DIELECTRIC RELAXATION TIME IN
NORMAL AND SUPERCOOLED SIMPLE LIQUIDS AND
ITS RELATION TO OTHER LIQUID PROPERTIES.

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Philosophy in the University of London

by

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ABSTRACT.

Measurements have been made on viscosity, density, static dielectric constant and dielectric constant at wavelengths of 3.279 cm and 0.847 cm. For some liquids measurements have also been made at 29.89 cm and 19.88 cm. The critical wavelength has been calculated from the results and its temperature dependence compared with that of viscosity.

The present viscosity measurements allow investigation of the dependence of viscosity of liquids on temperature over a great range of temperature, and the viscosity at normal pressure of a large number of liquids can be described successfully by Batschinski's relation $\eta = \frac{A}{V-b}$, where A and b are constants and V is the specific volume. No discontinuity is apparent between ordinary liquid and supercooled liquid states.

Reasonably consistent values of critical wavelengths are obtained from the two experimental wavelengths over a range of temperature from $+50^\circ$C to $-50^\circ$C, except for Iodobenzene, Quinoline and iso-quinoline. The measurements done for these three liquids at wavelengths of 29.89 cm and 19.88 cm suggest that there may be a second dispersion
region leading to abnormally high values of $\lambda$ at
the shorter wavelengths.

The results also suggest that in all cases studied
less free volume is required for molecular rotation
than for viscous flow so that the critical wavelength
varies less rapidly with temperature than the viscosity
does.
## CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Introduction</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Experimental methods</td>
<td>34</td>
</tr>
<tr>
<td>3</td>
<td>Experimental results</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>Experimental accuracy</td>
<td>105</td>
</tr>
<tr>
<td>5</td>
<td>Conclusion</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>Acknowledgements</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>Graphs of the experimental results</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>153</td>
</tr>
</tbody>
</table>
CHAPTER 1

Introduction:

Dielectric constant and polarisability 9
Relaxation time 17
Distribution of relaxation times 22
Relationship of relaxation time to molecular properties 25

In a non-conductor a plate between the plates of a condenser, it reduces the potential energy of the substance and is attributed to the dipoles in the substance. These dipoles may, in two ways: firstly, by the redistribution of electric charges within the molecule of a molecule, producing an electric moment in the direction of the external field (distortion polarization); secondly, by the orientation of permanent molecular moments, which, in the absence of external field have a random orientation and so produce no resultant moment (orientation polarization) (Debye "Polar Molecules"). If the external field does not alternate with too high a frequency, the first effect is always present. Substances where molecules possess permanent electric moments also exhibit the second effect, again provided the frequency is not too high. Such substances are characterized by high dielectric constants (e.g. chloroform 4.7, water 49.5, compared with the non-polar substance
1. INTRODUCTION

When a non-conductor is placed between the plates of a charged condenser, it reduces the potential difference between them. The effect is characterized by the dielectric constant of the substance and is attributed to the re-distribution of the charges in the substance (polarisation) by the action of the electric field between the plates. This commonly occurs in two ways: firstly, by the redistribution of electric charges within the molecules or atoms, producing an electric moment in the direction of the external field (distortion polarisation); secondly, by the orientation of permanent molecular moments, which in the absence of an external field have a random orientation and so produce no resultant moment (orientation polarisation) (Debye "Polar Molecules").

If the external field does not alternate with too high a frequency, the first effect is always present. Substances whose molecules possess permanent electric moments also exhibit the second effect, again provided the frequency is not too high. Such substances are characterized by high dielectric constants (e.g. chloroform 4.7, water 79.5, compared with the non-polar substance
benzene 2.27). As the frequency of the external field is increased, a point is reached beyond which it is not possible for the polar molecules to alternate in phase with the field owing to the resistance to their motion produced by the surrounding molecules. The molecular moments lag behind the field with a consequent absorption of energy and reduction of the dielectric constant. This observed lag in the attainment of equilibrium is referred to as 'relaxation' and the relaxation time $\tau$ of the system is defined as the time required for the orientation polarisation to fall to $\frac{1}{e}$ of its equilibrium value when the applied field is removed. At sufficiently high frequencies the orientation polarisation vanishes, and when optical frequencies are reached only the distortion polarisation remains. For this reason the distortion polarisation is also called the 'optical polarisation'.

