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The Construction and Use of an Apparatus for the Measurement of Dipole Moments by the Solution Method

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THE CONSTRUCTION AND USE OF AN APPARATUS
FOR THE
MEASUREMENT OF DIPOLE MOMENTS
BY THE
SOLUTION METHOD

BY

WILLIAM L. DUNCAN
SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS
OF
THE COLLEGE OF WILLIAM AND MARY
FOR THE
MASTER OF ARTS DEGREE
1938
OUTLINE

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CHAPTER 1

INTRODUCTION
CHAPTER I
INTRODUCTION

The understanding of any subject necessitates the recognition and definition of fundamental concepts. This treatment deals with a molecular property termed the "dipole moment" which involves the structure, dielectric constant and electric moment of molecules. From the standpoint of the electron theory, molecules are neutral systems of positive and negative electricity, that is, positive nuclei surrounded by negative electrons. In a dispersed field of electricity in a molecule some point in the system may be considered to be the "center of action" of the dispersed charged in a manner somewhat analogous to the consideration of the center of gravity as the "center of action" of the physical property we call mass. From the electrical point of view, however, there are two types of electrical charges--positive and negative--and each type of charge has its own "center of action". If these individual "centers of action" coincide the resulting molecule is termed non-polar; whereas if the "centers of action" do not coincide there results a polar molecule. It should be recognised here that non-polar molecules may become polar when placed in an electric field because of the distortion produced in these "centers of action" by the action of the field itself. It is therefore necessary to distinguish between a permanent polarity inherent in the structure of the molecule and a temporary or induced polarity which results from the distortion produced by an electric field. These polar molecules may be considered to act as electrical dipoles, that is, as if they were constituted of two electrical charged equal in magnitude but opposite in sign and separated by a finite distance. If this finite distance of displacement be multiplied by the value of one of the charges
there is obtained a product termed the dipole moment. Hence it will
be seen that the measurement of this important property may be expected
to afford valuable information concerning the structure of the molecule.
The dipole moment of a molecule is in turn related to its dielectric
constant which is a measurable factor. According to Smyth, "the
dielectric constant is generally familiar in the expression for the
force (f) between two charges (eo) and (e') separated by a distance (d);

\[ f = \frac{e_0 e' d^2}{2x} \]

in which (k) is a constant characteristic of the medium between the
charges, that is, the dielectric constant. (k) is also familiar as the
quantity to which the capacity (c) of a condenser is proportional, i.e.,
C = kC0, where C0 is the capacity of the condenser with a vacuum between
the plates and (k) is the dielectric constant of the medium between the
plates when (C) is measured. It is by means of this relation that (k)
is commonly obtained experimentally."

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1. Smyth, C. P., Dielectric Constant and Molecular Structure, page 15
CHAPTER XI

THEORETICAL DEVELOPMENT
CHAPTER II
THEORETICAL DEVELOPMENT

According to the classical theory the dielectric constant of a substance is independent of variations in temperature. Measurements of the dielectric constants of certain organic liquids taken over a wide range of temperatures revealed variations in the values of these dielectric constants. An inquiry into the causes of these variations was made in 1912 by P. J. W. Debye who discovered that the dielectric constant should be expected to be independent of temperature only for non-polar molecules. By application of the Clausius-Mossoti equation

\[ P = \frac{K-1}{K+2} \frac{M}{d} \]

Where: 
- \( P \) = polarisation
- \( K \) = dielectric constant
- \( M \) = molecular weight
- \( d \) = density

Debye was able to establish the existence of electrical moments for those liquids, the dielectric constant of which varied with temperature. A period of some fifteen years elapsed before any recognition was given to the value of this work in determining molecular structure. The real work on dipole moments may be considered to have started with the publication of Debye's "Polar Molecules" in 1929. In this monograph Debye drew attention to the fact that the polarization (\( P \)) of the classical Clausius-Mossoti formula included both the distortion effect of the applied electric field and the permanent effect resulting from the structure of the molecule. In the case of polar molecules this 'permanent' moment should contribute largely to the measured value of the polarization (\( P \)). Moreover, since this permanent moment should lead
to the orientation of the molecules in an electrical field, it was to be expected that this orientation would depend on the motion of these molecules and, hence, upon temperature. Debye concluded that those molecules whose polarisation varied with the temperature were polar in character, while those molecules which showed no temperature coefficient of their polarisation were non-polar. Debye then formulated a quantitative relation for the dependence of polarisation on temperature in which he showed that the polarisation (\( P \)) of the Clausius-Mossotti relation was made up of two parts—electronic and atomic polarisation due to distortion of the molecules and the polarisation resulting from the orientation of the molecules. The relation derived by Debye was:

