MEASUREMENT OF THE DIELECTRIC CONSTANTS OF DILUTE SOLUTIONS OF ALCOHOL IN NON-POLAR SOLVENTS

by

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A. B., College of Emporia, 1930

A Thesis submitted to the Department of Physics
and the Faculty of the Graduate School of
the University of Kansas, in partial
fulfillment of the requirements
for the Degree of Master
of Arts

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May 24, 1932

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I. INTRODUCTION

1. Preliminary Considerations

By taking into consideration the contribution of electronic displacement and molecular orientation to the polarization of a dielectric, Debye[1] has arrived at the following expression for the dielectric constant:-

$$\frac{K-1}{K+2} = \frac{4\pi}{3} N\left(e^2 \sum \nu_p \gamma_p L_p + \frac{1}{3} \frac{\mu^2}{kT}\right) \tag{1}$$

Now at a given temperature T, all terms on the right hand side of this expression are constant except N, the number of atoms (or molecules) per unit volume. This, however, is proportional to the density. Furthermore, we may multiply both sides through by M, the molecular weight of the dielectric, and thus obtain:-

$$\frac{K-1}{K+2} \frac{M}{d} = P \tag{2}$$

ih which P is the molecular polarization of the dielectric. Experimentally, it has been found that this expression quite closely describes the behavior of liquids such as benzene; that is, non-polar liquids. But it has been shown[2] that, in the case of polar liquids (water, alcohols, etc.), and in the case of solutions of polar liquids in non-polar solvents the expression does not hold at all.

When a solution is used as dielectric M of equa. (2) must be replaced by the weighted molecular weight of the solution. That is, the

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[1] Marx, Handbuch der Radiologie, 6, 614 (1925)

[2] Ibid., 6, 628 (1925)

the molecular weight of the solution is computed from the relation

$$M_1C_1 + M_2C_2$$

where M_1 and M_2 are the molecular weights, and C_1 and C_2 the mole fraction concentrations of the solvent, and the solute, respectively. We then have instead of (2), the relation:-

$$\frac{K-1}{K+2}\,\frac{M_1C_1 + M_2C_2}{d} = P \qquad (3)$$

On the basis of the additive law the polarization P of the solution is made up of two parts: one due to the solvent, the other due to the solute; that is

$$P = P_1C_1 + P_2C_2 \qquad (4)$$

where P_1 and P_2 are the molecular polarizations of the solvent and the solute, respectively. P_1 may be calculated from data on the pure solvent, and knowing C_1, we have P_1C_1. P may be calculated from the data on the solution, using (3). Hence, since C_2 is also known

$$P_2 = \frac{P - P_1C_1}{C_2} \qquad (5)$$

Debye[3], and one of his students,[4] have shown that the molecular polarization P_2 depends markedly on concentration. This behavior is usually attributed to association changes. It was suggested by Debye[5] that the polarization P_2 would approach that polarization corresponding to the unassociated state as the concentration C_2 is made to approach zero; that is, he believed that association would disappear as the concentration of the associating molecules approached zero.

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3. Marx, Handbuch der Radiologie, 6, 627-633 (1925)
4. Lange, Zeitschr. für Phys. 33, 169-182 (1925)
5. Polar Molecules, Debye: p. 49, 1929

Thus the solute, at sufficiently small concentrations, should approach the behavior of its vapor. The limiting value of P_2 for the solute might be obtained by plotting a curve of polarization P_2 versus concentration C_2, and extrapolating from this curve to zero concentration. This limiting value we may call P_o. Then if P_o represents the polarization at infinite dilution at temperature I, we should find that

$$(P_o - A)T = B \tag{6}$$

where B is a constant related to the electric moment of the molecule by

$$\mu = 1.27 \times 10^{-20} \sqrt{B} \tag{7}$$

and A is the molecular refraction.

2. Previous Investigations

A survey of the available literature on the subject reveals two interesting points. First, so far as the writer has been able to determine, there has been no deliberate attempt to measure the dielectric constant of solutions of polar solutes in non-polar solvents at such concentrations of the solute that the number of molecules of solute per unit volume was comparable to the number of molecules per unit volume of vapor at atmospheric pressure or less. It seems reasonable to suppose that, since the extrapolation of the P_2, C_2 curve to zero concentration is apparently justified by the close agreement[6] between the electric moment observed for the vapor and that calculated from the value of P_o obtained from the extrapolation

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[6] Stranathan: Phys. Rev., pp. 653-671, Vol. 31, No. 4, Apr., 1928; Williams & Ogg: J. Am. Chem. Soc., 50, 94, 1928.

we should find a continuation of the smooth curve when the polarizations, P_2, of solutions of extremely low concentration C_2, are measured and plotted.

Stranathan[6] obtained reliable data at lower concentrations than had been used by any previous investigator. That his values of P_0 were well defined is shown by the close agreement between the electric moments of a given solute calculated for different temperatures, and by the close agreement of the moments thus calculated, with the moments obtained from vapor data. However, because of experimental difficulties his points at lowest concentrations showed a tendency to deviate from a smooth curve, and while they were not inconsistent, they were given little weight by him.

Extensive investigations of such solutions have recently been made by Williams and Ogg.[7] Results obtained by them have led them to state that "the values of the electric moment for the solute molecules, calculated from the dielectric constant and density data in various non-polar solvents, is quite independent of the solvent used." However, their work using polar liquids as solutes was done at relatively high concentrations, in no case less than .1 mole fraction of solute. In several instances they used substances which were so sparingly soluble in the solvents used that they were forced to work at exceedingly low concentrations. In these cases they did not calculate P_2. Using their data, the writer has calculated P_2 for these substances. When these data were plotted in the usual manner very striking curves were obtained, as may be seen on page 5 in which P_2 is plotted against the corresponding C_2 for Benzoic acid in carbon disulfide. It will be seen later that this curve shows an effect which agrees with some observations made by the writer.

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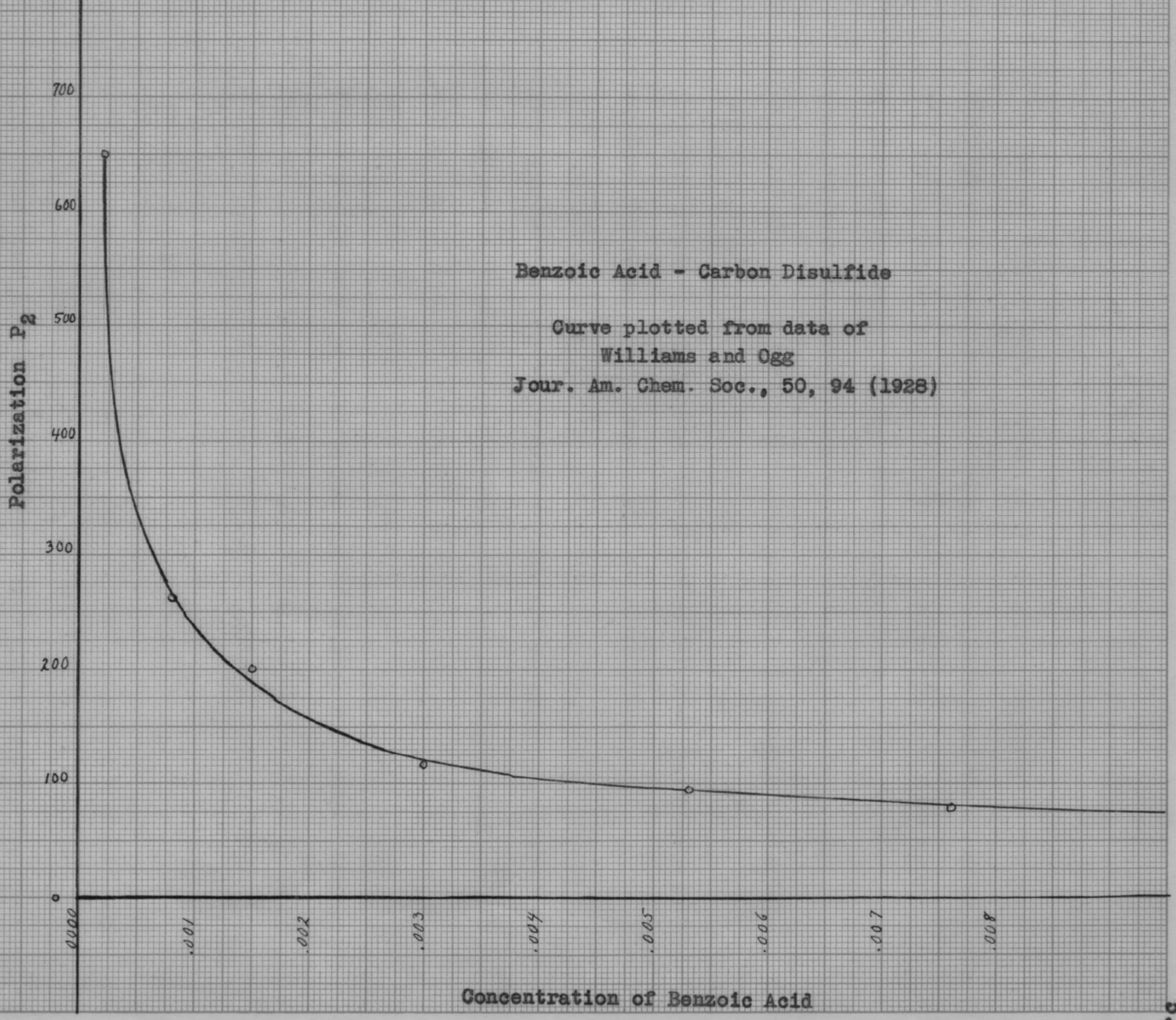
[7] Jour. Am. Chem. Soc., 50, 94 (1928)



Benzoic Acid - Carbon Disulfide

Curve plotted from data of
Williams and Ogg
Jour. Am. Chem. Soc., 50, 94 (1928)

We are led by such behavior of the curve to draw one of two conclusions:- (1) that there is in the method or apparatus one or more systematic errors which, because of the magnification of such error at low concentrations, vitiate the results; or (2) association changes are not eliminated even at these low concentrations; that is the solute when dissolved in a liquid does not behave in the same manner as where it is in vapor state.

Other workers have investigated the behavior of binary solutions, but none has worked in the region of such extremely low C_2.

A second point of interest is that in general there is rather poor agreement between the values of electric moment of some polar liquids as obtained from measurements in which different non-polar solvents were used. This, however, may be due to the fact that these values of electric moment were obtained by different workers using different apparatus, and not to the use of different solvents. Williams and his co-workers have obtained good agreement in electric moment of a substance using several different solvents.

3. Purpose of Present Research

In view of the conditions which were reviewed in section 2 of Introduction, it seemed desirable that an effort be made to determine whether or not the electric moment of some polar liquid were independent of the solvent in which it was dissolved. The writer undertook to use ethyl alcohol as the polar liquid, and to use as solvents three liquids which are generally considered to be non-polar: benzene, carbon tetrachloride and carbon disulfide.

In view of the results obtained from the first series of measurements (to be considered in detail in section III) the original purpose became submerged in what seemed a more important one. It seemed desirable to develop a method by which precise measurements could be made on solutions, such that the number of molecules per unit volume of solute in the solution was comparable to the number of molecules per unit volume of the vapor at ordinary pressures (1 atmosphere or less). This made imperative the design of apparatus and development of technique from which systematic experimental errors were eliminated.