The polarisability ($\alpha$) of a molecule is defined as the average, over a sufficient length of time, of the electric moment acquired per unit applied field. In the case of a polar molecule this is made up of two parts; the polarisability due to distortion ($\alpha$) and that due to orientation. Debye has shown that the average moment
in the direction of the field, due to the orientation of the permanent moment ($\mu$) of a molecule, is

$$\bar{m} = \frac{\mu^2 F}{3kT}$$

in a steady orientating field $F$ which is small so that $\frac{\mu^2 F}{kT} \ll 1$, $K$ being Boltzmann's constant, and $T$ the absolute temperature. $F$ is the local field at the molecule and is not in general equal to the external applied field. The total polarisability is then

$$\alpha = \alpha_0 + \frac{\mu^2}{3kT}$$

Debye also calculated (following the method of Einstein's theory of the Brownian movement) the average moment in the direction of the field produced by the orientation of a polar molecule in an alternating field $F = F_0 e^{i\omega t}$, as

$$\bar{m} = \frac{1}{1 + j\omega T} \frac{\mu^2}{3kT} F$$

and in this case the polarisability becomes

$$\alpha = \alpha_0 + \frac{1}{1 + j\omega T} \frac{\mu^2}{3kT}$$

The calculation is based on the assumption that a molecule rotating with an angular velocity $\frac{d\theta}{dt}$ experiences a resistive torque,

$$M = \zeta \frac{d\theta}{dt}$$

due to the surrounding molecules, where $\zeta$ is a constant measuring the 'inner friction', and

$$\tau = \frac{\zeta}{2kT}$$
An investigation of the behaviour of polar substances at frequencies at which the dielectric constant is falling from its static value to its optical value will yield information about the forces which are exerted on a rotating molecule by its neighbours. Conversely, knowledge of the forces of inner friction will allow the calculation of the relaxation time by assuming that the rotating molecule may be regarded as a sphere of molecular dimensions of radius 'a' rotating in a viscous medium which has the viscosity of the substance in bulk, that is

\[ \zeta = 8\pi \eta a^3 \]

From this Debye calculated that for water

\[ \tau = 0.25 \times 10^{-10} \text{ sec} \]

so that anomalous dispersion is to be expected at frequencies in the neighbourhood of

\[ \omega_0 = \frac{1}{0.25} \times 10^{+10} \text{ sec}^{-1} \]

i.e. at centimetre wave-lengths. It is thus to be expected that many liquids will show anomalous dispersion in the micro-wave region of the spectrum.

Relation between the dielectric constant and the polarisability

Actual measurements do not yield the polarisability directly. The quantities measured are related to the real
and imaginary parts of the dielectric constant (which is complex in the region of anomalous dispersion because the polarisation is out of phase with the field). To find the polarisability in terms of the dielectric constant it is necessary to make some simplifying assumption which will allow the local field $F$ experienced by a molecule to be calculated in terms of the external field and the bulk properties of the dielectric.

Debye's method was to imagine a sphere drawn in the substance about a particular molecule, the radius of the sphere being small compared with macroscopic dimensions but large compared with molecular dimensions. The field acting on the molecule was considered to consist of three components: the external field, the additional field due to the presence of the material outside the small sphere, and the field due to the presence of the material in the sphere. Debye then made the further assumption that the third component is zero, and so found that

$$F = E + \frac{4\pi I}{3}$$

$F$ being the field acting on the molecule, $E$ the external field and $I$ the polarisation of the medium. The polarisation is the electric moment per unit volume
produced by the field. If there are 'n' molecules per unit volume,

$$I = n\alpha F$$

Since the dielectric constant is

$$\varepsilon = 1 + \frac{4\pi I}{\varepsilon}$$

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi n\alpha}{3}$$

or

$$\frac{\varepsilon - 1}{\varepsilon + 2} \rho = \frac{4\pi n\alpha}{3}$$

where M is the molecular weight and \(\rho\) the density of the substance and \(N\) is Avagadro's number.

This argument does not take into account the effect of the dipole under consideration on the surrounding medium, except in so far as the bulk properties of the medium are determined by the averaged effect of all such dipoles, and for this reason cannot be expected to apply to pure polar liquids though it may be a reasonably good approximation for dilute solutions.