\[
P = \frac{k - 1}{k + 2} \frac{N}{V} = \frac{4\pi n}{3} \left( \frac{a + \mu^2}{3kT} \right)
\]

Where:
- \( P \) = molar polarisation
- \( k \) = dielectric constant
- \( n \) = molecular weight
- \( d \) = density
- \( a \) = polarisability
- \( u \) = dipole moment
- \( k \) = Boltzmann's constant
- \( T \) = absolute temperature

or in general:

\[
P = A + \frac{B}{T}
\]

This showed that the induced polarisation (\( A \)) was independent of the temperature, whereas the permanent polarisation (\( B \)) decreased as the temperature was increased. This relation held only for gases and for dilute solutions in non-polar solvents.
Early qualitative measurements served to settle questions of molecular structure, but it is now possible to make more accurate quantitative measurements from which conclusions may be drawn concerning small differences in dipole moments. These measurements become more valuable as a greater degree of accuracy is obtained by the elimination of experimental errors arising from outside influences such as the nature of the solvent, frequency effects, etc.

It is interesting to note that measurements conducted on the gaseous phase do not always agree with the measurements made by the solution method. Debye's equation for the calculation of dipole moments may also be derived by the modern methods of wave mechanics and, so, is consistent with the most recent theory of the nature of matter.

Most of the methods for the measurement of dipole moments involve the measurement of the dielectric constant. There are, however, two comparatively new methods which may be mentioned.

1. The molecular beam method, founded on the atomic beam experiments of Stern and Gerlach, was first applied to electrical dipoles by Wrede in his experiment on the alkaline halides and then greatly extended by Estermann in his work on organic substances. The experimental procedure described by Sidgwick² is as follows: "The substance to be investigated is heated in a minute oven to a temperature at which it has a perceptible but very low vapor pressure. A stream of molecules very far removed from one another, and with a velocity given by their temperature in accordance with the gas laws, issues from this oven through a narrow slit, about 0.01 mm. wide, into a high

² Sidgwick - The Covalent Link in Chemistry
vacuum. By means of a second slit this beam is cut down to a narrow and very thin ribbon of rays. This ribbon is passed through a highly inhomogeneous electric field, one pole being a knife edge in the line of the beam and the other a half cylinder enclosing this. Finally the molecules are received on a brass plate cooled with liquid air, and the trace that they form observed through a microscope.

Under these conditions the molecules are too remote to collide with one another. If the field is not on, they go straight through the apparatus and condense in a narrow vertical line on the receiver. If the field is put on it will affect even non-polar molecules; the electronic polarisation produced an induced dipole, and this leads to a movement towards the stronger part of the field, so that the trace is shifted. But as the direction of the induced dipoles is wholly determined by that of the field, all the molecules are affected equally and the trace shifts as a whole retaining its narrow form, less than 0.15mm. wide. If, however, the molecules are polar, the displacement caused by the field on any one of them depends upon the direction which the dipole has with respect to the field as it passes through; and as these directions are distributed at random the result is to broaden the trace, while the amount of broadening is a measure of the dipole moment. It has not yet been found possible to relate the broadening accurately to the moments, but comparative observations with substances whose dipole moments have been measured by means of the dielectric constant show a good qualitative agreement and make it possible to get a rough measure of other substances."

This method may be used with substances excluded by other methods because of their insolubility or high temperature volatility. Another advantage is that the measurements are made in the absence of
a solvent and with the molecules so far apart that complications through interactions are nearly impossible.

2. A still more recent and as yet little developed method depends on the determination of the dielectric losses, that is, of energy lost in heat when the substance is exposed to a rapidly alternating field.