The first series of measurements indicated that accurate measurement of the dielectric constant of solutions of $C_2 < .001$ mole fraction would be absolutely necessary in order to determine whether the effects which had been observed were due to systematic error or to unexpected association changes at these low concentrations of solute.

In order to be able to calculate the molecular polarizations of the solute at such extremely low concentrations, it was necessary to know the density of these solutions to a far greater degree of precision than that of any reference on the subject with which the writer is ac-

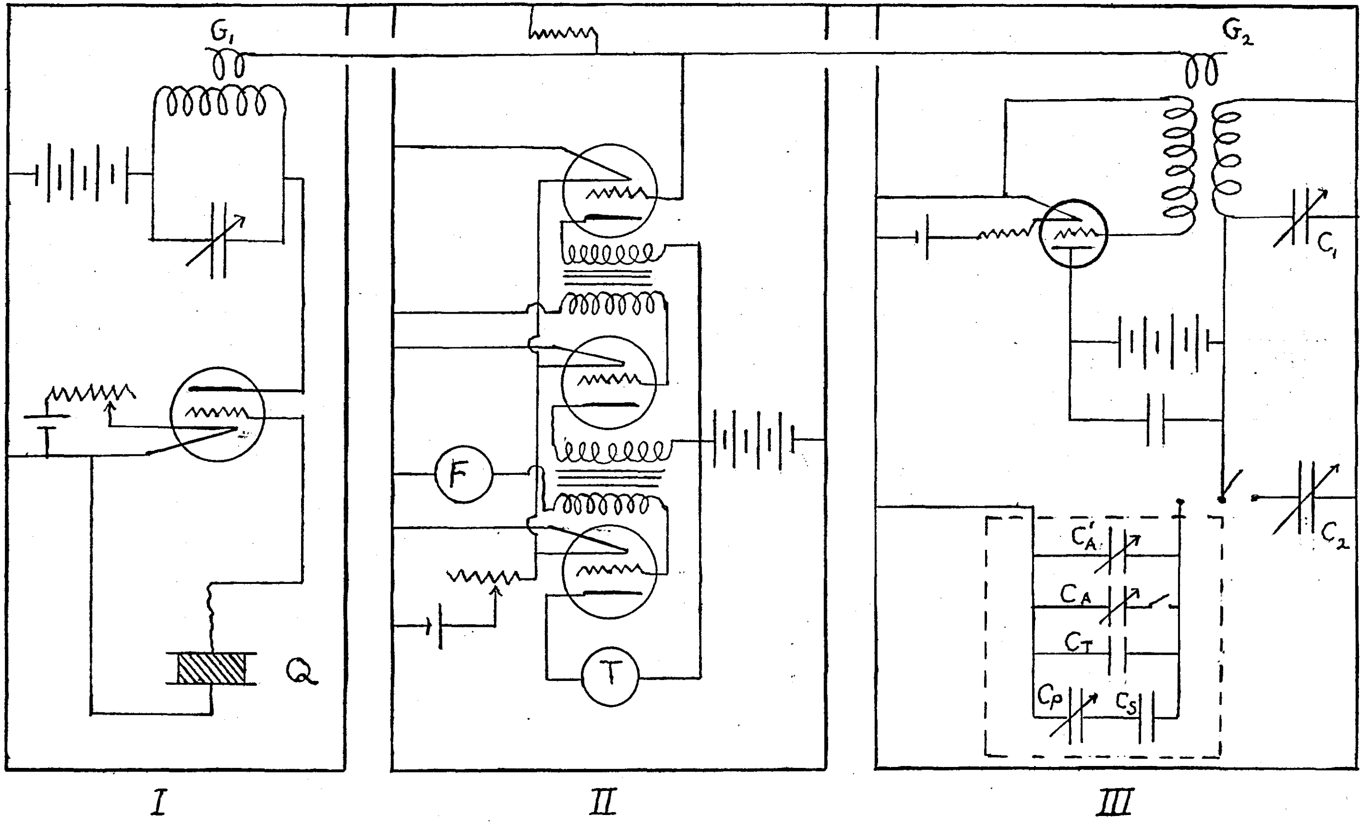


Fig. 1

quainted. Thus it was necessary to measure the density of dilute solutions of ethyl alcohol in the three solvents named above.

II. EXPERIMENTAL PROCEDURE AND APPARATUS

1. Description of Apparatus

This work may be divided into three practically separate parts so far as experimental procedure and method are concerned. With reference to each of these divisions there will be considered a separate set of data.

It was recognized that a relatively small error in the initial measurement of either the dielectric constant or density becomes greatly magnified during the process of calculation, and that the most precise method available should be used. In view of this the heterodyne beat method[8] was selected for the measurement of the dielectric constants.

A diagram of the apparatus is given in Fig. I. It consists of two high frequency oscillators I and III, the frequency of one of which is maintained constant at about 10^6 cycles by means of a quartz crystal. The frequency of the other oscillator is adjustable at will by variable condensers. In practice the frequency of this oscillator is adjusted accurately to 1000 cycles less than that of the other. The electric impulses from these two oscillators are impressed simultaneously upon the grid of the detector by means of the floating grids G_1 and G_2. The

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8. Zahn: Phys. Review, 24, 400, 1924.

beat note frequency is amplified by one stage of audio amplification. This amplified beat note together with the note from an electrically driven tuning fork is passed through another stage of audio amplification and the beat note between these two notes is impressed on the telephone receiver T. Obviously, the frequency of the variable oscillator can always be brought to a fixed value by bringing the beat note between the fork and the beat note between the two oscillators to zero value by varying the capacity of the second oscillatory circuit. The entire apparatus was housed in three separate metal boxes as indicated in the diagram. Thus the oscillators were shielded both from one another and from external influences. The oscillators were run from separate batteries which were new at the beginning of a series of measurements.

The test condenser C_T was completely submerged in a thermostatically controlled water bath. This water bath consisted of two separate metal boxes, one within the other. Space between them provided for a flow of cold water in case the room temperature exceeded the temperature of the inner bath.

Several forms of heater were tried. A coil of bare wire was discarded because the electrical influence communicated either through the water or magnetically to the test condenser caused measurable frequency changes. When an attempt was made to insulate this heater electrically a very large temperature lag was observed in the bath. Finally a 40 Watt incandescent lamp was found to be exactly suitable. The temperature of the bath was very constantly maintained at $25^\circ C \pm .1^\circ$.

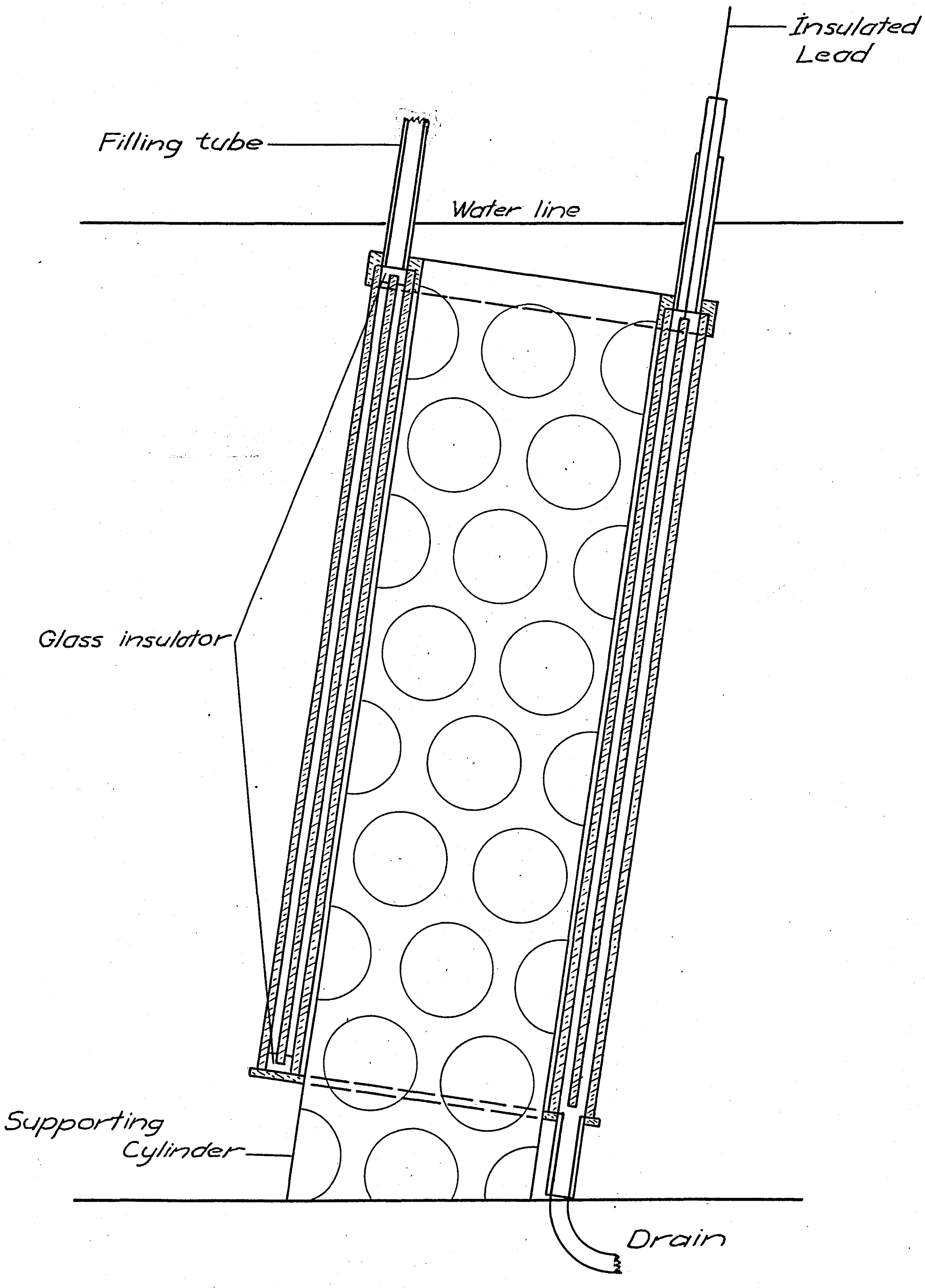
Three different schemes were tried, each of which required a different arrangement of the condenser assembly which is enclosed in the dotted rectangle in Fig. I. In the first scheme only condensers C_p and C_T, connected in parallel, were used. C_T will be described below. C_p was a General Radio precision condenser, type 222, No. 1074, having a maximum capacity of 1500 m.m.f. Any change in the capacity of this parallel arrangement due to the introduction of a different dielectric into C_T could be compensated for by a change in C_p. Since it was found that the greatest possible precision with this arrangement was inadequate, a second scheme was tried.

It seemed desirable that an arrangement be used such that a very small change in the capacity of C_T, would make a very large change in C_p necessary for compensation. The arrangement shown in Fig. 1 seemed to offer the best solution of this problem.