The impossibility of applying the Debye equation to liquids of considerable polarity becomes evident when an attempt is made to use it to calculate the dipole moment from the dielectric constant of the pure liquid. If we take the measured dielectric constant of water as 80, the density as 1, and neglect the small induced moment, the
inclusion of which would lower the calculated moment value a little, the Debye equation gives a moment value 0.95 $x 10^{-13}$ e.s.u. for the molecule as compared to the value 1.84 $x 10^{-13}$ measured in the vapour state. Water is rather an exceptional case, owing to the effects of hydrogen bonding, but similar considerations apply to other liquids.

A general difficulty in the application of the Debye equation to polar liquids becomes evident if, neglecting the induced polarisation for the sake of simplicity, we write

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi \eta \lambda^2}{9K\tau}$$

and

$$\frac{4\pi \eta \lambda^2}{9K} = T_c$$

So that

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{T_c}{T}$$

According to this equation, when $T$ becomes equal to $T_c$, $\varepsilon$ becomes infinitely large, that is, should be a curie point. Van Vleck has pointed out that this does not actually mean that the dielectric constant must really increase without limit, but, rather, that at temperatures below $T_c$, the polarisation cannot be treated as linearly dependant upon field strength, as assumed in the derivation of the Debye equation, since saturation
effects should occur, producing an electric analogue of ferromagnetism, that is, a stable state of permanent electric polarisation. In the case of water, putting the values of constants into the above equation gives $T_c = 1,140$, which means that, if the Debye equation were applicable, water should show ferroelectric behaviour throughout its liquid range. For most substances $\eta$ is smaller than water, which would lower the value of $T_c$ but still require ferroelectric behaviour of most polar liquids.

Onsager has calculated the relation between the bulk properties and the polarisability in a slightly different way. He considers the central dipole as being in a spherical hole of molecular radius in a medium which has the bulk properties of the substance, and calculates the field at the dipole in two parts: firstly, the field in the cavity due to an external field, in the absence of the central dipole, and, secondly, the field due to the polarisation of the walls of the cavity by the central dipole. The moment of the dipole is determined by its permanent moment and the moment induced in it by the field in the cavity.
In this way Onsager arrives at the equation,

\[
\frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d} - \frac{\eta^2 - 1}{\eta^2 + 2} \frac{M}{d} = \frac{3 \varepsilon (\eta^2 + 2)}{(2 \varepsilon + \eta^2)(\varepsilon + 2)} \frac{4 \pi N \mu^2}{9 kT}
\]

where \( \varepsilon \) is the dielectric constant of the bulk material, \( \mu \) is the permanent electric moment of the molecule, and \( \eta \) is the 'internal refractive index' of the polar molecule, defined in terms of the optical polarisability \( \alpha_0 \) by

\[\alpha_0 = \frac{\eta^2 - 1}{\eta^2 + 2} \alpha^3\]

where \( \alpha \) is the molecular radius.

Onsager's equation differs from that of Debye by the factor \( \frac{3 \varepsilon (\eta^2 + 2)}{(2 \varepsilon + \eta^2)(\varepsilon + 2)} \), since \( \mu \) of the Debye equation is not distinguished from \( \mu_0 \) of the Onsager equation. As \( \varepsilon \) approaches \( \eta^2 \), this factor approaches 1, i.e. the difference between the two equations approaches zero.

Kirkwood has pointed out that hindered rotation must play a part in the dielectric polarisation of polar liquids. He has generalized the Onsager theory by eliminating the approximation of a uniform local dielectric constant identical with a macroscopic dielectric constant of the medium, obtaining

\[
\left( \frac{\varepsilon - 1}{\varepsilon + 1} \right) \frac{M}{d} = \frac{4 \pi N}{3} \left( \alpha_0 + \frac{\mu^2}{3 kT} \right)
\]

where \( \mu \) is the molecular dipole moment in the liquid and \( \bar{\mu} \).
is the sum of the molecular dipole moment and the moment induced as the result of hindered rotation in the spherical region surrounding the molecule, \( \mu' \) may be replaced by
\[
\nu \mu = q \mu^2
\]

The calculation of the parameter \( q \) is, in principle, provided for by statistical mechanics, but is usually prevented by insufficient knowledge of liquid structure.

Kirkwood's equation, however, is incorrect because an incorrect approximation is used for the local field in calculating the distortion polarisability.