The better known methods for the measurement of dipole moments necessitate the measurement of dielectric constants and the elimination of the induced polarization. There are three principal methods for the measurement of dielectric constants:

I. The measurement of the electric force acting through a dielectric and the calculation of the dielectric constant by means of Columb's Law.

II. The measurement of the velocity of propagation of electromagnetic waves through a substance, which velocity is inversely proportional to the square root of the dielectric constant.

III. The measurement of the capacitance of a condenser when empty, \((C)\), and when filled with a liquid, \((C_x)\). The dielectric constant \((k)\) is then given by the ratio \(\frac{C_x}{C}\).

The most important methods for the measurement of dielectric constants fall in the third class. They are:

a. **The Bridge Method**

The bridge method applies the principle of the Wheatstone bridge circuit, and in this case consists of four condensers \(C_1, C_2, C_3, C_4\) and two resistances \(R_3, R_4\). If the condensers were

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3. Smyth - Dielectric Constant and Molecular Structure
perfect the resistances would be unnecessary but since the dielectric cell acts as a leaky condenser it becomes necessary to balance the bridge for resistance as well as capacitance, giving a zero minimum current and a more accurate balance. The resistances used must be free from inductance and capacitance. Both high and low frequency bridges are used and each has its particular advantages.

![Diagram](image)

b. The Resonance Method. In a circuit consisting of an inductance \(L\), capacitance \(C\), and resistance \(R\) in series, the effective current is

\[
I = \frac{E}{\sqrt{R^2 + (\omega L + 1)^2}}
\]

where \(E\) is the electromotive force and

\[w = 2\pi f\]

\((f)\) being the frequency. \(I\) has a maximum value under conditions termed resonance, i.e., when

\[
\frac{WL}{WC} = 1 \quad \text{or} \quad f = \frac{1}{2\pi \sqrt{LC}}
\]

Oscillations are excited in a primary circuit (I) which is coupled to a secondary resonant circuit (II) containing capacitance, inductance and resistance. The capacitance is adjusted by means of a condenser until the current reaches a maximum value as shown by the
detector circuit (III) coupled to it. The cell to be measured is connected in parallel with the precision condenser. Difference in readings gives the capacitance of the cell.

**c. The Heterodyne Beat Method.** This is one of the most accurate methods and is of especial interest here since it is the method employed in our measurements.

The frequency of an electronic oscillator depends upon the resistance capacitance and inductance in the circuit. In diagram II oscillators I and II are simple Hartley oscillating circuits loosely coupled to a resistance-capacitance coupled amplifier. From considerations in general physics it is known that when two oscillating systems are coupled the resultant frequency is the difference between the individual frequencies of the systems. The general frequency used for dielectric measurements if $10^6$ cycles per second or a wavelength of about 3000 meters. This frequency is beyond the audible range so the second oscillator is made to oscillate at about 1000 cycles above or below the first, giving a "beat frequency" of about 1000 cycles per second which is in the audible range and can be used as an indicator or reference point. Changes in capacitance in oscillator II increase or decrease this "beat frequency" note since it changes the frequency of that oscillator. For some value of the capacitance both systems will be oscillating at identical frequencies and no "beat note" will be produced. If an amplifier is used as shown in diagram II this region of silence may be narrowed down to a point on the precision condenser. Thus changes in capacitance produced by the addition of the dielectric cell

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4. General Radio Company Precision Condenser 722-M
in parallel with the precision condenser may be accurately measured by adjustment of the precision condenser to the null point with the dielectric cell out of the circuit followed by a readjustment to the same null point when the dielectric cell is in the circuit. The construction and use of this apparatus will be discussed in Part IV.

There are two principal methods for the calculation of dipole moments from dielectric constants. The polarisation term (P) of the Clausius-Mossotti relation may be considered to consist of several components.