C_p and C_T were the same condensers as used in the first scheme. C_s was a variable air condenser of exceptionally rigid construction which was kept at a fixed capacity throughout the period of its use. C_A and C'_A were also variable air condensers of rigid construction. C'_A was inserted in the system merely for the purpose of increasing the total capacity of the system which had been greatly reduced by the use of the series arrangement. C_A was set at a value exactly equal to the capacity of C_T when the pure solvent was used as the dielectric. C_A was connected to the circuit by means of a switch which was so designed as to eliminate the possibility of changes in that part of the total capacity which was due to the switch itself. When C_T was not connected C_A was connected, thus providing the necessary capacity for oscillation of the circuit, and C_p was set at its maximum useable value. When C_T was filled with a solution and connected, C_A was disconnected and any change necessary in C_p was then due to the change in the capacity of C_T which change was in turn due to the amount of solute present in the solution. From the change made in C_p the change in C_T could be calculated; from this, and from the previously determined value of C_T when the pure solvent was used alone, the dielectric constant of the solution could be calculated.

During a series of measurements made with this second arrangement of condensers, much trouble was experienced because of uncontrollable drift in the frequency of the oscillator. It was found impossible to obtain consistent readings since it was constantly necessary to alter the setting of C_A.

It was difficult to locate the exact cause of this change in the zero point since several possibilities were present. It was necessary to remove the test condenser from the bath in order to empty it of one solution, dry it thoroughly and refill it with the next solution. Although every precaution was observed to avoid bumping the condenser against the leads, it was possible that some change was caused in this manner. When the condenser was removed and replaced, the very slightest change in position of the condenser, indeed, even the slightest rotation of the condenser about a very rigid vertical axis produced measurable changes. It is believed now that temperature changes in the room were also causing trouble but these were not detected until the above


Insulated Lead
Filling tube
Water line
Glass insulator
Supporting Cylinder
Drain

sources of error were eliminated.

In the third scheme, the same condenser arrangement was used as that of the second scheme except that it was no longer necessary to use C_A. The test condenser C_T was fastened very rigidly to the bottom and sides of the metal water bath. A small copper tube was attached to the drain plug in the bottom of the test condenser, passed through the bottom of the water bath and thence through the large shield box which contained the entire oscillator and condenser system. It was thus possible to fill, drain and dry the test condenser without disturbing its position or connections in any way.

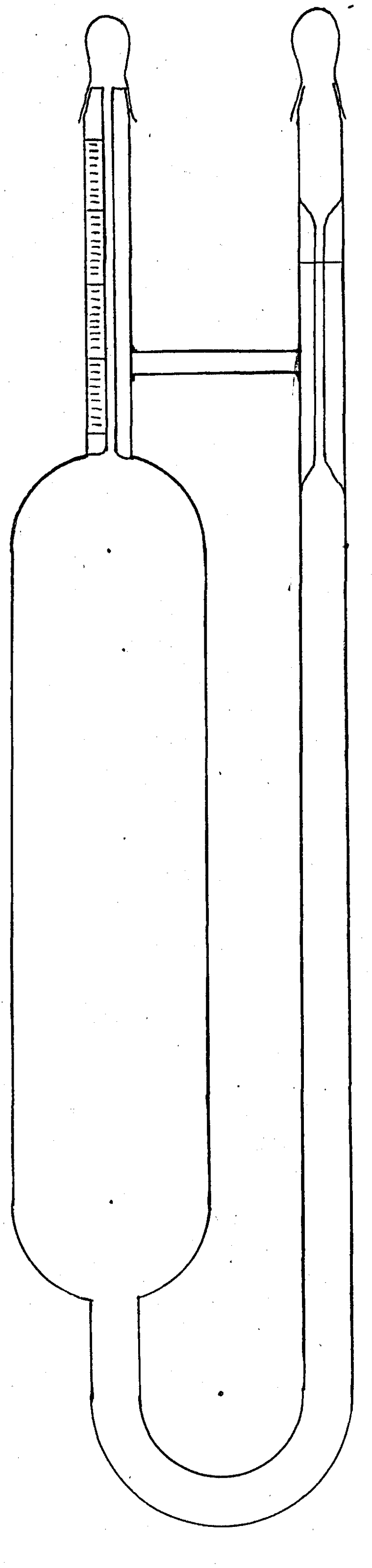
The test condenser is shown in Fig. II. It consisted of 3 pieces of brass tubing arranged concentrically. The two outer pieces were soldered to a brass ring at either end, while the inner cylinder, the insulated plate, was supported at each end by pyrex glass insulators as shown. The insulated lead wire to this plate passed through a large hole in the upper ring and through a piece of brass tubing which was shrunk on to the glass insulator through which the lead wire passed. Diametrically opposite to this lead wire tube was a filling tube and slightly to one side of this was a small tube which was opened when filling or drying the condenser. This small tube served to allow the escape of bubbles which were conveyed to it by a small v-shaped groove on the inner surface of the brass ring. This v-shaped groove also served to prevent the gathering of bubbles between the upper edges of the plates since the center of the groove was well above the top of the insulated plate.

A drain tube was soldered into the bottom ring on the opposite side of the condenser from that of the filling tube. When the condenser was placed in the bath, it was not placed vertically but at a slight angle with the vertical. In this way the drain hole was made the lowermost point at the bottom and the filling tube hole was the uppermost point at the top.

The test condenser had a liquid capacity of approximately 93 cc. Its electrical capacity with air as dielectric was 294.75 m.m.f.

A section of brass tubing having an outside diameter equal to the inside diameter of the top and bottom rings of the test condenser was securely soldered to the bottom of the water bath at the angle at which the condenser was to sit in the bath. This tube was completely perforated with large holes to allow for free circulation of water through and around it. The test condenser was placed in the bath by slipping it over this section of tubing, and thus was always replaced in exactly the same position each time and was held securely in this position.

Substances Studied. It was proposed to use ethyl alcohol as the polar liquid and to use as the non-polar liquids, benzol, carbon tetrachloride and carbon disulfide. Pure 95% ethyl alcohol was dried just before it was needed for a series of measurements. It was boiled over CaO for 24 hours and then distilled, the first and last portions of the distillate being rejected. No signs of coloration were observed when some of the dried alcohol was allowed to stand in contact with carefully dried $CuSO_4$ for several days. The benzol, carbon



PYKNOMETER

tetrachloride and carbon disulfide were Mallinckrodt's regular C.P. quality. No further effort was made to dry these since it was believed that the small amount of water present would not effect the results.

It was necessary to determine very accurately the relation between density and concentration over the range of concentrations to be used. Several methods were tried, by far the most precise of which was that in which a specially designed pyknometer was used. This design is due to Parker and Parker[9], the general scheme of which is shown in Fig. III.

The balance on which all the weighings of solutions, both for density and dielectric constant measurements, were made was very carefully selected. It was a large Paul Bunge balance having a maximum load capacity of 1 kg. in each pan and a sensitivity under maximum load of .1 mg. The balance was used on a stone pier.

A new set of gold plated weights was calibrated especially for and used throughout this work.

2. Calibration of Apparatus.

The precision condenser C_p used in this apparatus had been previously calibrated with special care by Knowles and Stranathan. This was accomplished by measuring the capacity change for every hundred divisions in terms of a fixed interval on another similar precision condenser which was placed in parallel with it. The worm gear was checked at 10 points in a similar manner. Capacity changes as measured on C_p should be in error by less than .06 m.m.f. at all

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[9] Jour. Phys. Chem. 29, p. 132, 1925.

points between 300 and 2400 scale divisions.

Since the changes in capacity to be measured were quite small, an air condenser was placed in series with the precision condenser. Neither terminal of this series condenser C_s could be grounded in use. It was found by Knowles[10] that the capacity of a condenser when used in this manner was quite different from its capacity when used with one set of plates grounded. He found that an entirely different method[10] was necessary for the evaluation of the capacity of a condenser when used in this manner. This method was followed in evaluating the capacity of C_s used in this apparatus.

The capacity of the test condenser with air as dielectric was measured by breaking the connection to C'_A and shorting across C_s. C_T was then directly in parallel with C_p, as used in the first series of measurements.

In order to measure the distributed capacity, that is, that part of C_T which is not changed by a change in the dielectric, the following procedure was followed:

$$K_A = \frac{C_A}{C_V} = 1.000536 \qquad \text{where}$$

C_A is the capacity of the condenser with air as dielectric

C_V is the capacity of the condenser with vacuum as dielectric

K_A is dielectric constant of air.

$$\text{or } C_V = \frac{C_A}{1.000536} = \frac{302.18}{1.000536} = 302.02 \text{ (approx.)}$$

Now assuming the dielectric constant of benzol to be 2.273, at 25°C,

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[10] Doctor's Thesis, K.U. 1931

we have

$$2.273 = \frac{677.14 - d}{302.02 - d}$$

in which d is the distributed capacity, hence

$$d = \frac{9.35}{1.273} = 7.34 \text{ m.m.f.}$$

3. Experimental Procedure

The density-concentration relationship for each type of solution was determined from a distinct set of solutions made up especially for the density determinations. The dielectric constants of these solutions were not measured. The set of solutions comprised 8 to 14 different solutions at regular intervals within the range over which it was expected to measure the dielectric constants.

Each of these solutions was weighed and mixed in a glass stoppered bottle which had been previously thoroughly cleaned and dried. Seven of these bottles were used, each being numbered so that successive weights could be checked and thus any change in weight of the bottle readily detected. All these bottles were cleaned and dried and placed inside the balance case at least five hours before any weighing was attempted. This was absolutely necessary in order that the bottles be in temperature equilibrium with the balance when they were weighed.

After the bottle was weighed, the required amount of alcohol was introduced into the bottle from an air tight dropping bottle which was also kept in the balance case. The weight of this alcohol was quickly determined, the benzol added immediately and the mixture weighed. The mixture was thoroughly mixed by shaking and then introduced into the pyknometer. The pyknometer was completely filled to the level of the top of the short tube. It was then immersed in the constant temperature water bath where it was left until complete temperature equilibrium was attained. The level of the liquid was adjusted to the scratch mark on the tube on which there is but one mark. Then the height of the liquid in the tube above the bulb was noted while the pyknometer was held in the bath. Then it was removed, dried thoroughly and weighed. Since the volume of the pyknometer was known and since the graduated capillary had been calibrated, any variation in the height of the liquid in the tube could be corrected for, and hence the density calculated.

A curve was plotted using density as ordinate and mole fraction concentration as abscissa. From the slope of this curve the rate of change of density with concentration was determined. The same procedure was followed in the case of the ethyl alcohol-benzol, ethyl alcohol-carbon tetrachloride and ethyl alcohol-carbon disulfide curves.

The method of preparing solutions, the dielectric constants of which were measured, was exactly the same as that described above for density determinations.

Several hours before a series of dielectric constant measurements was to be made, the oscillators were turned on and the stirrer of the water bath started (the bath was held at approximately 25°C even when not in use.) Thus it was determined that there was no drift in the frequency of the oscillators due to warming up of the apparatus. In general there was always a slight drift in frequency, the cause of which was unknown at the time of the first series of measurements. It was believed that any slight drift could be corrected for by adjustment of C_1.

First Series of Measurements.

In the first series of measurements, in which no series condenser was used, the condenser was thoroughly dried after washing with pure solvent, by opening all vents and blowing through it a strong current of heated air until it was certain that no traces of the liquid remained. The empty condenser was then placed in the bath, allowed to attain temperature equilibrium and its capacity measured. It was then removed from the bath, filled with solution, replaced in the bath and allowed to come to the temperature of the bath. The capacity of the condenser with the solution as dielectric was then measured.