By statistical reasoning Frohlich has obtained a more general expression which can be written
\[
\frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d} - \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d} = \frac{3\varepsilon (\varepsilon + 2)}{(2\varepsilon + 6)(\varepsilon + 4)} \frac{4\pi N a^2}{K^2}
\]

This equation is identical with Onsager's, except that \( \mu^2 \) is replaced by \( 3\mu^2 \).

It is evident that Kirkwood's equation represents a theoretical advance beyond the Onsager equation, in that it takes into account the hindrance of molecular orientation by neighbouring molecules. Since, however, the correlation parameter \( q \) which expresses this effect can be calculated only roughly from knowledge of the
liquid structure, which is usually lacking, the principal value of the equation consists in the introduction of a correction factor which is normally empirical. Kirkwood points out that the departure of $q$ from unity is a measure of the degree of hindered relative molecular rotation arising from short-range intermolecular forces. 'Normal' liquids show values of $q$ which do not depart much from unity, while 'abnormal' or 'associated' liquids show values which depart significantly from unity. Like the Onsager equation, the Kirkwood equation contains the approximation involved in treating the polar molecules as spherical, whereas Frohlich avoids this approximation by treating the liquid as made up of rigid dipoles in a continuum having the appropriate optical polarisability.

A group of measurements upon a considerable number of pure liquids has been used to compare the Debye, Onsager and Kirkwood equations written in the forms:

$$\mu_o^2 = \frac{9kT}{4\pi\varepsilon_0} \frac{M}{d} \left( \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right)$$  
Debye

$$\mu_o^2 = \frac{9kT}{4\pi\varepsilon_0} \frac{M}{d} \left( \frac{2\varepsilon + n^2}{3\varepsilon (n^2 + 2)} \right) \left( \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right)$$  
Onsager

$$q\mu_o^2 = \frac{9kT}{4\pi\varepsilon_0} \frac{M}{d} \left[ \frac{(\varepsilon - 1)(2\varepsilon + 1)}{q\varepsilon} - \frac{n^2 - 1}{n^2 + 2} \right]$$  
Kirkwood
Since there is no way of calculating $g$ with accuracy, it is lumped with the moment. The following table shows a comparison of dipole moments ($x 10^{18}$) calculated by Debye, Onsager and Kirkwood equations with observed values at $25^\circ C$. The value obtained are sensitive to the value chosen for $n$, which introduces some uncertainty.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Debye</th>
<th>Onsager</th>
<th>Kirkwood</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl Bromide</td>
<td>1.28</td>
<td>1.80</td>
<td>1.90</td>
<td>2.02 (gas)</td>
</tr>
<tr>
<td>n-Butyl Bromide</td>
<td>1.41</td>
<td>1.80</td>
<td>1.92</td>
<td>2.15 (gas)</td>
</tr>
<tr>
<td>t-Butyl Bromide</td>
<td>1.62</td>
<td>2.39</td>
<td>2.40</td>
<td>2.21 (solution)</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>1.22</td>
<td>1.45</td>
<td>1.54</td>
<td>1.72 (gas)</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>1.17</td>
<td>1.37</td>
<td>1.52</td>
<td>1.77 (gas)</td>
</tr>
<tr>
<td>α-Chloronaphthalene</td>
<td>1.20</td>
<td>1.35</td>
<td>1.33</td>
<td>1.50 (solution)</td>
</tr>
<tr>
<td>α-Bromonaphthalene</td>
<td>1.13</td>
<td>1.25</td>
<td>1.29</td>
<td>1.48 (solution)</td>
</tr>
</tbody>
</table>

The relaxation time

The relaxation time $\tau$ is a quantity which is independent of the expression for the internal field. The significance of $\tau$ can be illustrated by reference to Debye's theory of the dielectric relaxation of a viscous liquid. $\tau$ in this case is related to mean square angular deviation of a molecule in a given time and is of the order of magnitude of the time required for a given
molecule, if fixed and released, to revert to random orientation in the absence of resultant macroscopic polarisation due to the surrounding molecules. On the other hand, the measured quantity is the macroscopic dielectric constant \( \varepsilon = \varepsilon' - i \varepsilon'' \), and if the decay of the macroscopic polarisation of the dielectric with time is exponential it is found that, in an alternating field of frequency \( \omega \),

\[
\frac{(\varepsilon - \varepsilon_0)}{(\varepsilon_0 - \varepsilon_{\infty})} = \frac{1}{1 + i\omega \tau_m} \tag{1}
\]

The plot of \( \varepsilon'' \) versus \( \omega \) obtained by this equation has a maximum when \( \omega \tau_m = 1 \) i.e. \( \omega_c = \frac{1}{\tau_m} \) where \( \omega_c \) is defined as the critical angular frequency. \( \tau_m \) is then the experimentally measured quantity, the macroscopic relaxation time or decay time.

