diagram (Fig. I.) indicates the apparatus used. The crude hydrogen peroxide, made slightly alkaline with sodium hydroxide was placed in vessel (A).

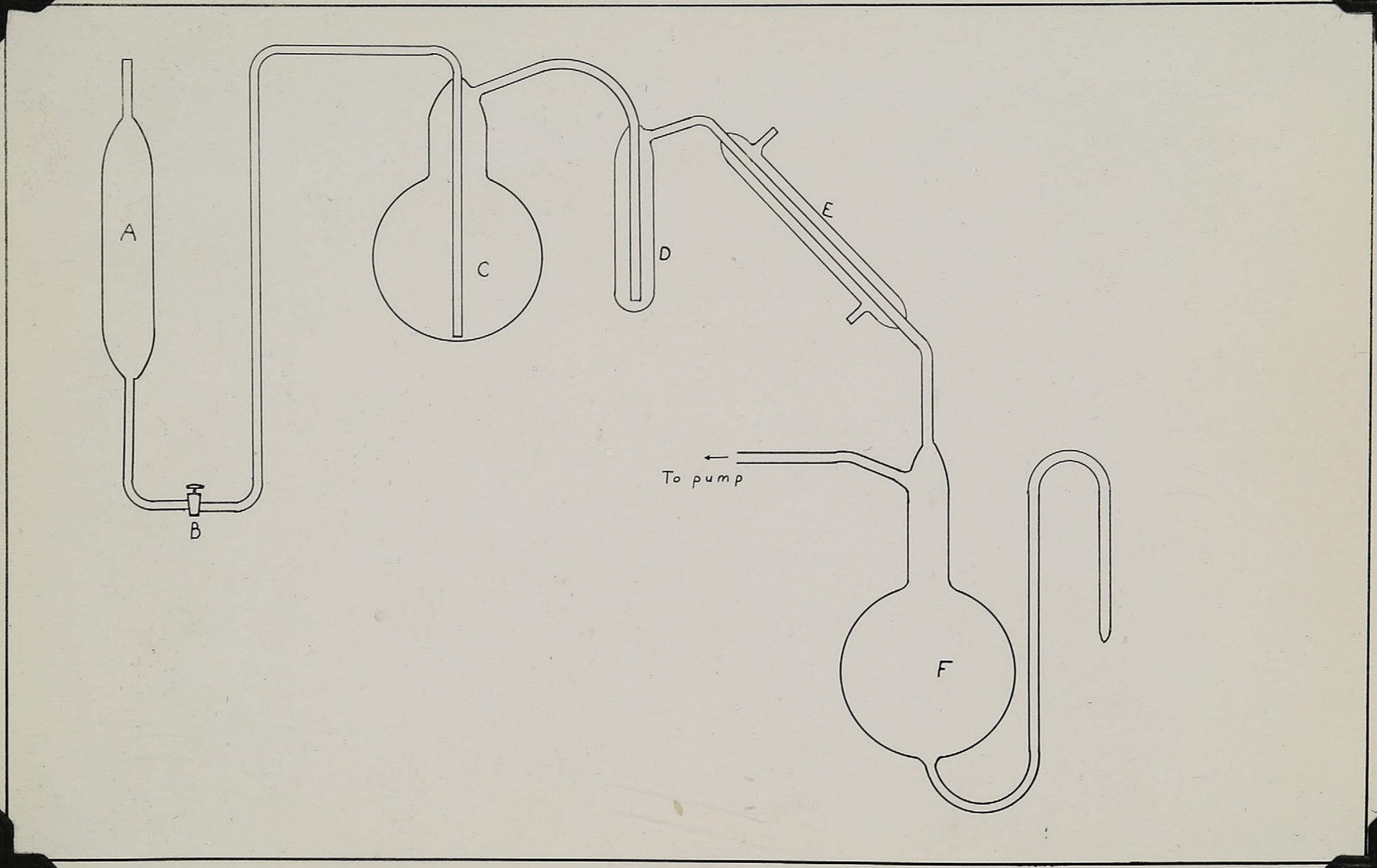


FIGURE I.

It was allowed to run slowly into vessel (C) through tap (B). The flasks (C) and (D) were heated to about 70° C. by means of water baths. The pressure varied from about one millimeter at the beginning of the distillation to around five millimeters at the end of the distillation. The liquid evaporated rapidly and left the impurities behind in (C). The pure distillate ix was collected in (F) which was cooled with crushed ice. About 300 cc was the maximum amount which could be distilled at one time, since the alkali accumulates in (C) and causes the peroxide to decompose near the end of the distillation. The distillate is about 20 percent H_2O_2 by weight and no traces of salicylic acid could be detected.

Throughout all this work, great care was necessary to prevent the hydrogen peroxide from becoming contaminated with impurities. It was kept in Pyrex flasks which were cleaned with chromic acid and dried in vacuo. The concentrated solutions take up water readily and consequently were kept in a dessicator.

The next step was the concentration of the twenty percent solution. The apparatus shown in Fig. II was used for this purpose, and it may be