The insulated plate of the test condenser was connected to the apparatus by means of a short piece of flexible wire. This could be disconnected or connected easily at will. When the condenser was placed in the bath this insulated lead was left unconnected until an accurate setting of the precision condenser had been made. This setting was found to remain practically[11] constant whether the condenser were empty or filled and hence was taken as a zero reference point, from which the amount and rate of drift of frequency of the oscillator could be observed. The insulated lead was then connected and another accurate setting of the condenser was made. From the

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[11] Often absolutely constant to the degree of accuracy to which measurement was possible with this condenser arrangement.

difference of these two settings the capacity of the test condenser could be calculated and from this the dielectric constant of the solution was found.

Second Series of Measurements.

In this series of measurements, a method which might be called a method of successive dilutions was used in the weighing and mixing of solutions. This consisted of weighing a relatively large amount of alcohol into a bottle and adding to this a correspondingly smaller amount of benzol. This solution was the "first dilution", and was used in the same manner as the pure alcohol had been used in the first series. Of course, the exact percentage of alcohol in this solution was known and hence the actual amount of alcohol in the successive "second dilutions."

The advantages of the above method of mixing solution are, first, that the amount of alcohol which evaporated during manipulation was a smaller fraction of the amount used than was the case when pure alcohol was used, and second, that a given error in the weighing introduced a smaller percentage error in the computed amount of alcohol. Errors in the amount of benzol used were relatively unimportant because of the large amounts used.

In this series of measurements the attempt was made to use the auxiliary condenser C_A, the capacity of which was equal to the capacity of C_T with pure solvent as the dielectric. It was hoped thus to measure only the small change in capacity of C_T, ΔC_T, due to the change in concentration of the alcohol in the solution. This change ΔC_T was, in the more dilute solutions, a very small one.

Now it was absolutely necessary that this small change be very precisely measured. In the series arrangement of condensers, a very small change in the capacity of C_T made necessary a comparatively large change in the capacity of C_p, especially in the case of the most dilute solutions.

In the measurements, the apparatus was set at zero beat with C_A connected, and C_T filled with solution in place but disconnected, by setting C_p near its maximum. The reading of C_p was noted. C_T was then connected and C_A disconnected. In order to compensate for the difference between the capacity of C_T with a solution containing alcohol, and C_A, it was necessary to reset C_p. From ΔC_p, ΔC_T was calculated.

Third Series of Measurements.

For the third series of measurements a large amount of pure solvent, of same purity as used above but all of the same manufacturer's lot number, was obtained. In order to further assure its uniformity, this was all poured into a single large bottle and thoroughly mixed. Otherwise the same procedure as described above was used in the mixing of solutions. Also the same apparatus was used and same procedure followed in the measurements of dielectric constants except that C_A was not used as a reference point. Furthermore, the test condenser was fastened permanently in the water bath as described above. Instead of C_A, the test condenser filled with pure solvent was itself used as the reference point, in the following manner.

Before any measurements on solutions were made, C'_A was disconnected and C_s was shorted from the circuit. This changed the circuit back to the arrangement as used in the first series of measurements. The test condenser, C_T, was thoroughly dried and its capacity when empty was measured. It was then filled with pure solvent and its capacity again measured. This procedure was repeated several times and the average values of C_T empty and C_T pure solvent were used in subsequent calculations.

The test condenser was filled with pure solvent and an accurate setting of C_p made. It was drained, dried and filled with solution immediately. A second accurate setting of C_p was made. It was again dried, refilled with pure solvent, and the first setting checked. If the settings of C_p in both cases in which pure solvent was used were identical, it seemed a safe assumption that no drift in frequency had occurred in the interval between these measurements. From the difference between the settings of C_p when C_T was filled with solution and when filled with pure solvent, ΔC_T, the change in the capacity of C_T due to the presence of a given amount of alcohol could be calculated. This calculated ΔC_T was added to the capacity of C_T when pure solvent was used as dielectric. This gave the actual capacity of C_T when the given solution was between the plates.

III. DATA AND CALCULATIONS

First Series

The polarization of the pure solvent was calculated from the expression

$$P_1 = \frac{K-1}{K+2}\,\frac{M}{d}$$

In the case of benzol

$$P_1 = \frac{2.27297-1}{2.27297+2}\,\frac{78.048}{.87288} = 26.63763$$

Sample Calculation Solution No. 1

Data

C_T solution No. 1 = 691.40 m.m.f. Calculated K = 2.321

Density of Sol = .87205 Calculated C_1 = .98777

Weight of Benzol = 87.6775 gr. Calculated C_2 = .012294

Weight of Alcohol = .6438 gr.

$$M_1C_1 \quad M_2C_2 = 77.093 \quad .566 = 77.659$$

Known Constants

Distributed Capacity = 7.34 m.m.f. $P_1 = 26.63763$

$C_{T_{vac}}$ - Distributed Capacity = 294.68 m.m.f.

Calculation

$$K_s = \frac{691.40 - 7.34}{294.68} = 2.3214$$

$$\frac{K-1}{K+2}\,\frac{M_1C_1 + M_2C_2}{d} = P_s = \frac{2.3214-1}{2.3214+2}\,\frac{77.659}{.87205} = 27.2257$$

$$P_2C_2 = P_s - P_1C_1 = 27.2257 - 26.311 = .91476$$

$$P_2 = \frac{.91476}{C_2} = \frac{.91476}{.012294} = 74.407$$

Density Data (First Series)

It is of interest to compare several determinations of the density of pure benzol, the first set made using a bottle type of pyknometer, the second set using the pyknometer as described in Section .

Bottle Type	U Type
.8728	.87288
.8725	.87289
.8735	.87288
.8737	.87290

Benzol from the same bottle was used in both sets, of course. Because of the great magnification of error in either K or d which occurs when the quantity P_1C_1 is subtracted from P_s, it is absolutely essential that the densities of the solutions be known accurately to 4, preferably to 5 decimal places. Obviously the accuracy of determinations made with the bottle type pyknometer is entirely inadequate.

The determinations made with the U type pyknometer, as shown above, and as shown by a later series of determinations in the next section, indicate a maximum variation of .00008, that is, one part in 10,000 or .01%. Every precaution and the greatest care was exercised to maintain this degree of precision in all density determinations and it is believed that the following data showing the variation of density with concentration of ethyl alcohol in the solvents used is the best available at the present time. This degree of precision was considered sufficient for the purpose in hand.

Ethyl Alcohol-Benzol

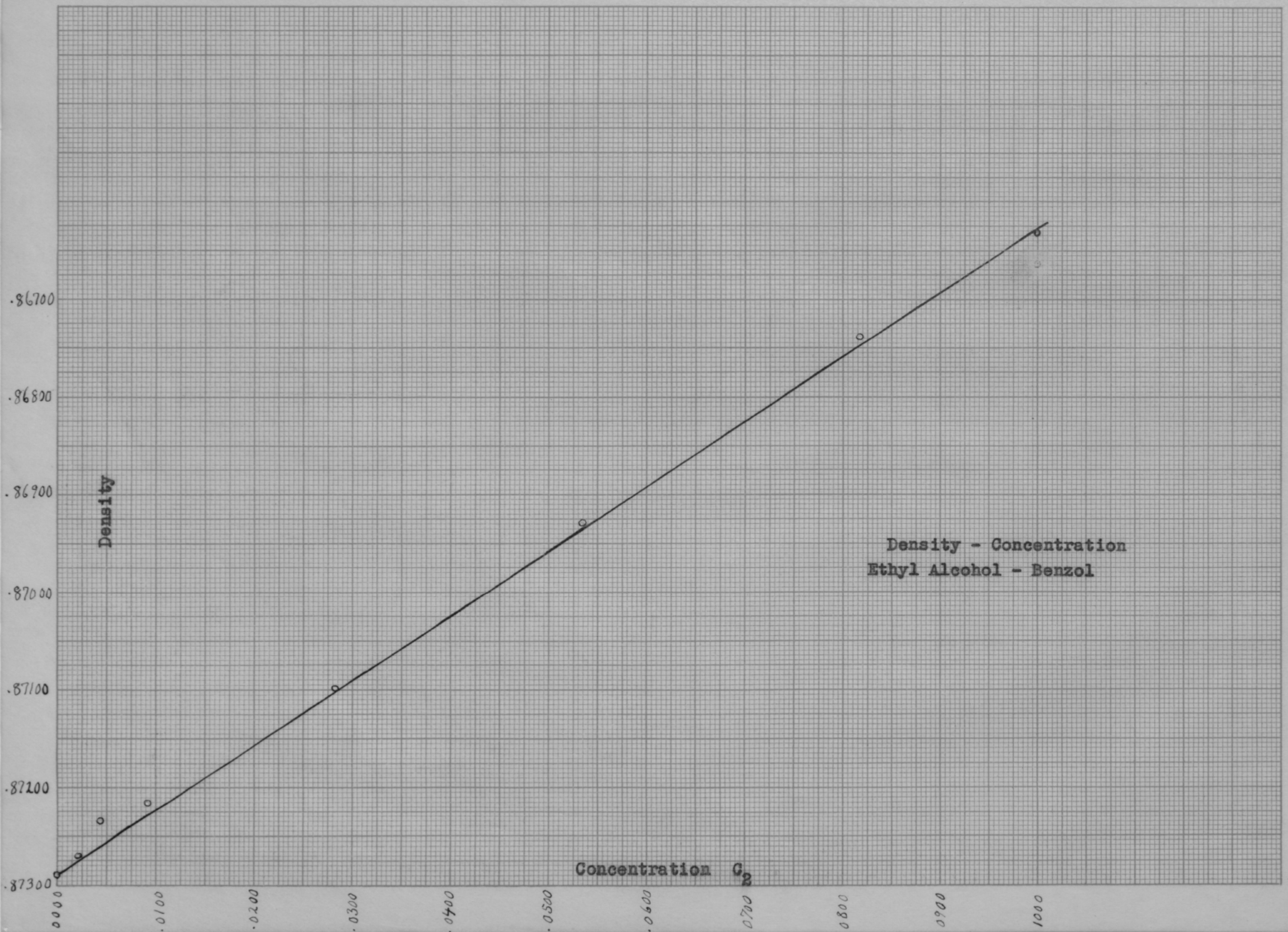
Concentration C_2	Solution Density
.00000	.87288
.00232	.87269
.00439	.87234
.00921	.87216
.02820	.87099
.05340	.86929
.08158	.86737
.10000	.86631