Let

\[ P_a = \text{the atomic polarisation}, \]
\[ P_e = \text{the electronic polarisation}, \]
\[ P_u = \text{the orientation polarisation}, \]
\[ P = \text{the total polarisation}, \]

Then from Debye's equation

\[ P_a + P_e + P_u = P = \frac{4\pi N (a + u^2)}{\epsilon + \epsilon_0} \]

and hence it is only necessary to eliminate (P_a) and (P_e) in order to calculate (P_u) if the value of (P) is known. (P_a) and (P_e) may be considered to be independent of the temperature (T), and equal to the distortion polarisation.

\[ P_a + P_e = 4\pi \chi A \]

Hence the total polarisation is plotted against the reciprocal of the absolute temperature a straight line is obtained in accordance with the general mathematical form

\[ P = A + \frac{B}{T} \]

If the substance is non-polar, \( u = 0 \) and \( B = 0 \) and the line will be horizontal, but if \( u \) has a finite value the line will be inclined and \( u \) may
be calculated from its slope. This is generally accepted as the most accurate method of eliminating (Pe) and (Pe) and can be applied to both gases and dilute solutions in non-polar solvents.

The refractive index method utilizes the Lorentz-Lorenz formula

\[ P = \frac{n^2 - 1}{n^2 + 2} \]

where \( P \) is the refractive index.

The elimination of the induced polarization by this method is accomplished because the molecules possess a finite inertia and when traversed by waves of sufficiently high frequency are unable to orientate themselves. The electronic distortion has so small an inertia that it will be unaffected up to the very high frequencies of ultra-violet light, while the atomic polarization, due to the greater mass of the nucleus, remains unaffected only as far as the infra-red region of the spectrum. It is also so very small compared to the electronic polarization that it may often be disregarded. According to Sidgwick the \( Fu \) term, due to the orientation of the permanent moment, is a relatively slow process requiring about 10-10 seconds, corresponding to a wavelength of about three centimeters. Actually measurements are never made using waves less than 2-5 meters because of dispersion and other difficulties of measurement.

The refractive index is measured somewhere in the visible spectrum and \( Fu \) \( Fu \) may then be calculated from the Lorentz-Lorenz relation. If this value be subtracted from the total polarization calculated from the measurements of the dielectric constant with radio waves the permanent polarization \( Fu \) and, thus, the dipole moment may be obtained.

The dielectric constants of solutions of different concentrations
in non-polar solvents are measured and extrapolated to infinite dilution, where the influence of the molecules is zero. A mixture of two liquids of molecular polarisation $P_1$ and $P_2$, density $d$, molecular weights $M_1$ and $M_2$, present in molar-fractions $f_1$ and $f_2$, gives

$$P_{11} = \frac{N}{d} \left( \frac{f_1 M_1 + f_2 M_2}{d} \right)$$

In this way the molecular polarisation of a substance when it is a component of a mixture may be determined.
CHAPTER III

STATEMENT OF THE PROBLEM
CHAPTER III

STATEMENT OF THE PROBLEM

The present work was undertaken with the object of constructing a heterodyne beat frequency oscillator for the measurement of dipole moments by the solution method. The apparatus was constructed as outlined below and the dipole moment of acetone was measured. The agreement between the value obtained and the accepted value for the dipole moment of acetone confirms the utility of the apparatus for making reproducible measurements of dipole moments by the solution method.
CHAPTER IV

DESCRIPTION OF APPARATUS
CHAPTER IV

DESCRIPTION OF APPARATUS

The heterodyne beat frequency oscillator circuit shown in diagram II was constructed using the values indicated. Each section was shielded with sheet copper. The inductances were hand wound on fiber cylinders and mounted on old tube bases for convenience in making connections. The leads to the condensers were made of shielded cable, and the B- of all current sources and one side of the precision condenser were grounded in order to avoid "drifting" and "hand capacitance". The dielectric cell was constructed after a considerable amount of research in the College library and a trip to Johns Hopkins University for a consultation with Dr. W. A. Patrick who has done a great deal of work with dielectrics. The cell in use there was inspected and found to be similar to that illustrated by Smyth. The measuring circuit used there is also similar to the one shown in Diagram II, except for crystal controlled frequency on the standard oscillator. A cell was constructed from copper sheet formed and soldered into three concentric cylinders with the approximate values suggested by Smyth. This cell is shown in diagram II. The cylinders were then cleaned with steel wool and nitric acid and plated with copper electrolytically to cover the soldered joints. The cylinders were insulated and spaced with mica blocks and mounted in a glass container constructed for the purpose.