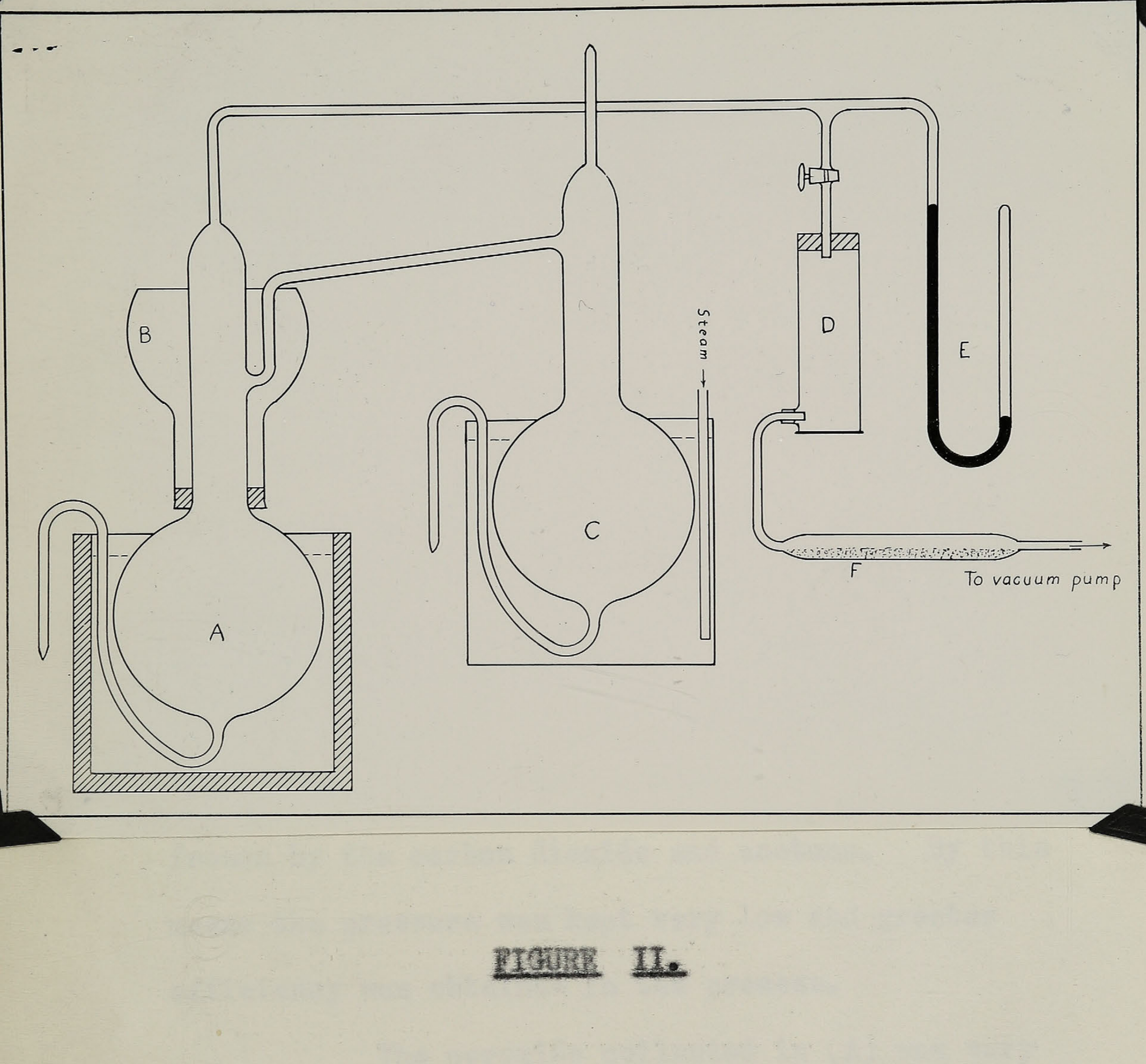


FIGURE II.

pointed out that this concentrator was original in design. The dilute solution was drawn into the two litre Pyrex flask (C) and heated to about 30°-35° C. by means of hot water. A "Hyvac" pump was used to maintain a low pressure during the concentration. The pressure always remained below one millimeter of mercury throughout the entire process. Since the vapor pressure of water was higher than the vapor pressure of the hydrogen peroxide, the water evaporated off more quickly and the solution remaining behind became more concentrated. The vapors were condensed by means of vessel (B) which contained crushed ice or snow. The flask (A) was a two litre Pyrex vessel which was cooled with carbon dioxide snow and acetone. The condensed vapors ran down into vessel (A) and were immediately frozen by the carbon dioxide and acetone. By this means the pressure was kept very low and greater efficiency was obtained in the process.

The peroxide collected in (A) was very pure and could be concentrated again if it was not too dilute. There was very little loss by decomposition and none of the vapors were carried over into the vacuum pump. It was convenient to concentrate the twenty peroxide to sixty eight or seventy percent and then concentrate the seventy percent to about ninety five percent. Starting with fifteen hundred grams of 21.2 percent, about 376 g of 68 percent and 1120 g of 6 percent H_2O_2 were obtained which shows a losss of less than one percent. A drying train of calcium chloride and phosphorus pentoxide was placed between the pump and the apparatus to prevent any vapors from contaminating the pump oil. When the 95 percent peroxide obtained by this process was analyzed for salicylic acid none could be detected.

To obtain the pure peroxide it was crystallized in the apparatus designed by Maass and Hatcher.[2] By freezing about four fifths of the liquid and forcing out the mother liquor an increase in concentration of about one percent was made. Repeating this process several times yielded peroxide of 99.5 percent strength.

SECTION II.

Part 1.

Apparatus and Experimental Method for Obtaining the Dielectric Constant.

The experimental method is the same as that used by Cuthbertson and Maass.[5] A diagram of the connections is shown in Fig. III. (I) is a variable oscillator. The inductances consist of two honeycomb coils. (A) is the dielectric cell containing the liquid whose dielectric constant is to be measured. (B) is a tuning condenser in parallel with the inductance and dielectric cell. The accuracy of the method depends to a large extent on the construction of this tuning condenser. It should be free from end effects and give a straight line relationship between capacity and dial setting. The tuning condenser used is accurate between a dial setting of 30 and 80. A glass mirror is mounted on the tuning condenser and the setting of the condenser is read accurately off a four foot millimeter scale by means of a reflected beam of light.

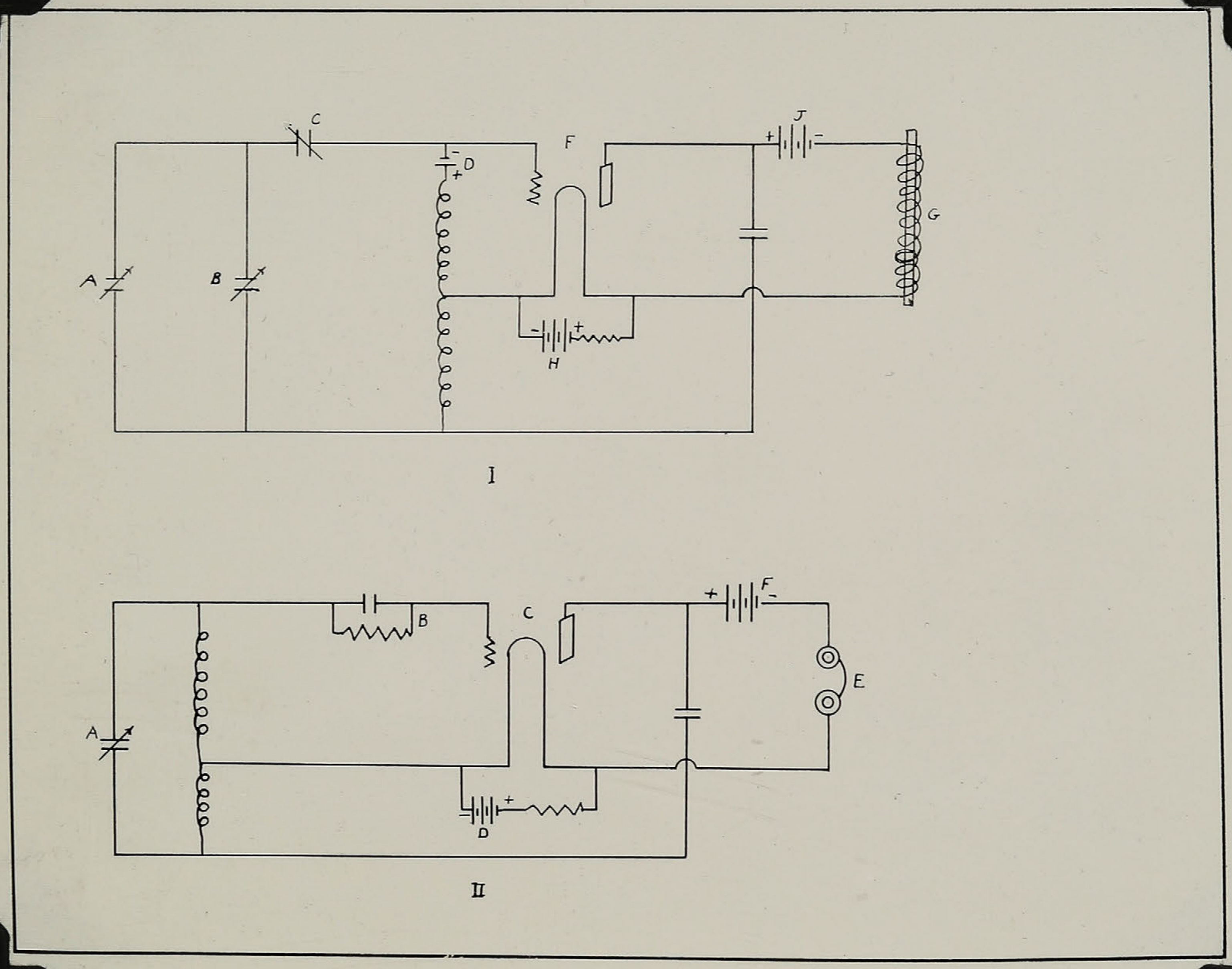


FIGURE III.