Ethyl Alcohol-Carbon Tetrachloride

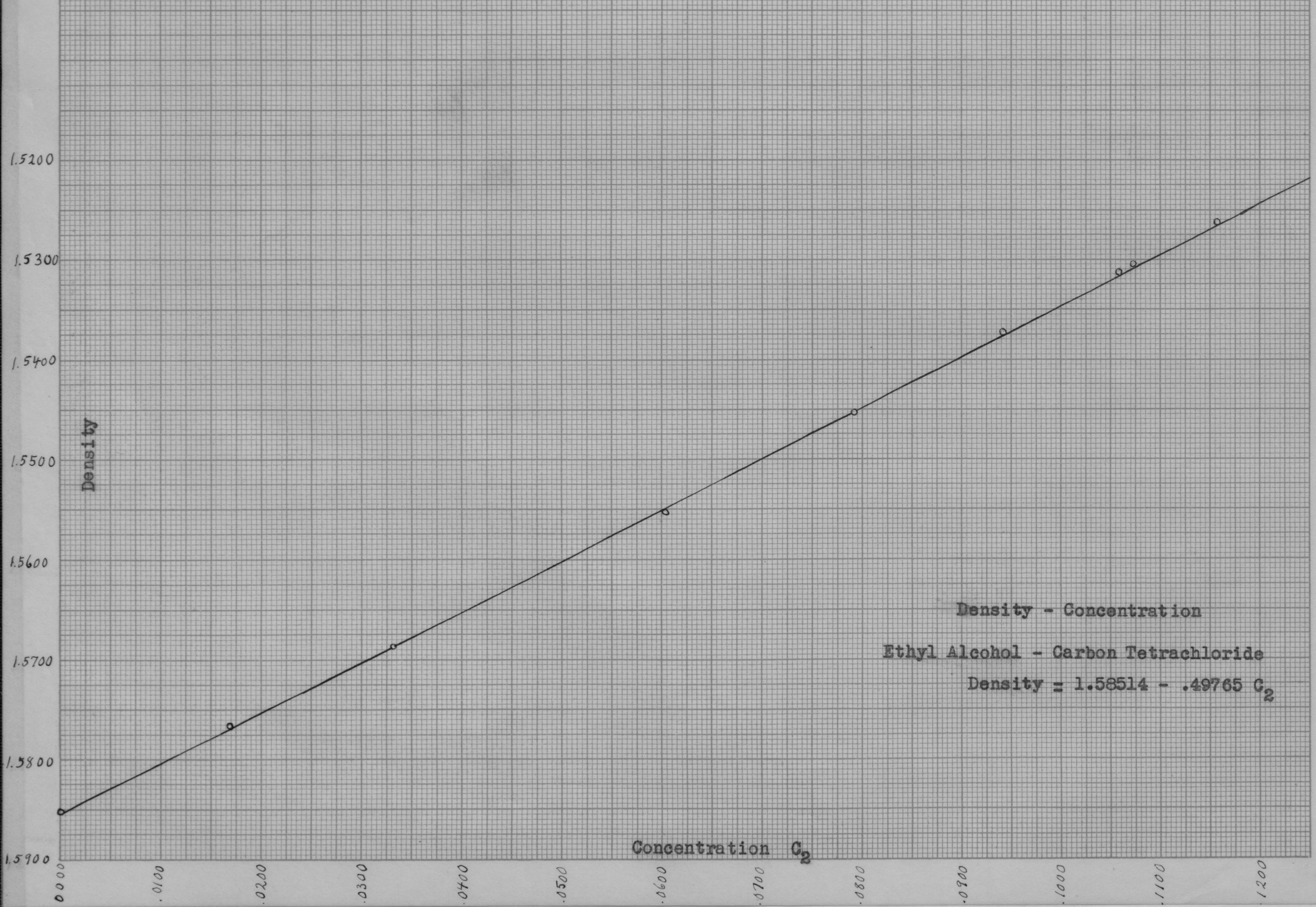
Concentration C_2	Solution Density
.00000	1.58519
.01690	1.57674
.03320	1.56872
.06030	1.55523
.07912	1.54533
.09423	1.53736
.10586	1.53130
.10727	1.53038
.11573	1.52603

Ethyl Alcohol-Carbon Disulfide

Concentration C_2	Solution Density
.00000	1.25617
.01723	1.25059
.03239	1.23995
.036713	1.23788
.05568	1.22926
.08295	1.21463
.10067	1.20652



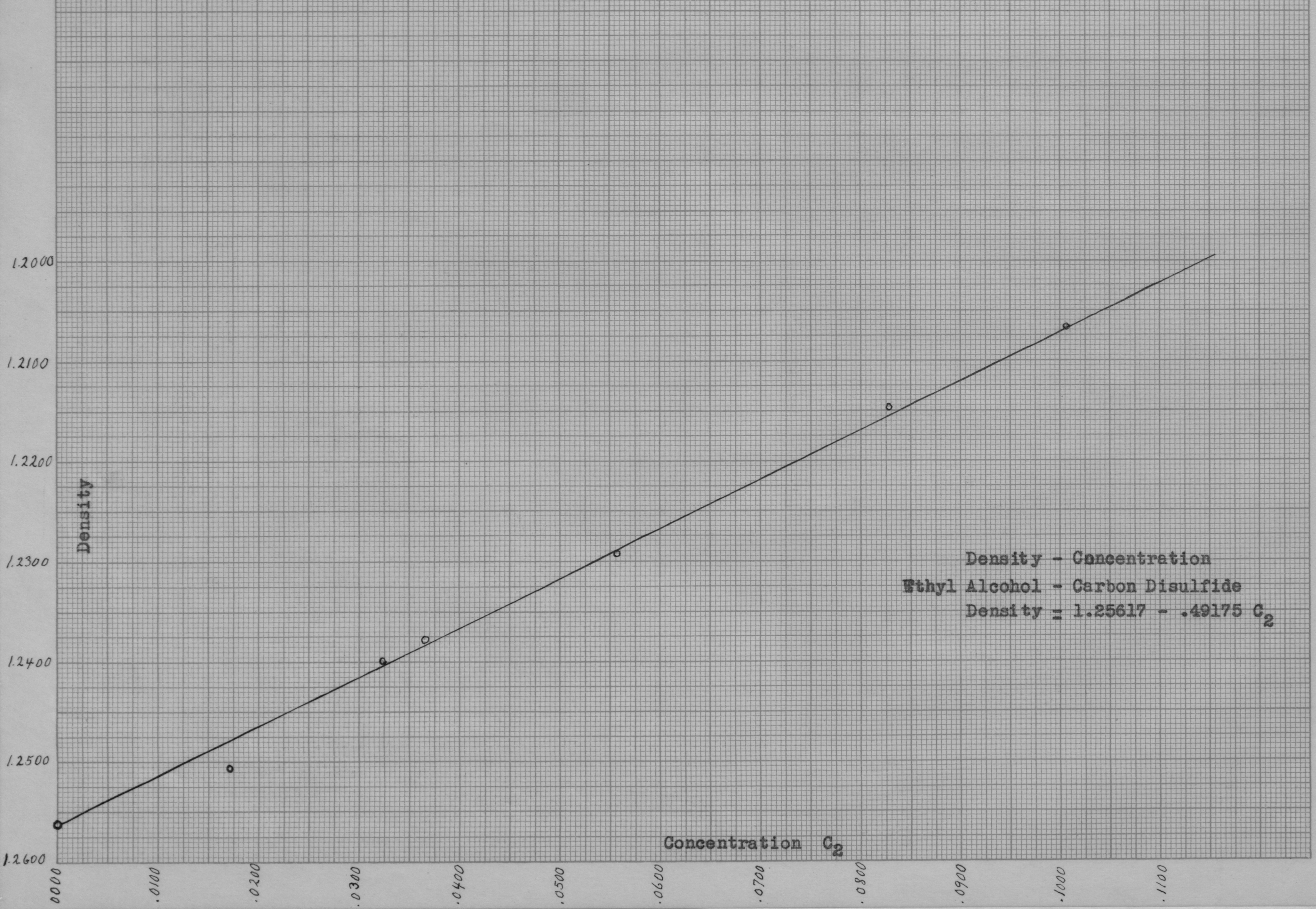
Density - Concentration
Ethyl Alcohol - Benzol



Density - Concentration

Ethyl Alcohol - Carbon Tetrachloride

Density = 1.58514 - .49765 C_2


Density - Concentration
Ethyl Alcohol - Carbon Disulfide
Density = 1.25617 - .49175 C_2
Density
Concentration C_2
1.2000
1.2100
1.2200
1.2300
1.2400
1.2500
1.2600
.0000
.0100
.0200
.0300
.0400
.0500
.0600
.0700
.0800
.0900
.1000
.1100

Second Series Data

Pure Benzol

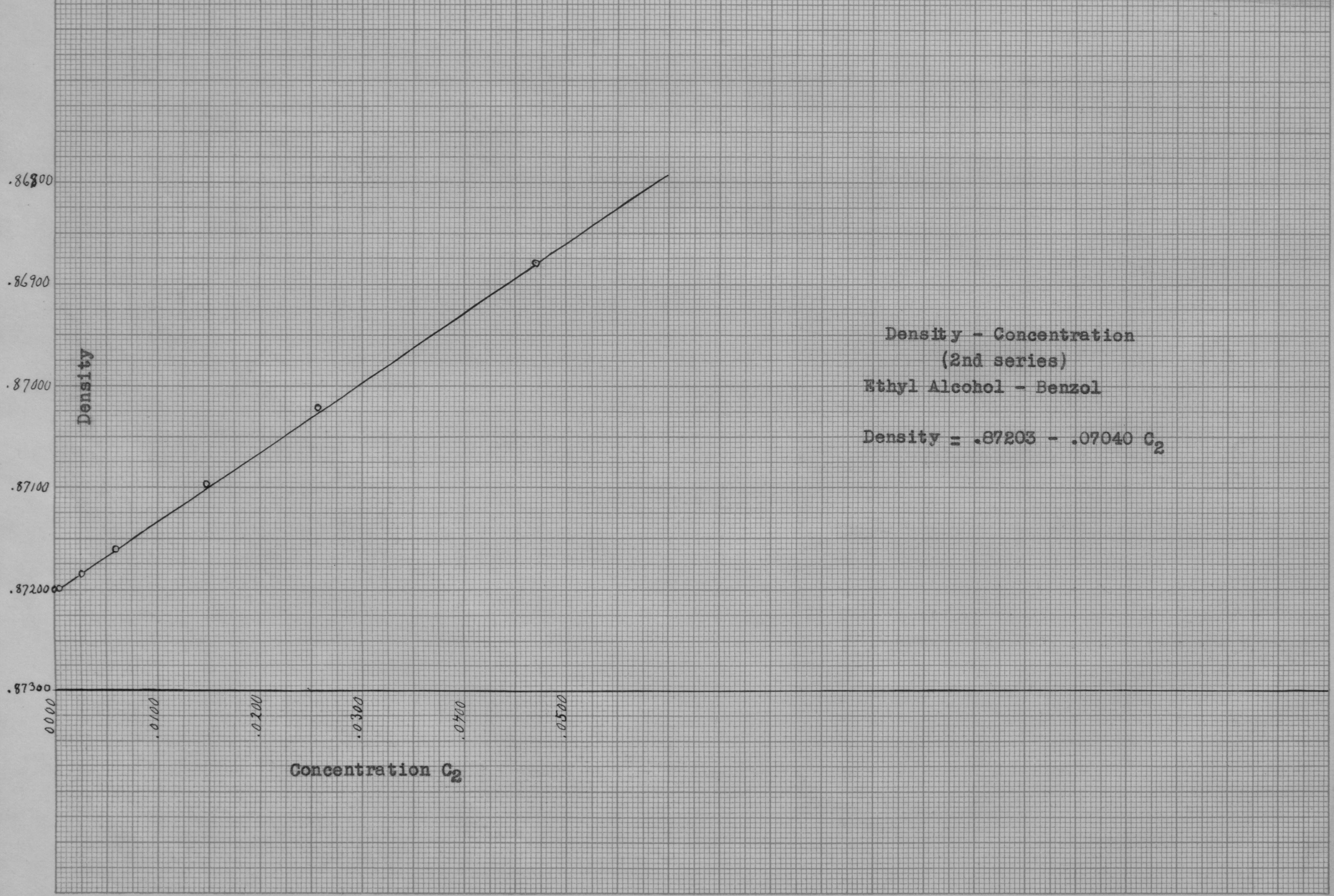
Density	Density*
.87203	.87187
.87196	.87214
.87195	.87282
.87196	.87195
.87204	.87189

* This set of determinations was made while trying out a new type of heater. It was found that there was a tremendous temperature lag which caused the temperature of the bath to vary about 3°C. That the variations in density were due to this temperature variation of the bath is shown by the other set of determinations made when no variation in bath temperature could be detected.