Debye, Onsager and Powles have worked out relations between the relaxation time and decay time for various internal fields.

(a) **Debye:**

In his theory of dielectric relaxation Debye has used implicitly the internal field

\[
F = \left[ \frac{\varepsilon + 2}{3} \right] E
\]

where \( \varepsilon \) is the complex dielectric constant and is
frequency dependent. This leads to Debye's equation

$$\frac{(\varepsilon - \varepsilon_{\infty})}{(\varepsilon_0 - \varepsilon_{\infty})} = \frac{1}{1 + i\omega \frac{(\varepsilon_0 + 2)}{(\varepsilon_{\infty} + 2)} \tau_m^*}$$

(where $\tau_m^*$ = Microscopic relaxation time)

which has the same form as (1) with

$$\tau_m^* = \frac{(\varepsilon_0 + 2)}{(\varepsilon_{\infty} + 2)} \tau_m$$

Debye's equation for a single microscopic relaxation time therefore corresponds to exponential relaxation of polarisation with a decay time $\tau \left[ \frac{\varepsilon_0 + 2}{\varepsilon_{\infty} + 2} \right]$. The factor $\frac{\varepsilon_0 + 2}{\varepsilon_{\infty} + 2}$ may be quite large. However, the evidence from the calculation of dipole moments from static dielectric constants suggests that the form of the internal field assumed here is not valid.

(b) Onsager - Cole:

Cole has given a modified form of the Debye theory in which he puts for the internal field in the alternating current case

$$F = \frac{3\varepsilon E}{2\varepsilon + 1}$$

in analogy to the static case where $F$ is the field in an actual spherical cavity in the dielectric. For $\varepsilon$, one obtains

$$\frac{(\varepsilon - \varepsilon_{\infty})(2\varepsilon + \varepsilon_{\infty})}{\varepsilon} = \frac{(\varepsilon_0 - \varepsilon_{\infty})(2\varepsilon_0 + \varepsilon_{\infty})}{\varepsilon_0} \frac{1}{1 + i\omega \tau_m^*}$$
This contains the implicit assumption that the reaction field is also now determined by \( \varepsilon \) rather than \( \varepsilon_0 \). This equation compared with (1) shows that \( \tau_M \equiv \tau_\mu \).

Substituting (1) in the Cole equation \( \tau_M \equiv \tau_\mu \).

\[
\frac{F}{E} = \frac{3\varepsilon_0}{2\varepsilon_0 + 1} + \left[ \frac{3\varepsilon_0}{2\varepsilon_0 + 1} - \frac{3\varepsilon_0}{2\varepsilon_0 + 1} \right] \left[ \frac{1}{1 + i\omega \tau_M \left( \frac{2\varepsilon_0 + 1}{2\varepsilon_0 + 1} \right)} \right]
\]

Thus the field in a real cavity in a medium characterized by a decay time \( \tau_M \) relaxes with a decay time \( \tau_M \left[ (2\varepsilon_0 + 1)/(2\varepsilon_0 + 1) \right] \) i.e. more slowly than the polarisation in a continuous medium.

(c) Powles:

Powles assumes for an internal field \( F \)

\[
\frac{F}{E} = \frac{3\varepsilon_0}{2\varepsilon_0 + 1} + \left[ \frac{3\varepsilon_0}{2\varepsilon_0 + 1} - \frac{3\varepsilon_0}{2\varepsilon_0 + 1} \right] \frac{1}{1 + i\omega \tau^*}
\]

where \( \tau^* \) is yet unknown.