In all these measurements a condenser is kept in series with the tuning condenser. It gives a much stronger note when measuring the dielectric constant of water. A UX-171-A Radiotron tube is used as the source of the oscillations and takes 90 volts on the plate circuit and 6 volts on the filament. A choke coil (G) is placed in the plate circuit to absorb the radio frequency currents and prevent them passing through the plate circuit.

(II) is a fixed oscillator operating on a definite frequency throughout any measurement. It consists of the ordinary regenerative hook-up. A UV-199 Radiotron tube is employed which uses a very small current on the filament. Six dry cells are used as the source of the filament current. The telephones (E) indicate the point of resonance, i.e. when the two oscillators are operating on the same frequency. By varying the tuning condenser the note in the phones is varied and the two oscillators are brought into resonance.

(A) the dielectric cell, is made of pure block tin. It is constructed on the principle of a variable condenser, the plates of which are immersed in the liquid whose dielectric constant is to be measured. The rotor is attached by means of an insulating bakelite board to the stator plates. By means of a vernier dial attached to the rotor, the variable condenser can be set at any desired capacity. This cell is supported in a Pyrex glass beaker which contains the liquid under measurement. This beaker is surrounded by a larger beaker containing ice and water. In this way the liquid under measurement can be kept at a constant temperature. The variable cell eliminates the necessity of correcting for the capacity of the leads.

During a measurement the cell is placed in the circuit and the two oscillators connected. The cell ~~was~~ is set at different readings and the corresponding positions of the tuning condenser noted. In this way a series of points is obtained which should give a straight line relationship provided both the tuning condenser and dielectric cell have no end effects. The liquid under measurement is placed in the dielectric cell and the slope of the straight line obtained. Then another liquid whose dielectric is known is placed in the cell and the slope of its line found. By multiplying the ratio of the two slopes by the dielectric constant of the known liquid, the dielectric constant of the unknown liquid is obtained.

In order to make sure that the apparatus was ~~is~~ in good working order a determination of the dielectric constant of benzene ~~is~~ was made. A nine plate cell was constructed with brass condenser plates which made possible a comparison between air and benzene. Since the benzene used was not purified no significance could be placed on the absolute result obtained. However, the values obtained agreed well among themselves and showed that the apparatus gave consistent results.

SECTION II.

Part 2.

The Effect of Conductivity on the Dielectric Constant of Water.

The dielectric constant of water was measured by Cuthbertson and Maass.[5] Since the values obtained with those found in the literature, the objection was raised that the conductivity, i.e. resistivity, played a part in the method used. The object of the following research was to find out whether the conductivity affected the dielectric constant, and if so, in what way.

In the resonance method for the measurement of the dielectric constant, the capacity of the solution was measured by tuning to a fixed frequency. the frequency of this circuit depends on the inductance, capacity and resistance of the circuit. Since the inductance and frequency are fixed, the end point depends on the capacity and resistance of the circuit. In the measurements of the dielectric constant of water, the resistance of the pure water was very high and the changing of the setting of the dielectric cell did not affect the resistance of the circuit appreciably. If the resistance of the circuit was changed by varying the dielectric cell, a straight line relationship between the setting of the dielectric cell and the tuning condenser would not be produced. Since straight line relationships were found in each case, it was apparent that the resistance of the circuit did not change to any extent. As will be seen from the following, the difference between the dielectric constant of conductivity and ordinary distilled water was negligible. That is, the resistance of these solutions was so high that the change in resistance did not affect the frequency of the oscillation of the apparatus. However, when the conductivity becomes greater than 4.5×10^{-6} the dielectric constant increased rapidly.

The apparatus used in these measurements was the same as that described in the preceding section. The three plate tin condenser with the glass container was used as the dielectric cell. All measurements were carried out at 25° C. and since the temperature coefficient of the dielectric constant of water is large, care had to be taken to keep the temperature of the water constant.

The conductivity of the water was measured by means of the ordinary Wheatstone bridge hook-up.

Ordinary tap water of the laboratory showed a conductivity of around 10^{-5}, while the distilled water gave a conductivity of 3.5×10^{-6}. By mixing small amounts of tap water with the distilled water, various conductivities from 3.5×10^{-6} to 1×10^{-5} were obtained. When an attempt was made to measure the conductivities greater than 10^{-5} the oscillations from the sending set became very weak and at about 1.3×10^{-5} water acted as a conductor and the set would not oscillate. For the preparation of conductivity water of the order of 1.5×10^{-6} a Hartley still was used.[5] The apparatus was steamed out for several days, the necessary precautions being taken to exclude dust and carbon dioxide. Finally about four or five litres of distilled water were made alkaline with sodium hydroxide and a small amount of potassium permanganate added. This water was distilled and the first third discarded. The water which then condensed had a conductivity of about 1.1×10^{-6} to 1.3×10^{-6}. As soon as some of the conductivity water was prepared, the dielectric cell was washed out with it and the plates covered. The dielectric constant of the water was then measured, the conductivity of the water being determined both before and after the measurement. The conductivity rose from 1.2×10^{-6} to 1.3×10^{-6} due to carbon dioxide from the air. The following table (Table I) gives the experimental results obtained. Table II then gives the slopes of the lines corresponding to each set of readings in Table I.

The curve in Fig. IV gives the relative dielectric constant of water plotted against conductivity. It is seen that as the conductivity decreases the difference between the corresponding dielectric constants decreases. Thus, at about 4×10^{-6} the curve flattens out and varies very little from the dielectric constant at 1×10^{-6}. Above a conductivity of 7×10^{-6} the dielectric constant rises very rapidly as is shown by the curve.

Cuthbertson and Maass measured the temperature coefficient of the dielectric constant of water, using water of a conductivity of about 4×10^{-6} at 25° C. Since the conductivity increased rapidly above 25° C. their value of the temperature coefficient is probably in error due

TABLE I.