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5. Smyth, C. P., Dielectric Constant and Molecular Structure, page 60
CHAPTER V

EXPERIMENTAL PROCEDURE
The oscillator as constructed was not crystal controlled and was subject to frequency variation. In order to cancel these variations the null point displacements on the precision condenser dial were averaged for several harmonics. By this procedure separate measurements checked to less than two parts in a thousand.

All measurements were made at 30°C in a constant temperature bath. Cell connections were made in such a manner as to reduce and stabilise stray capacitances. The cell was standardised with pure benzene and checked with chloroform. After each measurement the cell was cleaned with alcohol and ether and dried in an oven at 100°C. The capacitance of the cell was checked after drying and was found to give a small but expected variation, since the cell was constructed of rather heavy copper cylinders spaced less than 0.25 inches apart. Expansion was found to change this distance and thus to change the capacitance. When the cell was allowed to cool slowly after the drying process the capacitance variations, though still present, were greatly reduced.

Solutions of acetone in benzene of known concentration were prepared and their dielectric constants at 30°C were measured by this method. The total polarization \( P \) of each solution was calculated from the dielectric constant in accordance with the relation:

\[
P = \frac{k-1}{k+2} \left( \frac{f_n - f_m}{f_k} \right) \text{, where}
\]

\[
P = P_m f_n + P_n f_m \text{ and where}
\]
\text{P}_{ps} = \text{polarisation of acetone-benzene solution}\\
\text{P}_{a} = \text{polarisation of acetone}\\
\text{P}_{b} = \text{polarisation of benzene}\\
k = \text{electric constant of the solution}\\
\text{f}_{a} = \text{mol-fraction of acetone}\\
\text{f}_{b} = \text{mol-fraction of benzene}\\
d = \text{density of solution at the temperature of measurement}\\

and the extrapolated value of \text{P} at infinite dilution was obtained graphically.

The refractive index of acetone was measured and the approximate value of \( (\text{P}_{a} + \text{P}_{b}) \) was obtained from the Lorents-Lorentz relation

\[
\text{P}_{a} + \text{P}_{b} = \frac{n^2 - 1}{n^2 + 2} \times \frac{\text{M}}{d}
\]

Where \text{P} and \text{P} are the atomic and electronic polarisations and were "n" is the refractive index. The difference between the total polarisation of acetone \( (\text{P}_{a}) \) and the distortion polarisation \( (\text{P}_{a} + \text{P}_{b}) \), gave the orientation polarisation \( (\text{P}) \) from which the dipole moment of acetone could be calculated using the Debye relation;

\[
\text{P}_{a} = \frac{4}{3} \pi \text{M} \frac{u^2}{kT}
\]
CHAPTER VI

RESULTS
CHAPTER VI

RESULTS

(a) Standardization of cell with benzene at 30°C.

Let $C_0$ stray capacitance,
$C$ capacitance of the empty condenser,
$C_x$ capacitance of condenser filled with a liquid of dielectric constant ($k$).

Then $C_0 + C$ measured capacitance of cell in air
and $C_x + C$ is the measured capacitance of cell containing a liquid with a dielectric constant ($k$).

Now ($k$) for benzene at 18°C 2.288, and the calculated value at 30°C is 2.260

Co $C$ was determined for the empty cell by averaging several readings:

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<th>Cell out</th>
<th>Difference</th>
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</thead>
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<td>560.20</td>
<td>488.70</td>
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<td>315.10</td>
<td>241.85</td>
<td>71.25</td>
</tr>
<tr>
<td>360.70</td>
<td>197.55</td>
<td>71.15</td>
</tr>
</tbody>
</table>

| II      |          |            |
| 899.55  | 828.50   | 71.05      |
| 851.65  | 786.40   | 71.25      |
| 607.60  | 736.45   | 71.15      |
| 730.25  | 668.80   | 71.65      |
| 655.45  | 563.80   | 71.65      |
| 560.25  | 488.70   | 71.55      |
| 446.75  | 377.50   | 71.25      |
| 370.65  | 299.55   | 71.10      |
| 315.00  | 241.75   | 71.25      |
| 268.80  | 197.40   | 71.40      |