This leads for an expression for \( \varepsilon \),

\[
\frac{\varepsilon - \varepsilon_0}{\varepsilon_0 - \varepsilon_0} = \frac{2\varepsilon_0 + \varepsilon}{3\varepsilon_0} = \frac{\varepsilon_0 - \varepsilon}{1 + 2\varepsilon_0 + \varepsilon_0} \frac{1}{1 + i\omega \tau^*}
\]

and this reduces to the form (1) if

\[
\tau^* = \tau_M = \left[ \frac{3\varepsilon_0}{2\varepsilon_0 + 1} \right] \tau_\mu
\]
in which case one can write

$$\frac{\epsilon - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + i\omega \tau_\mu \left( \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \right)}$$

Hence the internal field with \( \tau^* = \tau_\mu = \left( \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \right) \tau_\mu \) gives for a process with a single relaxation time a dielectric behaviour characterized by a single decay time. For this internal field the tendency of the polarization to maintain itself is much less than for the Debye expression, and the maximum error incurred in assuming \( \tau_\mu \) and \( \tau_\mu \) identical is 33 per cent, which is likely to be of little significance in relating \( \tau_\mu \) to molecular processes. In the analysis of variation of \( \tau_\mu \) with temperature the use of \( \tau_\mu \) rather than \( \tau_\mu \), neglecting possible variations of \( \epsilon_0 \) and \( \epsilon_\infty \) with temperature, leads to a deduced value of the entropy of activation too small by 0.8 cal/°C/mole at the most. There is, however, no real justification for the assumption made here that the dielectric polarisation must be characterized by an exponential decay.

It is therefore possible to represent the behaviour of all dielectrics by (1), and by considering \( \tau_\mu \) instead of \( \tau_\mu \) the error incurred is extremely small.
Distribution of Relaxation Time

If a molecule is not spherical the processes of orientation about different axes should require different relaxation times. Thus in Debye's equation for a complex polarisation which is

$$\frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d} = \frac{4\pi N}{3} \alpha_o + \frac{4\pi N \mu^2}{9kT} \frac{1}{1+j\omega\tau}$$

$$\mu^2 \frac{1}{1+j\omega\tau}$$ will have to be replaced by $$\mu_1^2 \frac{1}{1+j\omega\tau_1} + \mu_2^2 \frac{1}{1+j\omega\tau_2} + \mu_3^2 \frac{1}{1+j\omega\tau_3}$$

where $$\mu_1, \mu_2$$ and $$\mu_3$$ are the components of $$\mu$$ along these axes and $$\tau_1, \tau_2$$ and $$\tau_3$$ are the corresponding relaxation times, and similarly in the other equations.

Variation in the local environment of the molecules may also give rise to variations in the relaxation times.

In the case of a single relaxation time Debye's theory gives

$$\varepsilon = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau} \quad (2)$$

which can be written

$$\varepsilon' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + (\omega\tau)^2} + \varepsilon_\infty \quad (3)$$

and

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + (\omega\tau)^2} \quad (4)$$
Cole and Cole developed an equation for $\varepsilon$, in the presence of a distribution of relaxation times resulting in a modification of eq. (2) to give

$$\varepsilon = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega \tau_0)^{-\alpha}}$$

where $\tau_0$ is the most probable relaxation time corresponding to the frequency at which $\varepsilon'' = \varepsilon''_{\text{max}}$ and $\alpha$ is an empirical constant with values between 0 and 1, a measure of the distribution of relaxation times.

This leads to the following equations instead of (2) and (3).

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 + \varepsilon_\infty}{2} \left[ 1 - \frac{\sinh [(1-\alpha)x]}{\cosh [(1-\alpha)x] + \sin (\alpha \pi/2)} \right]$$

(5)

and

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty) \cos (\alpha \pi/2)}{2 \left\{ \cosh [(1-\alpha)x] + \sin (\alpha \pi/2) \right\}}$$

(6)

when $X = \ln \omega \tau$. When $\alpha = 0$ these equations reduce to (3) and (4). Equation (5), however, differs from the original Cole and Cole expression in having $\sin(\alpha \pi/2)$ in the denominator instead of $\cos(\alpha \pi/2)$, which appears to be incorrect.

Equations (3) and (4) can be combined and written
in the form of the equation of a circle

\[ (e' - \frac{e_\infty + e'_\infty}{2})^2 + e''^2 = \left(\frac{e_\infty - e'_\infty}{2}\right)^2 \]