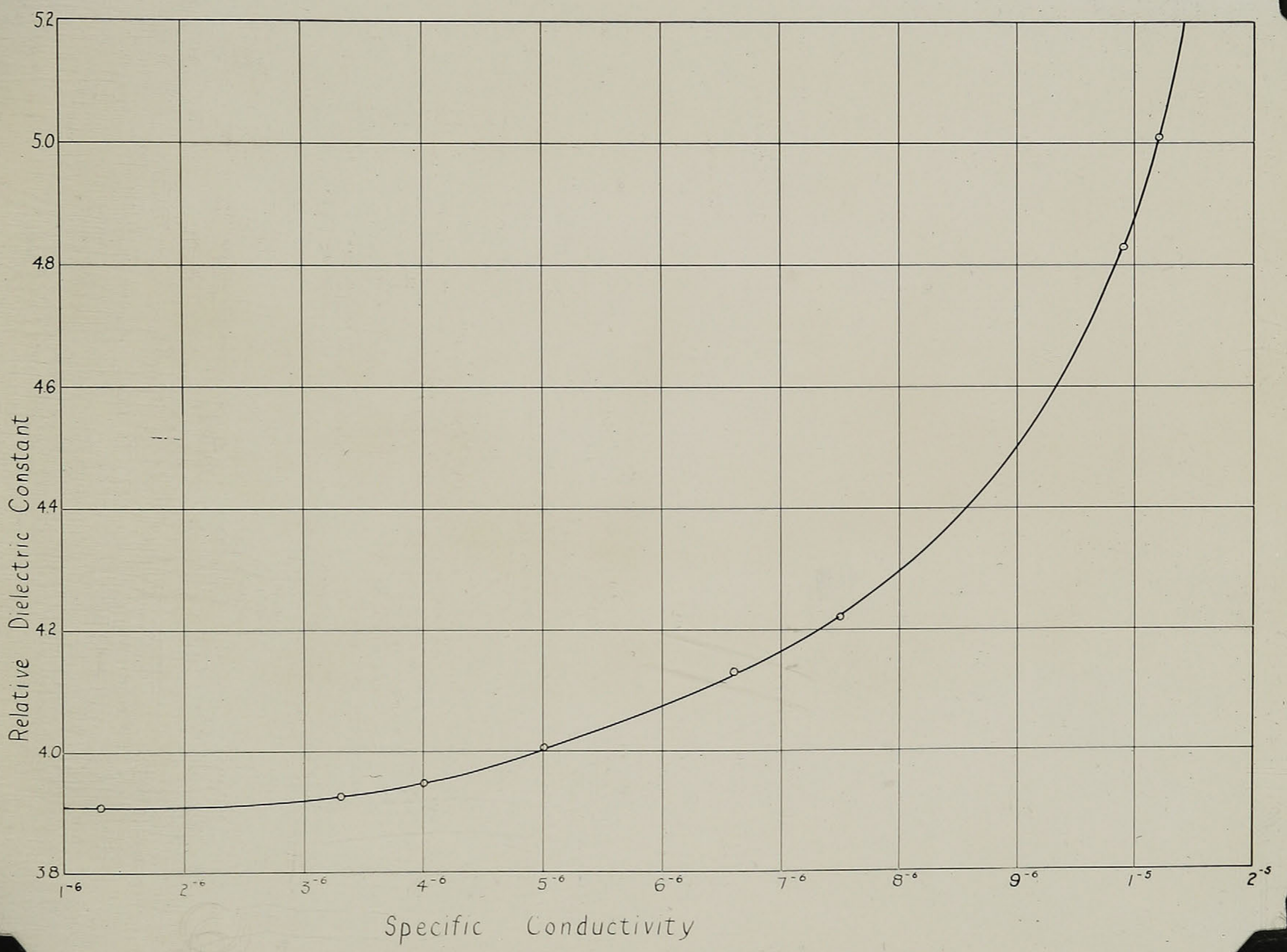
Experimental Results.

Dial Setting:	30	40	50	60	70
Sp. Cond. =					
= 1.3 x 10^{-6} :	30.4	71.0	112.1	148.5	186.6 .
= 3.3 x " :	31.4	71.5	112.6	150.0	187.6 .
= 4.0 x " :	56.9	97.8	138.9	178.4	216.0 .
= 5.0 x " :	31.0	71.6	113.9	152.5	190.2 .
= 6.6 x " :	31.0	72.3	115.0	155.0	195.0 .
= 7.5 x " :	33.2	75.2	118.8	159.5	200.0 .
= 9.9 x " :	30.0	73.4	122.0	173.3	227.0 .
=12.0 x " :	52.3	100.6	152.5	204.5	--- .

TABLE II.

Variation of Dielectric Constant with Conductivity.

Specific Conductivity.		Relative D. E. C.
1.3×10^{-6}	-	3.910 .
3.3 "	-	3.925 .
4.0 "	-	3.950 .
5.0 "	-	4.04 .
6.6 "	-	4.13 .
7.5 "	-	4.22 .
9.9 "	-	4.82 .
12.0 "	-	5.03 .


Relative Dielectric Constant
52
5.0
4.8
4.6
4.4
4.2
4.0
38
1^{-6}
2^{-6}
3^{-6}
4^{-6}
5^{-6}
6^{-6}
7^{-6}
8^{-6}
9^{-6}
1^{-5}
2^{-5}
Specific Conductivity

<u>**FIGURE IV.**</u>

to neglecting the above fact.

The specific effect of the material causing the conductivity has not been investigated in the above measurements. It is possible that the nature of the salt plays a very important part at high conductivities. The effect of increasing the power of the sending set on the resonance method for the measurement of the dielectric constant offers another field for investigation.

It will be interesting to make an investigation of the above problems, not only as having a bearing on the use of the resonance method for the accurate measurement of the dielectric constant, but also on the results of Cuthbertson and Maass.

SECTION III.

Part 1.

The Dielectric Constant of Ethereal Solutions of Hydrogen Peroxide.

Since the dielectric constant of ether was around 4 and that of hydrogen peroxide nearly 90^{e}, dielectric cells of different capacity had to be used for the determinations of the dielectric constant of mixtures of the two substances. A three plate dielectric cell was used to measure the dielectric constant of solutions between 30 and 60 percent hydrogen peroxide. The dielectric constant of these strong solutions could be measured directly by comparing with the dielectric constant of pure water, but it was found more convenient to standardize a sample of nitrobenzene against water and use this in the measurements. The dielectric constant of nitrobenzene (35) was of the same magnitude as the dielectric constant of the stronger peroxide solutions and the two solutions could be compared without changing the setting of the variable oscillator.

For the more dilute solutions a seven plate condenser with removable plates was made. A mixture of nitro benzene and benzene was prepared which had a dielectric constant midway between nitrobenzene and ether. By means of this mixture the dielectric constant of the sample of nitrobenzene could be checked against a sample of pure ether. It was found that the dielectric constant of ether agreed with value of Cuthbertson and Maass using their value of water as a standard.

To avoid the evaporation of ether from the solution under measurement as much as possible, a sheet of rubber was glued to the bakelite cover of the dielectric cell. This rubber fitted tightly over the top of the beaker and kept the moisture from the air out of the solution.

All the measurements of the dielectric constant were carried out on a wave length of 250 to 300 meters.

The hydrogen peroxide was purified as described in Section 1. The 95 percent peroxide was recrystallized about six times and in this way peroxide of 99.4 percent strength was prepared.

In order to purify the ether for the measurements, ordinary commercial ether was shaken with water five or six times, and the water layer discarded. The ether was then dried over calcium chloride and distilled. It was allowed to stand over sodium wire until no more bubbles were given off. Any sodium oxide or sodium hydroxide which dissolved in the ether would cause the hydrogen peroxide to decompose. To avoid this the ether was distilled from fresh sodium in a moisture-free Pyrex still.

Ether dissolves hydrogen peroxide up to a concentration of about 60 percent by weight, heat being generated in the mixing. It was evident that a volume change took place on mixing, and it was considered advisable to measure the density of these solutions. Since the dielectric constant and density are very closely related, it was thought possible that the density would be useful in extrapolating the curve to a hundred percent H_2O_2: The density was measured by means of a dilatometer with a graduated stem. A tight fitting glass cap was made to cover the end of the glass tube, so as to avoid as much as possible, the loss of any ether by evaporation. The measurement of the densities of these solutions was carried out at 0° C. and at 20° C.

The composition of the solution could be determined by analyzing for hydrogen peroxide with standard potassium permanganate, or by making the solution up to a known composition by weighing the hydrogen peroxide and ether separately. In the more concentrated bydrogen peroxide solutions, no difficulty was found in obtaining an end point with potassium permanganate, but when the concentration of ether was over seventy percent, it was difficult to obtain the correct end point. The excess ether had to be evaporated off before diluting with water. If a large excess of water, i.e. about one and a half litres was used, the end point could be obtained more easily.

By mixing together known weights of hydrogen peroxide and ether, the solutions could be made up to any strength desired. The first solution made up was the most concentrated solution of hydrogen peroxide and ether that could be obtained. This was diluted down with known weights of ether and the more dilute solutions were obtained in this way. Thus the strength of the solutions were determined in two ways and the two methods checked very well.

Any inorganic impurities dissolved in the hydrogen peroxide or ether would not ionize to any extent in the ether solution. Hence the conductivity of the solution will be low and will not effect the measurement of the dielectric constant.