Ethyl Alcohol-Benzol

Concentration C_2	Solution Density
.000000	.87199
.000444	.87196 **
.000607	.87198 **
.002603	.87184
.005993	.87159
.014882	.87096
.025766	.87021
.047058	.86880

** It will be observed that in the case of these two solutions the change in density is reversed. However, it must be remembered that the maximum variation to be expected as shown by a series of determinations on pure solvent was .00008, and that at these very low concentrations of alcohol, the change in density is well within this limit. It would be necessary to know the density accurately to .00001 in order to make precise determinations of density at such low concentrations of alcohol.



Density - Concentration
(2nd series)
Ethyl Alcohol - Benzol

Density = .87203 - .07040 C_2

The density-concentration relationships for the above solutions may be summarized by the following statements:-

At 25° C

the density of any given solution of:

Benzol-Ethyl Alcohol is given by:- Density $= 0.87203 - 0.07040C_2$

Carbon disulfide-Ethyl Alcohol is given by:-
Density $= 1.25617 - 0.49175\ C_2$

Carbon tetrachloride-Ethyl Alcohol is given by:-
Density $= 1.58514 - 0.49765\ C_2$

in which C_2 has the same significance as that attached to it throughout this paper.

Polarization Data (First Series)

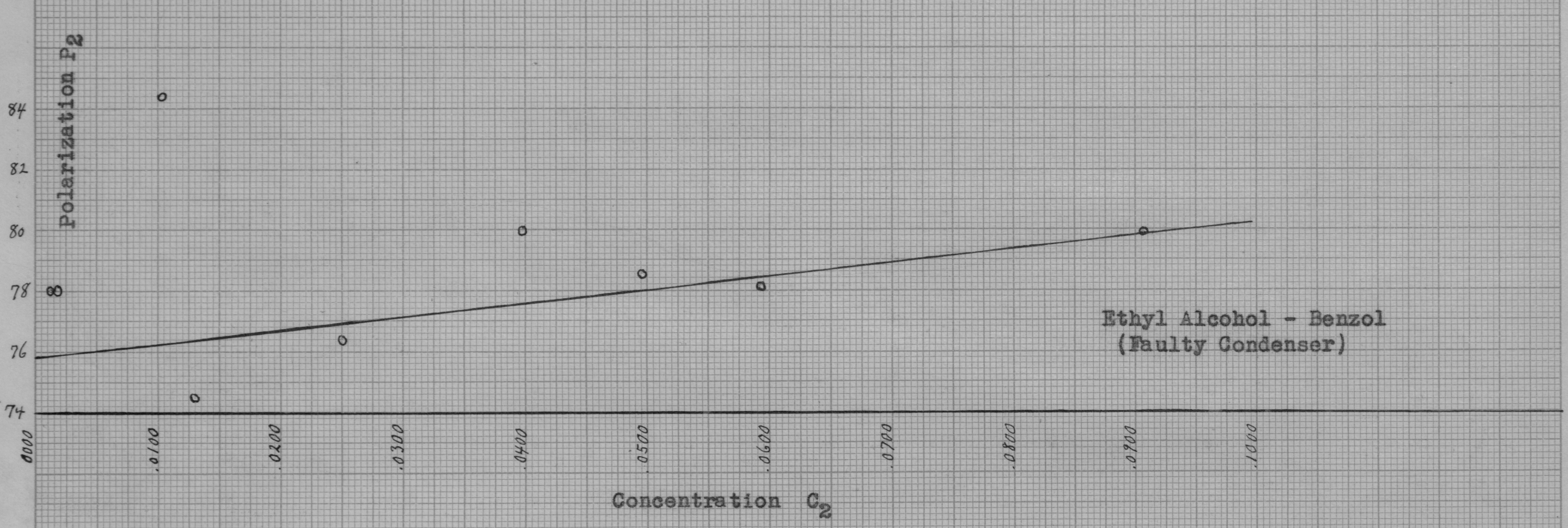
Ethyl Alcohol-Benzol

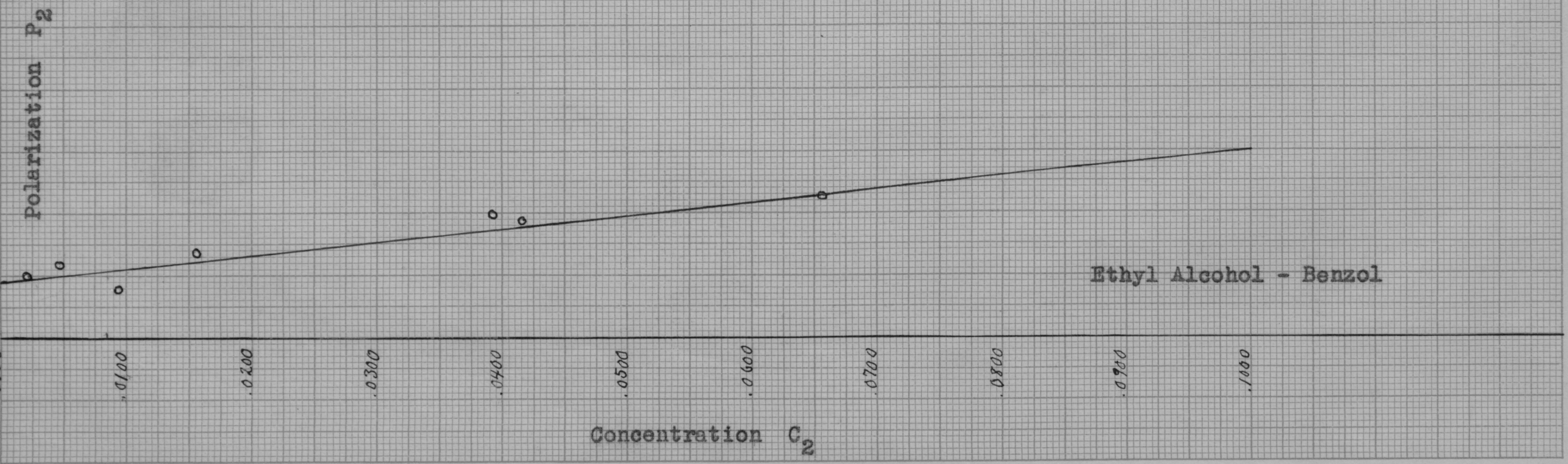
C_2	K	d	$\frac{K-1}{K+2}\ \frac{1}{d}$	P	P_1C_1	P_2C_2	P_2
.00117	2.27765	.87280	.34221	26.69590	26.6553	.09056	76.93
.00155	2.27915	.87277	.34250	26.7147	26.5953	.11937	76.91
.01039	2.32072	.87217	.35047	27.2368	26.3594	.87745	84.37
.01229	2.32100	.87205	.35058	27.2250	26.3110	.91476	74.40
.02503	2.37500	.87117	.36090	27.8789	25.9699	1.90891	76.26
.03964	2.44197	.87023	.37303	28.6412	25.5808	3.16046	79.73
.04951	2.49182	.86958	.38193	29.2038	25.3177	3.88610	78.48
.05936	2.53736	.86892	.38993	29.6925	25.0555	4.63703	78.12
.09065	2.70958	.86683	.41876	31.4692	24.2220	7.24720	79.95

During the taking of the above set of data, quite a large drift in the frequency was noted, which was finally traced to the reference Condenser C_2. This was replaced by a higher grade condenser and the following data taken. Comparison of the two curves over the same range will show clearly the effect of the poor condenser.

Polarization Data (first series) Ethyl Alcohol-Benzol (continued)
After elimination of faulty condenser

	C_2	K	d	$\frac{K-1}{K+2}\frac{1}{d}$	P	P_1C_1	P_2C_2	P_2
	* .000261	2.27104	.87206	.34125	26.63149	26.60604	.02545	97.43
	* .000265	2.27104	.87206	.34125	26.63144	26.60692	.02552	96.02
	.000531	2.27591	.87284	.34186	26.67626	26.62346	.05280	99.37
	* .000535	2.27229	.87205	.34149	26.64723	26.59873	.04850	90.63
	* .000845	2.27524	.87242	.34190	26.67581	26.60283	.07298	86.35
	.001057	2.27752	.87281	.34218	26.69503	26.60944	.08559	80.91
	.001106	2.27769	.87281	.34221	26.69697	26.60814	.08827	80.25
	.001112	2.27830	.87281	.34232	26.70567	26.60801	.09766	87.98
	* .001512	2.27630	.87198	.34228	26.69753	26.57273	.12480	82.51
1	✓ .002265	2.28196	.87273	.34305	26.74926	26.57726	.17199	75.92
2	✓ .004666	2.29167	.87257	.34492	26.86928	26.51331	.35597	76.29
3	✓ .009513	2.31481	.87224	.34861	27.10251	26.38419	.71831	75.51
4	✓ .015575	2.33667	.87184	.35353	27.41649	26.22272	1.19377	76.65
5	✓ .039304	2.44275	.87026	.37315	28.65467	25.59066	3.06401	77.95
6	✓ .041752	2.45340	.87010	.37508	28.77310	25.52540	3.24770	77.78
7	✓ .065753 P77 book I	2.57065	.86847	.39568	30.04968	24.88610	5.16359	78.53


Polarization P2
84
82
80
78
76
74
0000
.0100
.0200
.0300
.0400
.0500
.0600
.0700
.0800
.0900
.1000
Concentration C_2
Ethyl Alcohol - Benzol
(Faulty Condenser)