Since all values are positive, this gives a semicircular plot of \( e'' \) against \( e' \), typical of Debye's theory. However, Cole and Cole found for a considerable number of liquids and solids that the values of \( e'' \) commonly fell below the semicircle, but could be represented by a semicircular arc intersecting the abscissa axis at the values of \( e_\infty \) and \( e'_\infty \). The centre of the circle of which this arc was a part lay below the abscissa axis, and the diameter drawn through the centre from the \( e_\infty \) point made an angle \( \alpha \pi /2 \) with the abscissa axis. This is represented by equations 5, and 6.
To determine $\alpha$, it may be assumed that the lines drawn between adjacent plotted points are chords of a circle with its centre below the real axis. The centre of the circle is given by the intersection of the perpendicular bisectors of these chords and the perpendicular bisector of the abscissa axis between and $\xi_0$. $\tan \frac{\pi \alpha}{2}$ is measured on the plot, and is calculated from it. The relaxation time may be calculated from the relation

$$\frac{\nu}{\omega} = (\omega \tau)^{1-\alpha}$$

where $\nu$ is the distance on the Cole-Cole plot between $\xi_0$ and the experimental point, and $\omega$ is the distance between the point and $\xi_\infty$. If $\alpha$ is zero, $\frac{\nu}{\omega} = \omega \tau$ which is true for the Debye equations.

The relationship of relaxation time to molecular properties.

Debye (1929) calculated the dielectric relaxation time of a polar molecule, assuming it behaved as a sphere rotating in a viscous medium which had the bulk viscosity $\eta$ of the liquid, as

$$\zeta_\nu = \frac{4 \pi \eta a^3}{K \tau}$$
where $\tau_{\mu}$ is the microscopic relaxation time defined as the time taken for the molecular polarisation due to dipole rotation to fall to $\frac{1}{e}$ of its steady value when the orienting field is removed,

$\mathbf{a}$ is the molecular radius and $k$ the Boltzman constant.

Hill (1954) has shown that a similar equation

$$\tau = \frac{A \eta K^2 \sigma}{kT}$$

can be written, where $A$ is a constant (2.4), $K$ is the mean radius of gyration of the molecule about any axis normal to the dipole axis and $\sigma$ the intermolecular distance. This equation is justified by assuming that the resistance to rotation experienced by a molecule is due to intermolecular collisions.

This equation is derived on the assumption that the viscosity of a liquid arises from molecular collisions in which two molecules become temporarily so closely associated that no macroscopic relative motion is possible between them. This type of an association, which prevents relative motion between the parts of a substance, is what is recognised as freezing when it involves a large number of molecules instead of a pair. It is also assumed to prevent
relative rotation of a pair of molecules, and this equation will be valid only if this is true.

For substances having molecules with no permanent dipole moment the dielectric constant depends on the induced polarisation and is almost independent of the physical state and temperature, except in so far as these factors determine the number of molecules in unit volume, and a small change in the dielectric constant when the phase is changed (solid to liquid) is caused by a small change in the number of molecules per c.c. as in diagram (a) on page 23. However, for most substances having molecules with permanent dipole moment the molecules are fixed with such rigidity in the solid state that little or no orientation in the dipoles in an externally applied field is possible. Thus, the dielectric constant depends only on the displacement of charges inside the molecule. When the solid changes into the liquid state the polar molecules acquire the freedom of rotation and the orientation polarisation increases sharply at the melting point as in diagram (b) on page 23. The very slight increase in the dielectric constant with temperature at low temperatures, and the more pronounced rise just below the melting point are typical.
For such substances the assumptions made in deriving the equation above are valid. However, there are dipolar substances for which the dielectric constant is not altered much on solidification, which indicates that the dipoles still have some freedom of rotation which is lost at a transition point considerably below the freezing point.

Hill (1957) has suggested classifying these substances which lose their freedom of dipole rotation on solidification "class II substances" and those which show no appreciable loss of dipole rotation on solidification "class I substances", and these terms should be used. It appears that the relaxation time of substances belonging to these two classes are controlled by different mechanisms. Thus, for class I substances the type of association which gives rise to van der Waals interactions may have little or no effect on dipole rotation, whereas there is no reason why the dielectric relaxation time should be related to viscosity. According to Hill, the amplitudes can be explained for class I liquids and not for class II liquids in which freezing does not involve cessation of rotational motion.

It has been suggested by Curtis et al. that the
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Hill (1957) has suggested calling those substances which lose their freedom of dipole rotation on solidification "class I substances" and those which show no appreciable loss of dipole rotation on solidification "class II substances", and these terms will be used. It appears that the relaxation times of substances belonging to these two classes are controlled by different mechanisms. Thus, for class II substances the type of association which gives rise to viscosity may have little or no effect on dipole rotation, and there is no reason why the dielectric relaxation time should be related to viscosity. Accordingly the equation \( \tau = \frac{A_1 K^{\alpha}}{kT} \) can be expected to hold for class I liquids and not for class II liquids in which freezing does not involve cessation of rotational motion.