The mol fraction of the hydrogen peroxide was calculated from the percentage composition. The mol fraction gives the relation of solute and solvent much better than the percentage composition since one is dealing with relative molecular amounts. The results of the measurements are recorded in Table III.

TABLE III.

Percent H_2O_2.	M. F. of H_2O_2.	D:E:C: of Soln.
5.2	.1022	6.4 .
10.0	.195	8.3 .
17.8	.323	13.0 .
26.3	.436	17.5 .
38.2	.574	26.2 .
46.3	.654	32.8 .
58.2	.750	42.5 .

The curve in Fig. V gives the dielectric constant plotted against mol fraction. The different points fall on the curve within the experimental error of the measurements, which was about one percent.

The density of the solution was measured as soon as it was made up in order to avoid any errors due to the loss of ether by evaporation. The dilatometer was standardized with water at 20° C. The calibration and results of the density determinations were corrected to vacuo. The aberration from the mixture rule was calculated by using the following formula:

$$V = 1 - \left(\frac{\frac{\% H_2O_2 \times D_1}{100}}{D_2} + \frac{\frac{(1 - \% H_2O_2) D_1}{100}}{D_3} \right).$$

where,

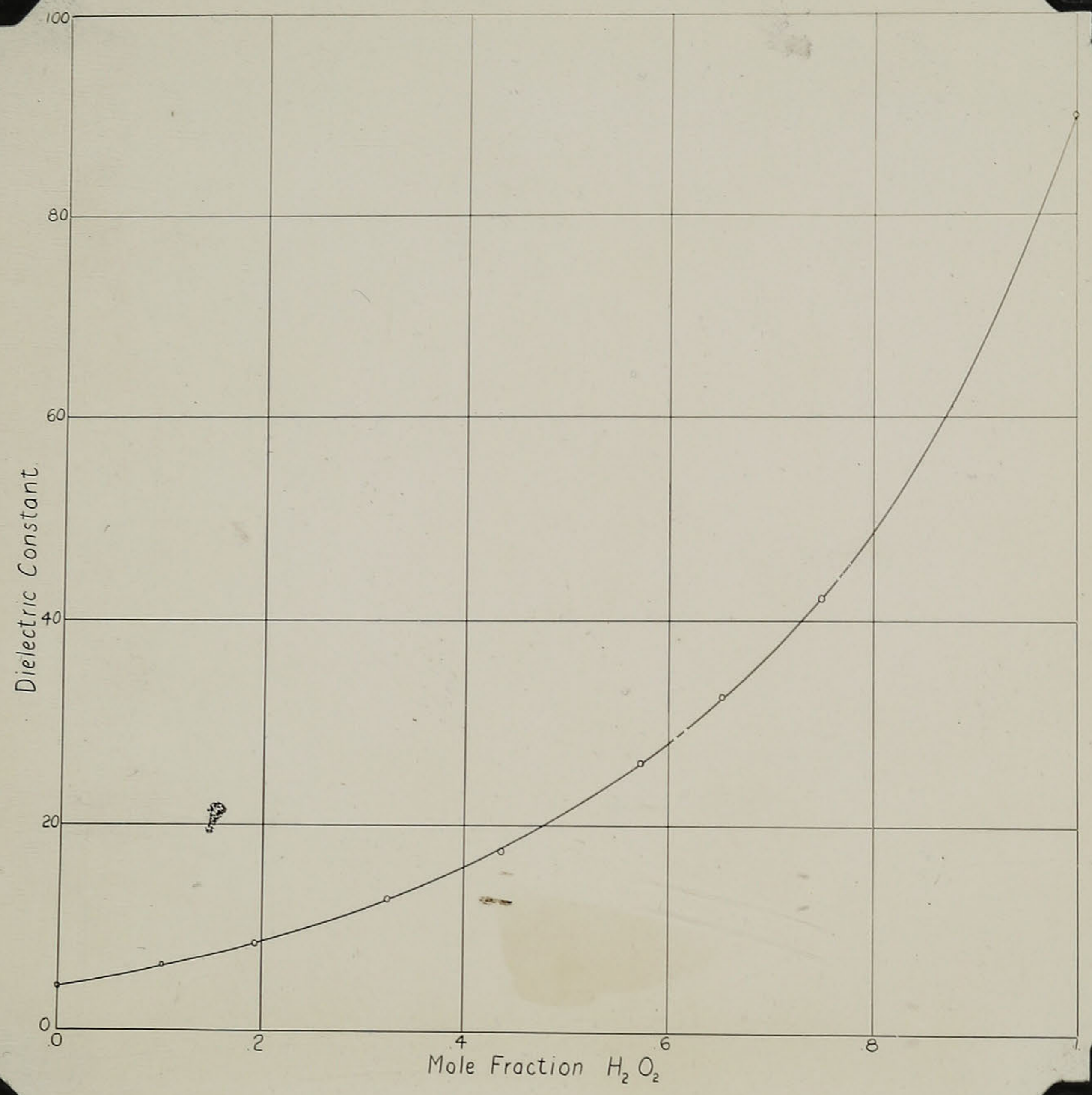
V = Volume of 1 cc,

D_1 = Density of the Solution,

D_2 = Density of Hydrogen Peroxide,

D_3 = Density of Ether.

The following table (Table IV) gives the densities and aberrations from the mixture rule of the various solutions.



100
80
60
40
20
0
.0
.2
.4
.6
.8
1.
Dielectric Constant
Mole Fraction H_2O_2

FIGURE V.

TABLE IV.

Densities and Aberrations from Mixture Rule.

M.F.		D_1		Aberration.
.1022	-	.769	-	.029 .
.195	-	.791	-	.032 .
.323	-	.834	-	.042 .
.436	-	.892	-	.064 .
.574	-	.954	-	.061 .
.654	-	.997	-	.051 .
.750	-	1.071	-	.042 .

These points are plotted in the graph of Fig. VI. The density plotted against mol fraction falls on a smooth curve, but a large increase in density occurrs between 60 and 100 percent hydrogen peroxide. In the case of the aberration from the mixture rule the points do not fall on so smooth a curve. A maximum occurs at about a density of 0.93 which corresponds to a mol fraction of about .5 H_2O_2. The maximum occuring at a mol fraction of .5 would seem to indicate that a compound of ether and hydrogen