$C_0 + C = \frac{1426.25}{20} = 71.31$
The cell was then filled with pure benzene and (Cz) determined by averaging several readings;

<table>
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<tr>
<th>Cell in</th>
<th>Cell out</th>
<th>Difference</th>
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<tbody>
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<td>359.75</td>
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| II      |          |            |
| 970.45  | 828.55   | 141.90     |
| 922.45  | 780.45   | 142.00     |
| 978.75  | 756.40   | 142.35     |
| 801.80  | 665.80   | 142.00     |
| 706.80  | 563.90   | 142.90     |
| 651.55  | 488.60   | 142.90     |
| 520.05  | 377.40   | 142.65     |
| 441.90  | 299.50   | 142.30     |
| 384.00  | 241.80   | 142.20     |
| 359.90  | 197.40   | 142.40     |

\[ Cz = C_0 - EC = \frac{264.96}{20} = 142.45 \]

Then \[ C(\text{b-1}) = 142.45 - 71.31 - 71.14 \]
and \[ k = 2.280 \]

therefore \[ C = \frac{71.14}{1.28} = 56.45 \text{ micro-micro farads} \text{ the cell constant} \]

(b) Calculation of the polarization of pure benzene at 30°C.

\[ P_B = (k-1)/(k 2) \times \mu/\delta \]
\[ = (1.28)/(4.28) \times 78.05/0.865 \]

(c) Measurement of the dielectric constants of solutions of acetone in benzene of known strength and the calculation of the total polarization \(P_{AB}\) and the polarization of acetone \(P_A\).
For example, 15cc of acetone were pipetted into a 100cc volumetric flask and diluted to the mark with pure bensene. All solutions and apparatus were kept at 20°C. The mole-fraction \( f_A \) was then calculated from

\[ f_A = \frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}} \]

Where \( W_A \) is the weight of acetone = \( V_A \times D_A = (15)(.792) = 11.880 \) grams,

where \( W_B \) is the weight of bensene = \( V_B \times D_B = (85)(.879) = 74.715 \) grams,

and where \( M_A \) and \( M_B \) are the molecular weights of acetone and bensene, respectively.

\[ f_A = \frac{11.880}{58.05 + 74.715} = \frac{2046}{2046 + 9572} \text{, or} \]

\[ f_A = .1761 \]

A density determination of the solution was made at 50°C with a pyrometer.

\[ D = \frac{m}{v} = \frac{42.553}{50} \]

\[ D = .8510 \text{ g/cc} \]

The sample of the solution was then transferred directly from the pyrometer to the dielectric cell. The capacitance of the cell with the liquid medium (Cx) was then measured in a similar manner.
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<th>Cell out</th>
<th>Difference</th>
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<td>736.30</td>
<td>244.75</td>
</tr>
<tr>
<td>903.70</td>
<td>656.45</td>
<td>244.25</td>
</tr>
<tr>
<td>809.70</td>
<td>565.60</td>
<td>244.10</td>
</tr>
<tr>
<td>734.75</td>
<td>496.60</td>
<td>248.15</td>
</tr>
<tr>
<td>622.60</td>
<td>377.30</td>
<td>245.30</td>
</tr>
<tr>
<td>544.50</td>
<td>299.60</td>
<td>244.90</td>
</tr>
<tr>
<td>485.60</td>
<td>241.85</td>
<td>244.95</td>
</tr>
<tr>
<td>442.20</td>
<td>197.40</td>
<td>244.80</td>
</tr>
</tbody>
</table>

\[ Cx = \frac{4411.95}{18} = 245.11 \text{ (average)} \]
From the change in capacitance of the cell when empty and when filled with the sample of solution, the dielectric constant was calculated.

\[ C_0 + C = 71.50 \]
\[ C_0 + kC = 245.11 \]

subtracting \( C(k-1) = 173.81 \)
hence \( k \approx 3.078 \)
since \( C \approx 58.46 \)