Polarization P_2
80
78
76
74
0.000
.0100
.0200
.0300
.0400
.0500
.0600
.0700
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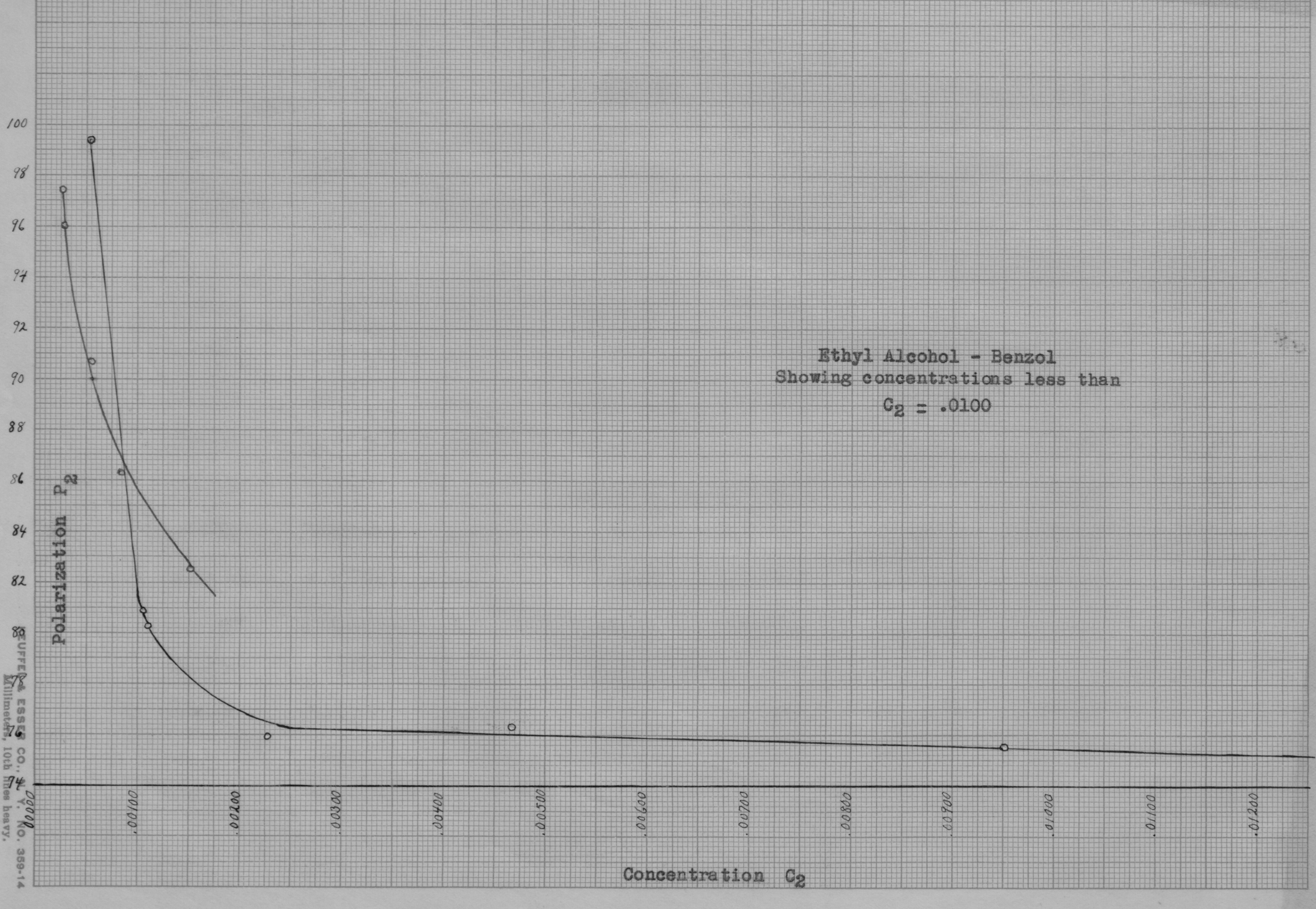
.0900
.1000
Concentration C_2
Ethyl Alcohol - Benzol

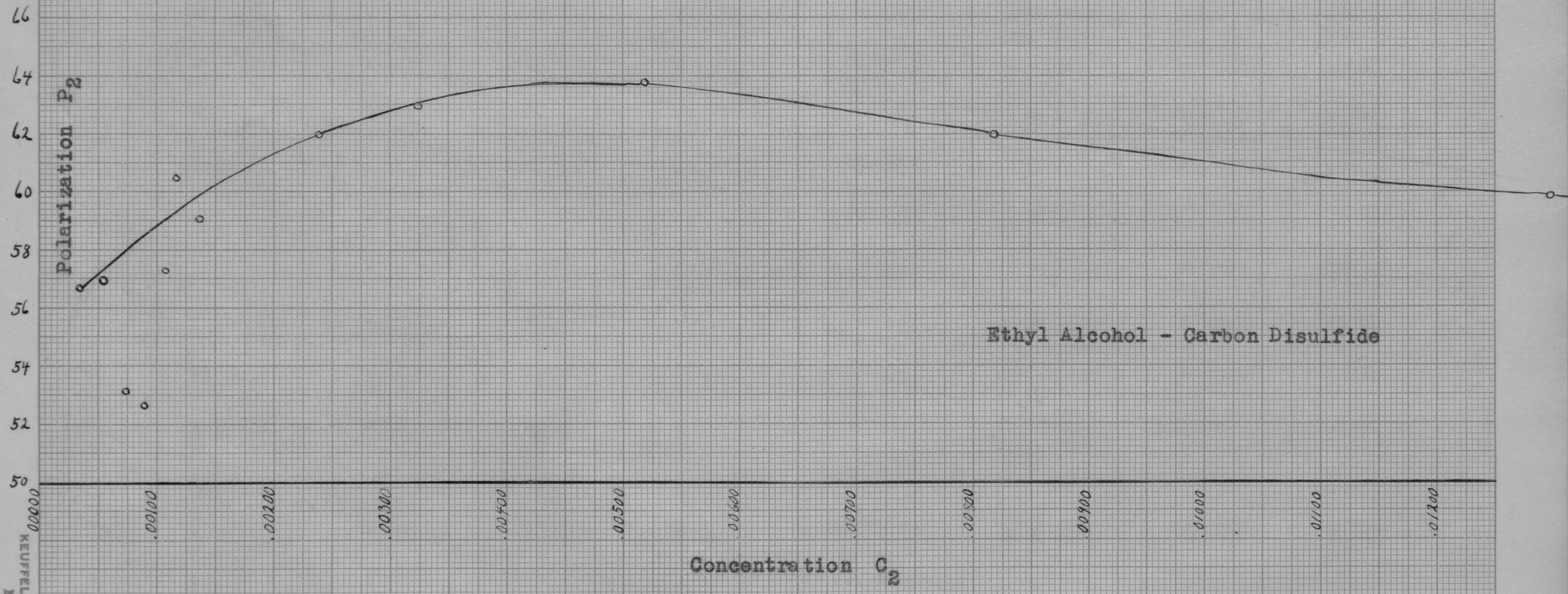


Ethyl Alcohol - Benzol
Showing concentrations less than
C_2 = .0100

Ethyl Alcohol - Carbon Disulfide

Polarization Data (first series continued)

C_2	K	d	$\frac{K-1}{K+2}\frac{1}{d}$	P	P_1C_1	P_2C_2	P_2
.000346	2.62739	1.25601	.280003	21.31216	21.29350	.019658	56.67
.000540	2.62821	1.25591	.280116	21.32013	21.28937	.030767	56.87
.000744	2.62875	1.25582	.280197	21.32456	21.28504	.039525	53.12
.000900	2.62926	1.25573	.280274	21.33122	21.28383	.047391	52.61
.001070	2.63048	1.25565	.280427	21.33937	21.27809	.061280	57.26
.001169	2.63133	1.25560	.280534	21.34663	21.27598	.070641	60.42
.001358	2.63201	1.25551	.280630	21.35225	21.27195	.080307	59.11
.002388	2.63740	1.25499	.281346	21.39809	21.25001	.148080	61.99
.003241	2.64188	1.25457	.281938	21.43588	21.23185	.204040	62.95
.005186	2.65206	1.25362	.283279	21.52126	21.19040	.330860	63.79
.008179	2.66553	1.25213	.285104	21.63425	21.12667	.507582	62.05
.012905	2.68542	1.24980	.287819	21.79936	21.02600	.773357	59.93
.029019	2.75981	1.24020	.298115	22.43467	20.68275	1.751920	60.37
.056686	2.93162	1.22650	.319348	23.76682	20.09343	3.673400	64.80


66
64
62
60
58
56
54
52
50
Polarization P_2
.00000
.00100
.00200
.00300
.00400
.00500
.00600
.00700
.00800
.00900
.01000
.01100
.01200
Concentration C_2
Ethyl Alcohol - Carbon Disulfide

Polarization Data (first series continued)

Ethyl Alcohol-Carbon Tetrachloride

C_2	K	d	$\frac{K-1}{K+2}\ \frac{1}{d}$	P	P_1C_1	P_2P_2	P_2
.000294	2.22543	1.58495	.182979	28.14155	28.11614	.02541	86.47
.000591	2.22604	1.58485	.183059	28.14683	28.10777	.03906	66.09
.000879	2.22682	1.58471	.183154	28.15695	28.09966	.05729	65.15
.000309	2.22665	1.58505	.183097	28.15943	28.13051	.02892	93.44
.000460	2.22726	1.58500	.183168	28.16728	28.12629	.04099	89.05
.000611	2.22787	1.58493	.183241	28.17552	28.12203	.05349	87.50
.001213	2.22825	1.58466	.183311	28.17444	28.08073	.09371	77.20
.001837	2.23106	1.58440	.183639	28.21242	28.06318	.14924	81.20
.003882	2.23781	1.58350	.184404	28.28934	28.00572	.28363	73.06

In the above data on alcohol benzol solutions, it will be observed that five solutions are starred. These five solutions were mixed from a different lot of benzol than the unstarred solutions. The data on the five starred solutions is self-consistent, as is that of the unstarred solutions, that is in both sets of data the polarizations increase steadily and consistently with decrease in concentration of alcohol, C_2. The explanation for the disagreement between the two sets of data is that the density of the second lot was different from that of the first lot, and it was not realized that the density of two different bottles of benzol would be sufficient to cause such discrepancies until after the solutions had been mixed and used.

The data given above on alcohol-carbon tetrachloride solutions show a similar behavior. Several solutions mixed from the same bottle are self consistent, but not with solutions mixed from another bottle; this, in spite of the fact that all the bottles were stamped with the same lot number. As noted above, this difficulty was overcome by pouring all the solvent to be used in a large bottle and mixing the various solutions from this bottle. Only sufficient data was taken on carbon tetrachloride solutions in this series of measurements to make certain that the behavior in the region of low concentrations, C_2, was the same as that observed for the benzol solutions.

The data on these solutions, and the curves plotted therefrom, indicated a very peculiar behavior in the region of concentrations extending from $C_2 = .0025$ to $C_2 = 0$. It will be observed from the curve plotted from the data on benzol solutions that the expected linear relation between C_2 and P_2 was found to exist at concentrations above .0025, within the limit of experimental error. Below this the polarization P_2 begins very abruptly to increase rapidly with decrease in C_2, and the curve apparently approaches the zero concentration axis asymptatically. This behavior is noted for both benzol and carbon tetrachloride solutions.

This was exactly the bahavior of the extremely low concentration solutions of Williams and Ogg referred to above.

Two explanations of this unexpected behavior presented themselves. First, that very peculiar association phenomena were taking place at these extremely low concentrations. If this were true, the extrapolation of the curve to zero concentration in order to determine the intercept was completely vitiated. However, in support of this extrapolation we have the close agreement between the electric moment of alcohol valculated in this way and the electric moment calculated from data on the vapor.

The alternative explanation was that this apparent behavior was due to a systematic experimental error which because of the great magnification of error as P approaches nearer and nearer the value of P_1C_1 rendered data taken on such dilute solutions worthless. One condition which indicated this as a very probably explanation was the serious limitation imposed upon the precision of measurement of the dielectric constant of the solution by the apparatus as used.

It will be recalled that what really determined the behavior of the curve was the very small change in the dielectric constant of the solution due to the addition of a small amount of alcohol. But with this apparatus, it was impossible to measure just this small change. The entire dielectric constant of the solution had to be measured.

The precision condenser could be read accurately to four places; to obtain the fifth place, it was necessary to estimate tenths of the distance between two graduation marks. If an error of only 1 were made in this estimation a surprisingly large error was introduced into the calculated P_2. In the case of a solution of which $C_2 = $ Ca .001, an error of Ca 3% was introduced in the value of P_2; and as C_2 becomes smaller, the percentage error becomes much larger. Incidentally, it may be mentioned here that an error of .0001 in the density of this solution would introduce an error of Ca 4% in P_2. Since it was believed that the densities were known much closer than this, it was believed that if the uncertainties of capacity measurement could be greatly reduced, it would be possible to determine definitely whether the apparent peculiar behavior were due to systematic error or to actual association changes.