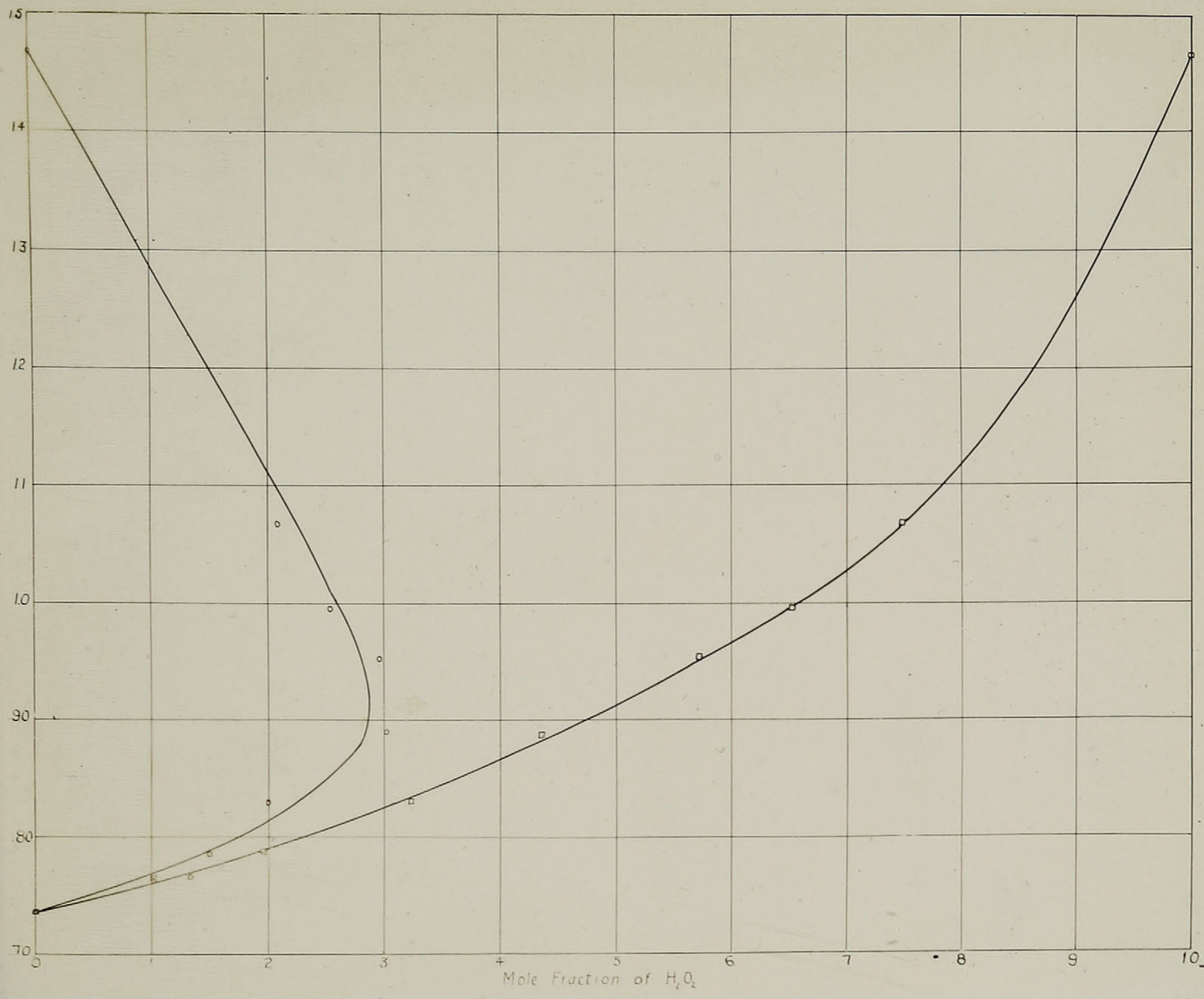


FIGURE VI.

peroxide was formed. This compound of ether and hydrogen peroxide probably caused a minimum in the curve when dielectric constant was plotted against mol fraction.

In order to obtain the dielectric constant of hydrogen peroxide as accurately as possible from the above data, an attempt was made to establish a straight relationship between dielectric constant and mol fraction. The following table (Table V) gives the logarithm of the dielectric constant and mol fraction of the mol fraction of the hydrogen peroxide of the various solutions:

TABLE V.

M. F.	Log. (D.E.C.)
.1022	.8062
.195	.9191
.323	1.114
.436	1.243
.574	1.418
.654	1.516
.75	1.628

These points are plotted in the graph of Fig. VII. As will be seen, the points fall fairly well on a straight line. When the straight line is extrapolated to 100 percent hydrogen peroxide the dielectric constant is shown to be 91. This value agrees with that of Cuthbertson and Maass viz. 89.2 within the accuracy of the measurements.

Since hydrogen peroxide is a polar substance and ether relatively non-polar, an attempt was made to calculate the electric moment of hydrogen peroxide.[7] The molar polarization of the mixture of the two substances is given by the expression:

$$P_1P_2 = \frac{E-1}{E+2} \cdot \frac{\overline{M}}{D_1} = C_1P_1 + C_2P_2.$$

where,

P_1 = Polarization of Ether,

P_2 = Polarization of Hydrogen Peroxide,

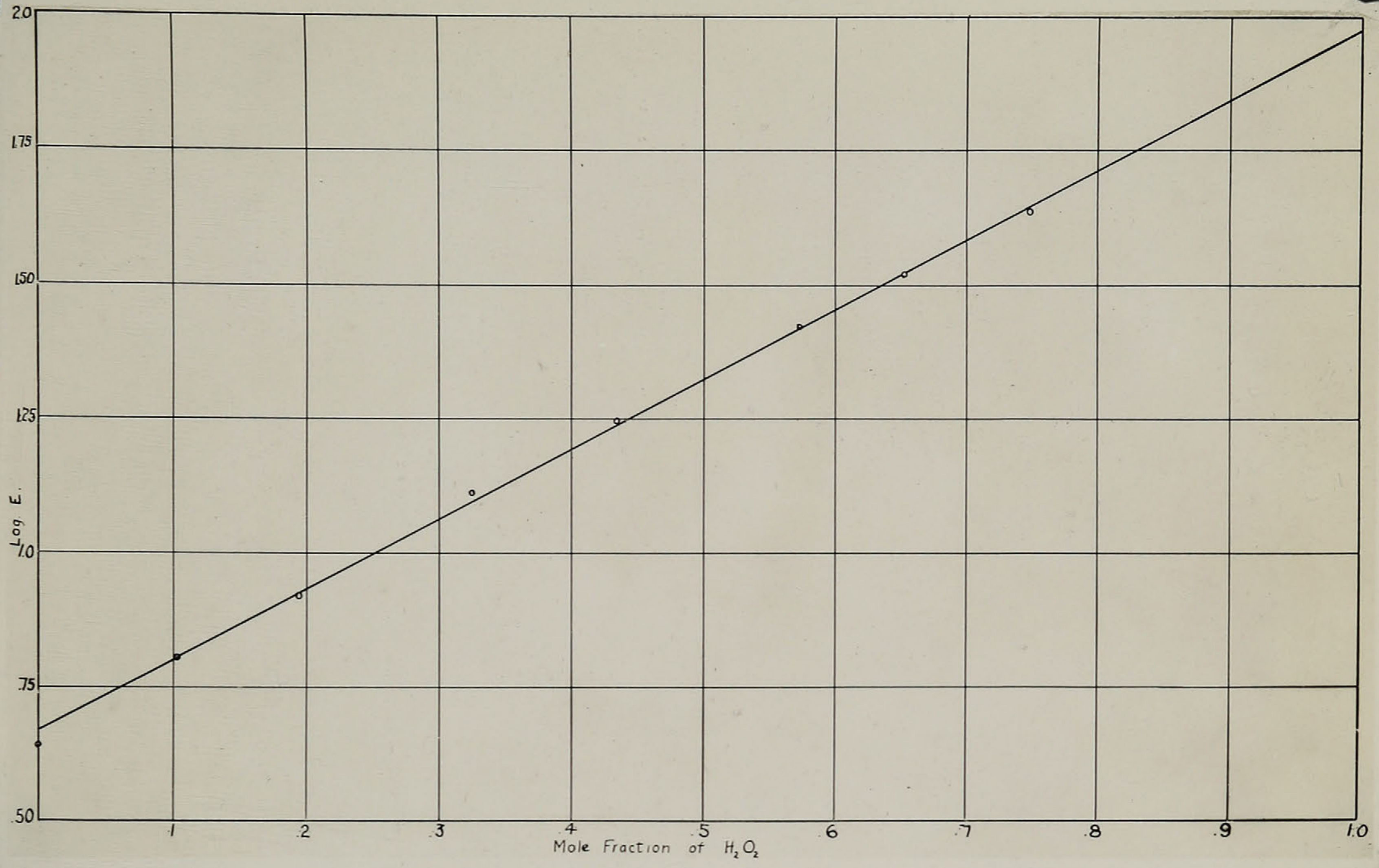
E = Dielectric Constant of the Solution,

$\overline{M}$ = Average molecular weight.