The polarization \( (P_{AB}) \) was then calculated from the dielectric constant \( (k) \)

\[ P_{AB} = k-1 \left( \frac{E_{A}^{M} + E_{B}^{M}}{E_{A}^{M} + E_{B}^{M}} \right) = 3.078 \times \frac{1.761 \times 58.46 + 0.6239 \times 75.06}{6.078} \times 0.5558 \]

\[ = 44.21 \]

The polarization \( (P_{A}) \) was then calculated from the total polarization of the solution \( (P_{AB}) \) and the polarization of benzene \( (P_{B}) \) from the relation

\[ P_{AB} = P_{A}A_{A} + P_{B}A_{B} \]

\[ 44.21 = 1.761 P_{A} + 0.6239 (26.65) \]

\[ P_{A} = 126.46 \]

This procedure was followed for solutions containing 5, 10, 15, 20, and 25 milliliters of acetone in 100ml of acetone-benzene solution at 20°C. The results are shown in Table X.

(d) Calculation of the polarization \( (P_{A}) \) at infinite dilution.

The mole-fractions of acetone were plotted against the polarization \( (P_{A}) \) and extrapolated to infinite dilution as shown graphically, giving

\[ (P_{A}) = 160.00 \]
(e) Measurement of the refractive index of acetone and the calculation of the distortion polarization \((P_a, P_b)\)

<table>
<thead>
<tr>
<th>(V)</th>
<th>Incident</th>
<th>Normal</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>156 47' 10&quot;</td>
<td>291 44' 00&quot;</td>
</tr>
<tr>
<td>B</td>
<td>156 46' 00&quot;</td>
<td>291 44' 30&quot;</td>
</tr>
<tr>
<td>A</td>
<td>156 47' 20&quot;</td>
<td>291 44' 00&quot;</td>
</tr>
<tr>
<td>B</td>
<td>156 46' 10&quot;</td>
<td>291 44' 40&quot;</td>
</tr>
<tr>
<td>A</td>
<td>156 47' 40&quot;</td>
<td>291 44' 18&quot;</td>
</tr>
<tr>
<td>B</td>
<td>156 47' 40&quot;</td>
<td>156 56' 58&quot;</td>
</tr>
</tbody>
</table>

(Average angles)

\[ \text{Angle } A \text{ of prism} = (180 - 156 \ 56' \ 38") = 45 \ 05' \ 22" \]

and \(U_a\) (index of refraction of prism) = 1.72

<table>
<thead>
<tr>
<th>(V)</th>
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<th>Normal</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>177 57' 40&quot;</td>
<td>186 23' 40&quot;</td>
</tr>
<tr>
<td>B</td>
<td>357 59' 20&quot;</td>
<td>346 21' 40&quot;</td>
</tr>
<tr>
<td>A</td>
<td>177 56' 20&quot;</td>
<td>346 21' 40&quot;</td>
</tr>
<tr>
<td>B</td>
<td>357 57' 20&quot;</td>
<td>346 21' 40&quot;</td>
</tr>
<tr>
<td>A</td>
<td>141 52' 40&quot;</td>
<td>150 15' 40&quot;</td>
</tr>
<tr>
<td>B</td>
<td>531 69' 20&quot;</td>
<td>310 16' 00&quot;</td>
</tr>
</tbody>
</table>

\[ \text{Angle } I' \text{ (angle of refraction)} = 11 \ 37' \ 00" \]

and \(U_b\) (index of refraction of acetone) = 1.351

\[
\text{Then} \quad P_a + P_b = \frac{(n^2 - 1)}{(n^2 + 2)} \frac{N}{d}
\]

\[
= \frac{(1.351)^2 \ 1 \ \cdot \ 58.05}{(1.351)^2 \ \frac{N}{d} \ \ \frac{57.9}{57.9}}
\]