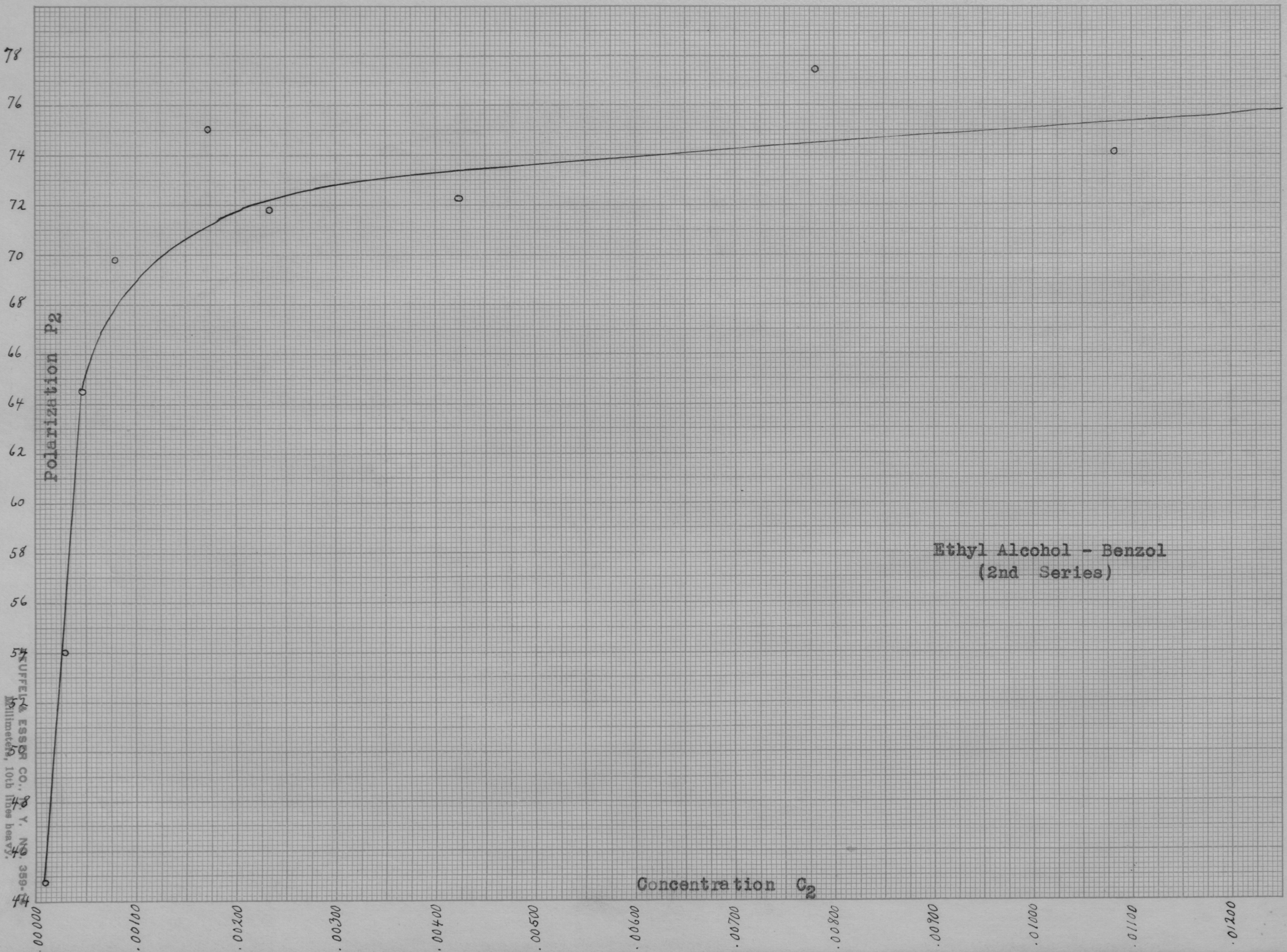
Although the behavior of the carbon disulfide solutions was not similar to that of the benzol and carbon tetrachloride solutions, it was extremely erratic and further investigation seemed desirable.

In order to eliminate the large error introduced into P_2 due to error in the measurement of K, the second arrangement of apparatus was decided upon. This permitted the measurement of the small change, to a far greater degree of precision than did the first arrangement. The following set of data was taken.

Polarization Data (Second Series)

Ethyl Alcohol-Benzol

C_2	K	d	$\frac{K-1}{K+2}\frac{1}{d}$	P	P_1C_1	P_2C_2	P_2
.0000976	2.27006	.87202	.34108	26.62001	26.61565	.00436	44.68
.0002907	2.27060	.87201	.34119	26.62623	26.51050	.01573	54.11
.0004589	2.27134	.87200	.34133	26.63562	26.60600	.02962	64.53
.0007859	2.27267	.87198	.34159	26.65213	26.59728	.05485	69.80
.0017318	2.27664	.87191	.34237	26.70223	26.57214	.13009	75.10
.0023334	2.27851	.87189	.34273	26.72364	26.55612	.16752	71.80
.0042364	2.28566	.87175	.34412	26.81164	26.50546	.30618	72.30
.0078062	2.30195	.87154	.34725	27.01551	26.41047	.60504	77.51
.0108690	2.31206	.87127	.34923	27.13544	26.32891	.80653	74.20



Ethyl Alcohol - Benzol
(2nd Series)

The above series of measurements indicated almost without doubt that the apparent peculiar behavior was due to some systematic error since the polarization P_2 now decreased with decrease in C_2 -- an exact reversal of the results of the first series. Furthermore, greater variations from the straight line at higher concentrations are evident from the data and curve.

In view of these results it appeared advisable to abandon for the time being the original purpose and make a determined effort to eliminate the sources of error if possible. To this end several refinements were made in procedure and apparatus as described in Section II. A very important feature was the holding of the room temperature constant to within ca. .5° C. It was found that very considerable drift in frequency was caused in the variable oscillator by increase or decrease in room temperature. This amounted to a change in the zero point for which no compensation could be made in this method. The effect of an accidental change in room temperature is shown by the two red points which lie off the curve plotted from the following data.

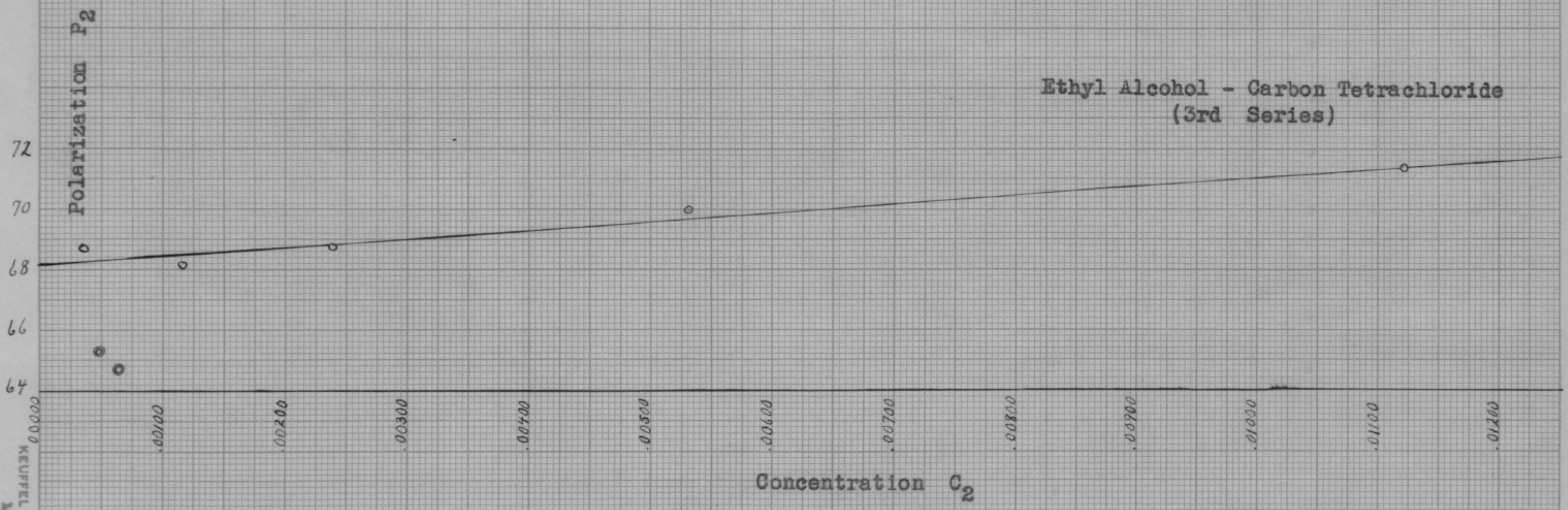
In the table of data below, there is given in Column 1 the vapor pressure corresponding to the respective concentrations of alcohol used; that is, the pressure which the amount of alcohol used in that particular solution would exert if the benzol were not present and the alcohol vapor alone occupied the full volume of the condenser.

Polarization Data (Third Series)

Ethyl Alcohol-Carbon Tetrachloride

Equivalent Pressure	C_2	K	d	$\frac{K-1}{K+2}\ \frac{1}{d}$	P	P_1C_1	P_2C_2	P_2
1.2 mm.	.0003559	2.22351	1.58496	.182774	28.108777	28.084330	.024446	68.67
1.67 "	.0004823	2.22381	1.58490	.182183	28.112235	28.080762	.031473	65.25
2.14 "	.0006431	2.22425	1.58482	.182870	28.117853	28.076267	.041586	64.66
3.80 "	.0011613	2.22602	1.58456	.183086	28.140834	28.061686	.079148	68.15
8.12 "	.0023897	2.22995	1.58396	.183572	28.191386	28.027186	.164200	68.71
18.20 "	.0053146	2.23966	1.58250	.184769	28.316797	27.945010	.371787	69.95
38.70 "	.0112165	2.25942	1.57956	.187190	28.568750	27.779200	.789550	70.39
74.80 "	.0204250	2.28606	1.57498	.190514	28.886840	27.520360	1.366480	66.91

This data seems to indicate that the experimental difficulties met in an attempt to measure the dielectric constants of extremely dilute solutions have been overcome.



Ethyl Alcohol - Carbon Tetrachloride
(3rd Series)

IV. SUMMARY AND CONCLUSIONS

1. The behavior of solutions of ethyl alcohol in benzol, carbon disulfide and carbon tetrachloride has been studied at far lower concentrations of alcohol than ever before attempted.

2. The cause of peculiar effects observed by the writer as well as other investigators in measurement of the dielectric constants of extremely dilute solutions, has been definitely traced to defects in apparatus and method of measurement.

3. The manner of variation of density with concentration at 25° C, of alcohol in benzol, $C\ S_2$ and $C\ Cl_4$, has been measured to a greater degree of precision than that of any available data of which the writer is aware.

4. A method of successive dilution has been introduced in the mixing of solutions in order to reduce the effects of evaporation during manipulation.

5. A method and apparatus has been outlined by means of which it is believed the behavior of highly dilute solutions of polar liquids in non-polar solvents can be investigated.

In conclusion, the writer wishes to express to Dr. J. D. Stranathan, under whose direction this work was undertaken, his gratitude for his interest in the work and for his many helpful suggestions.