D_1 = Density of the Solution.

C_1 = Mol Fraction of Ether,

C_2 = Mol Fraction of Hydrogen Peroxide.



2.0
1.75
1.50
1.25
Log. E.
1.0
.75
.50
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
Mole Fraction of H_2O_2

FIGURE VII.

Assuming P_1 to be constant but P_2 to vary with concentration, P_2 may be calculated from the equation;

$$P_2 = \frac{P_{12} - P_1}{C_2} + P_1.$$

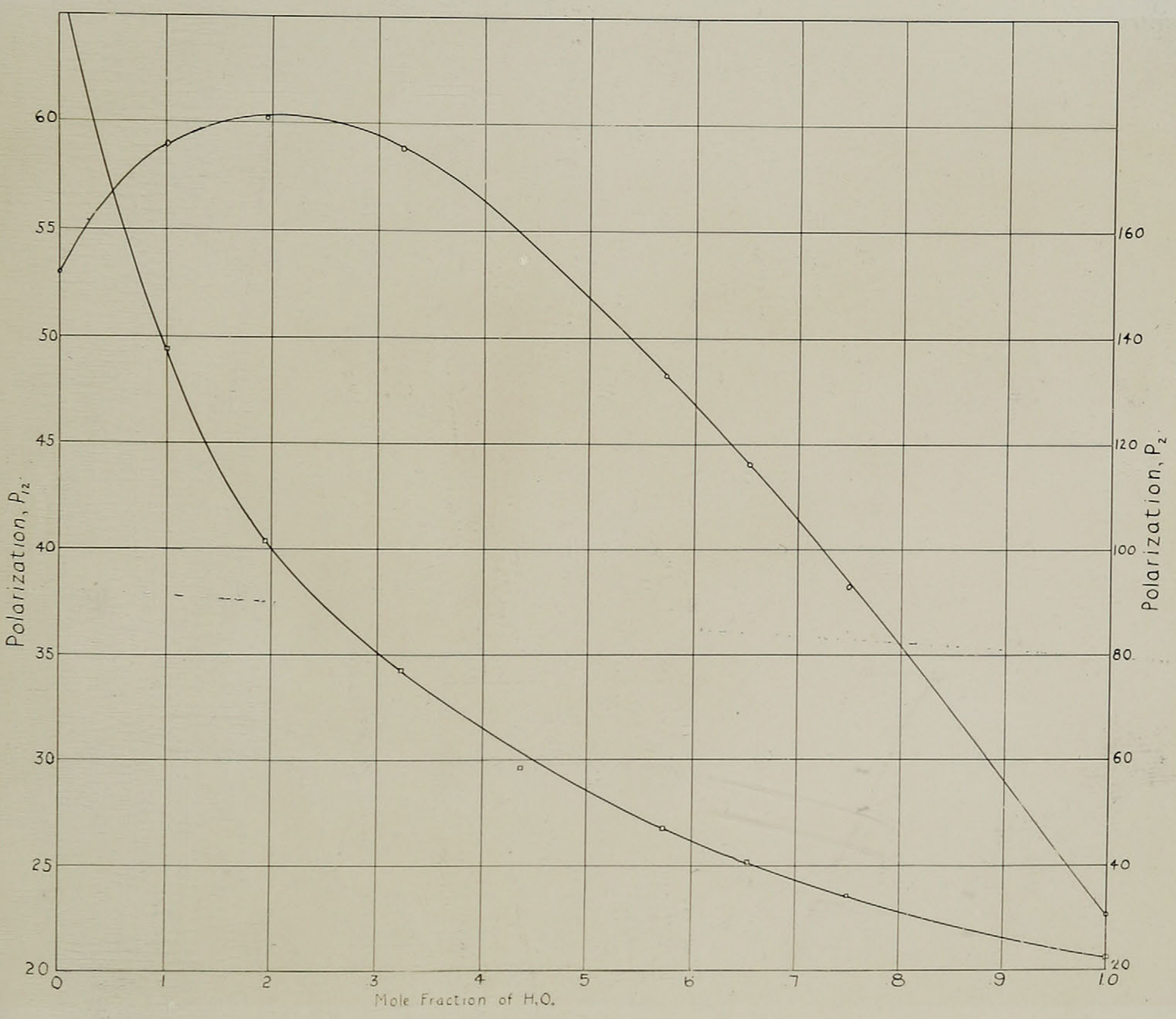
The following table (Table VI) gives the results of these calculations for the mixtures of ether and hydrogen peroxide:

TABLE VI.

M.F. H_2O_2	$\bar{M}$	P_{12}	P_2
.000	74.0	53.0	137.5
.1022	70.0	59.0	137.5
.195	66.2	60.0	101.6
.323	60.8	58.8	76.9
.436	56.4	53.6	58.0
.574	51.1	48.2	46.7
.654	47.8	44.0	40.7
.75	44.0	38.2	34.2
1.00	34.0	22.6	22.6

The graph in Fig. VIII gives the mol fraction plotted against P_{12} and P_2. As will be seen from the curve for the molar polarization of the mixture of the two substances, a maximum occurs around a mol fraction of 0.2 H_2O_2. This is quite typical of a polar molecule dissolved in a non polar solvent.

In order to calculate the electric moment of the hydrogen peroxide the curve for P_2 would have to be extrapolated to zero concentration of H_2O_2. The extrapolation in this case would not be accurate enough to calculate the electric moment since the curve rises rapidly near a zero concentration of hydrogen peroxide. In order to calculate the moment a large number of points at a very dilute concentration would have to be measured. As ether is not a true non-polar solvent, the effect of the ether would come into play and this also makes the extrapolation uncertain.



60
55
50
45
40
35
30
25
20
Polarization, P_{12}
160
140
120
100
80
60
40
20
Polarization, P_2
0
1
2
3
4
5
6
7
8
9
1.0
Mole Fraction of H_2O.

FIGURE VIII.

SECTION III.

Part 2.

Measurement of the Dielectric Constant of Ether, Hydrogen Peroxide and Water Mixtures.

Cuthbertson and Maass have determined the dielectric constant of aqueous solutions of hydrogen peroxide[6]. By measuring the dielectric constant of mixtures of water, hydrogen peroxide at different concentrations in an ether solution, it was possible to extrapolate to zero percentage of ether and find the dielectric constant of the mixture of water and hydrogen peroxide.

Difficulty was found in obtaining a solution of 50 percent H_2O and 50 percent hydrogen peroxide - ether mixture. Only a three percent mixture of this solution could be obtained. An 85 percent H_2O_2, 15 percent water, would dissolve quite readily in ether up to a concentration of 50 percent. The dielectric constant of these solutions at various dilutions with ether was measured. The concentration of the different constituents was determined by weighing the amounts added to make up the solution.

Both dielectric cells were used in the measurement of the dielectric constant of the solutions and were standardized against the samples of nitrobenzene and ether. The densities of these solutions were determined as in the preceding part and also the aberrations from the mixture rule. The following table (Table VII) gives the values obtained:

TABLE VII.

D.E.C	M.F. H_2O_2	M.F. H_2O.	M.F. Ether	D_1	M.F. $H_2O.H_2O_2$	No.
5.7	.032	.061	.907	.746	.093	(1).
8.0	.103	.099	.80	---	.202	(2).
8.4	.171	.049	.780	.792	.220	(3).
12.4	.190	.180	.630	.824	.370	(4).
18.1	.352	.095	.547	.872	.447	(5).
28.0	.476	.127	.397	.944	.603	(6).
40.0	.547	.157	.297	1.005	.703	(7).