(f) The calculation of the dipole moment of acetone

The difference between the polarization \((P_a)\) at infinite dilution and the distortion polarization \((P_a + P_b)\) gave the orientation polarization \((P_u)\) from which the dipole moment of acetone was calculated from the Debye relation:

\[
P_u = \frac{4 \pi \mu \mu^2}{9 \ \text{m}^2}
\]
\[
P = \frac{(1.23)^2 - 1}{(1.23)^2 + 2} \cdot \frac{59.05}{2.93} = 47.91 = 14.08
\]

\[
P_A - (P_u P_o) = 160 - 14.08 = 145.92
\]

\[
P_u = \frac{4 \times 9}{64t}
\]

\[
\]

\[
u = 2.66 \times 10^{-15}
\]
TABLE I

First Determination

<table>
<thead>
<tr>
<th>Va</th>
<th>fα</th>
<th>fb</th>
<th>d</th>
<th>Co C</th>
<th>Cx</th>
<th>k</th>
<th>Pab</th>
<th>Pb</th>
<th>Pa</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0599</td>
<td>0.9401</td>
<td>0.861</td>
<td>71.95</td>
<td>177.99</td>
<td>2.881</td>
<td>54.10</td>
<td>26.65</td>
<td>152.0</td>
<td>57.0</td>
</tr>
<tr>
<td>10</td>
<td>0.1198</td>
<td>0.8812</td>
<td>0.858</td>
<td>71.95</td>
<td>210.57</td>
<td>3.432</td>
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<td>26.65</td>
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<td>0.852</td>
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<td>246.59</td>
<td>4.064</td>
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<td>128.4</td>
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<tr>
<td>25</td>
<td>0.2876</td>
<td>0.7124</td>
<td>0.846</td>
<td>71.95</td>
<td>319.18</td>
<td>5.387</td>
<td>50.51</td>
<td>26.65</td>
<td>109.5</td>
<td>57.0</td>
</tr>
</tbody>
</table>

Pa fα 163.0
Pa fβ 16.06
Pa 143.92
u 2.66

Second Determination

<table>
<thead>
<tr>
<th>Va</th>
<th>fα</th>
<th>fb</th>
<th>d</th>
<th>Co C</th>
<th>Cx</th>
<th>k</th>
<th>Pab</th>
<th>Pb</th>
<th>Pa</th>
<th>C</th>
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</thead>
<tbody>
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<td>3</td>
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<td>0.9639</td>
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<tr>
<td>5</td>
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<td>0.9401</td>
<td>0.8655</td>
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<td>176.55</td>
<td>2.867</td>
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<td>26.65</td>
<td>151.0</td>
<td>56.46</td>
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<td>210.50</td>
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<td>0.8239</td>
<td>0.8528</td>
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<td>246.01</td>
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<td>0.7124</td>
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<td>50.71</td>
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<td>110.5</td>
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</tr>
</tbody>
</table>

Pa 163.0
Pa fα 16.06
Pa 143.92
u 2.66
CONSTANTS FOR DIAGRAM II

$L_3, L_4$ -------------- 25 turns
$L_1$ -------------- 55 turns
$L_2, L_6$ -------------- 50 turns
$L_5$ -------------- 100 turns
$C_1$ -------------- 1500 uuf precision condenser
$C_2$ -------------- Cell
$C_3$ -------------- 1500 uuf condenser
$C_4$ -------------- 0.00025
$C_5, C_6$ -------------- 0.01 uf.
$R_1, R_3$ -------------- 0.25 Meg.
$R_2, R_4$ -------------- 0.5 Meg.
$E_1, E_3, E_7$ -------------- 6.0 Volts
$E_2, E_4$ -------------- 90.0 Volts
$E_5$ -------------- 15.0 Volts
$E_6$ -------------- 27.0 Volts
$E_7$ -------------- 135.0 Volts
$E_9$ -------------- 5.0 Volts
The accepted value for the dipole moment of acetone measured in benzene is $2.71 \times 10^{-18}$ e.s.u. The agreement between this value and the value obtained in this work confirms the reliability of the apparatus as an instrument for dipole moment measurements. An interval of several days elapsed between the measurements of the first determination and those of the second determination on new and freshly prepared solutions and the agreement between the values obtained in the two determinations shows that the apparatus gives reproducible results.

Further refinements such as a platinum cell, a crystal frequency control, more efficient shielding, etc. should make it possible to ensure even greater accuracy in the measurement of this important property.

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