If the logarithm of the dielectric constant is plotted against mol fraction of H_2O_2 plus mol fraction H_2O, a straight line is produced for numbers (3), (5), (6), and (7). These solutions contain about 13 percent water. The dielectric constant of 87 percent H_2O_2 - 13 percent H_2O mixture from the data of Cuthbertson and Maass is about 98. When the above values for 87 percent hydrogen peroxide, 13 percent H_2O are extrapolated to zero concentration of ether, the dielectric constant of the mixture is found to be 100. This shows that the dielectric constant of water and hydrogen peroxide is greater than the individual substances.

For the solutions (1), (3) and (4) the logarithm of the dielectric constant plotted against mol fraction does not give a straight line relationship. These solutions contain between 60 and 70 percent Hydrogen peroxide and the dielectric constants are therefore much higher.

The above points are plotted in the graph in Figure IX. The curve for the points numbers (3), (5), (6) and (7) is linear while points number (1), (3) and (4) are on a curve which shows a minimum and would probably show a value of over 100 for the dielectric constant of the mixtures.

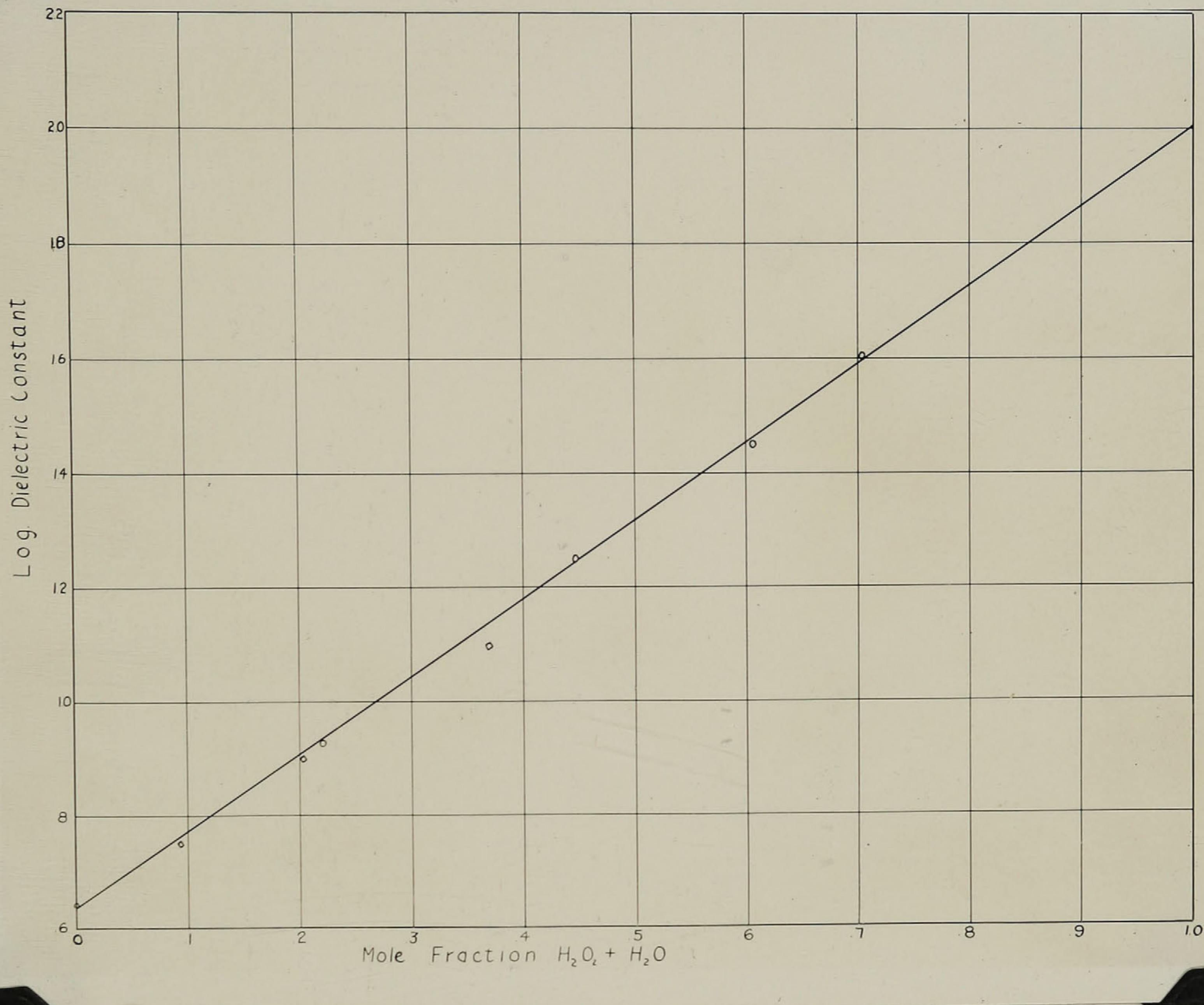

22
20
18
16
14
12
10
8
6
Log. Dielectric Constant
0
1
2
3
4
5
6
7
8
9
10
Mole Fraction H_2O_2 + H_2O

FIGURE IX.

SUMMARY.

Pure anhydrous hydrogen peroxide was prepared and innovations were made in the method which gave better yields.

The objection, that the resonance method for the dielectric constant was inaccurate due to the conductivity of the water, was shown to be unfounded. As long as the specific conductivity was below 4 x 10^{-6} no appreciable change could be noted in the dielectric constant. However, when the specific conductivity exceeds 4 x 10^{-6}, the dielectric constant increases very rapidly.

The dielectric constant and density of hydrogen peroxide at various dilutions with ether were measured. By extrapolating to 100 percent hydrogen peroxide, the dielectric constant of pure hydrogen peroxide was obtained and agreed with the value of Cuthbertson and Maass within the error of the measurements.

The aberration from the mixture rule was calculated. The results seem to point to a compound of ether and hydrogen peroxide being formed in equimolecular proportions.

The molar polarization of the mixture of hydrogen peroxide and ether was calculated from the Debye equation. The polarization of hydrogen peroxide was calculated but the electric moment could not be calculated since not enough measurements had been made on the dilute ether solutions. Since ether was not a true non-polar solvent the values for the electric moment of hydrogen peroxide would have no significance.

The dielectric constant and density of mixtures of hydrogen peroxide and water were measured at various dilutions with ether. By extrapolating the measurements of the dielectric constant to zero concentration of ether, the dielectric constant of mixtures of hydrogen peroxide and water were obtained. The values obtained for the dielectric constants of the mixtures agreed with those of Cuthbertson and Maass within the error of the measurements.

BIBLIOGRAPHY.

[1] Maass and others, I, J.A.C.S., 42: p 2548, 1920; II, Ibid., 42: p 2569, 1920; III, Ibid., 44: p 2472, 1922; IV, Ibid., 46: p 290, 1924; V, Ibid., 46: p 2693, 1924; VI, Ibid., 51: p 674, 1929; VII, Ibid., 52: p 489, 1930.

[2] Maass and Hatcher, I above.

[3] Cuthbertson and Maass, J.A.C.S., 52: p 483, 1930.

[4] Williams and Krchma, J.A.C.S., 48: p 1892, 1926.

[5] Hartley, J.C.S., 1908, p 428.

[6] Cuthbertson and Maass, VII above.

[7] Smyth, Morgan and Boyce, J.A.C.S., 50: p 1536, 1928.