It has been suggested by Curtis et al that the
independence of the inner friction constant (The inner friction constant is the resistive couple acting on a molecule rotating with unit angular velocity) and the viscosity for approximately spherical molecules may be due to the fact that their high symmetry enables them to rotate without appreciably displacing their neighbours.

This aspect of the difference between the two types of liquids is brought out by the following considerations.

Batschinski's relation as to the temperature dependence of the viscosity is

\[ \eta = \frac{A}{(V-b)} \]

where A and b are constants and V is the specific volume. The constant b turns out to lie between the specific volumes of the solid and the liquid at the freezing point and is interpreted as the minimum specific volume at which flow can occur and hence \((V-b)\) is regarded as free volume.

Hill (1959) has suggested that a similar relation may be written

\[ \mathcal{G} = \frac{A'}{(V-b')} \]
where $\zeta$ is the inner friction and $b'$ is the minimum volume at which rotation can occur so that at $v = b'$ rotational freezing will occur.

Comparing the above two relations it is easily seen that for class I substances $b = b'$, that is, viscous flow and dipole rotation both cease at the same temperature, i.e. at the same specific volume, and hence,

$$\frac{\zeta}{\eta} = \frac{A'}{A}$$

and is independent of temperature.

For class II substances $b' < b$ so that the dipole rotation persists at temperatures below that at which viscous flow ceases and

$$\frac{\zeta}{\eta} = \frac{A'}{A} \frac{(v-b)}{(v-b')}$$

is dependent on temperature, and no direct interpretation of it in terms of molecular dimensions is possible.

Hill (1959) has calculated the ratio $\frac{A'}{A} = \frac{\zeta}{\eta} = \text{const} = k\sigma^2$ for class I liquids, where $\sigma$ is the mean distance between neighbours in the liquid.
### Class I

<table>
<thead>
<tr>
<th>Compound</th>
<th>$A'/AK^2\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furan</td>
<td>6.26</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>6.02</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>6.15</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>6.50</td>
</tr>
<tr>
<td>α-Bromonaphthalene</td>
<td>5.90</td>
</tr>
<tr>
<td>Quinoline</td>
<td>6.20</td>
</tr>
<tr>
<td>Isoquinoline</td>
<td>8.00</td>
</tr>
</tbody>
</table>

### Class II

<table>
<thead>
<tr>
<th>Compound</th>
<th>$A'/AK^2\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:2-dichloropropane</td>
<td>17.00</td>
</tr>
<tr>
<td>Methyl chloroform</td>
<td>11.40</td>
</tr>
<tr>
<td>6-buty1 bromide</td>
<td>20.20</td>
</tr>
<tr>
<td>Thiophene</td>
<td>4.80</td>
</tr>
</tbody>
</table>

As can be seen $A'/AK^2\sigma$ is not a constant for the class II liquids.

The above results are based on measurements over a rather limited temperature range, which is frequently quite remote from the freezing points of the liquids considered. The aim of the present work is to obtain values of the relaxation time and viscosity over a wide range of temperature down to, and possibly below,
the freezing point in order to make a more rigorous test of the theory.

The measurements required for this purpose are:

1) The dielectric constant and loss factor of polar liquids over a wide range of temperature down to and possibly below the freezing point at wavelengths of approximately 3 cm and 1 cm.

2) The static dielectric constant of the liquid over the same range of temperature as in (1).

3) The viscosity of the liquids over the same range of temperature as in (1).

4) The density of the liquids over the same range of temperature as in (1).
### CHAPTER 2.

**Experimental methods:**

<table>
<thead>
<tr>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Measurement of complex dielectric constant</td>
<td>35</td>
</tr>
<tr>
<td>Variable short circuit method</td>
<td>37</td>
</tr>
<tr>
<td>Roberts and Von Hippel method</td>
<td>42</td>
</tr>
<tr>
<td>Matched line method</td>
<td>46</td>
</tr>
<tr>
<td>Bridge method</td>
<td>61</td>
</tr>
<tr>
<td>2) Measurement of static dielectric constant</td>
<td>64</td>
</tr>
<tr>
<td>Substitution method</td>
<td>65</td>
</tr>
<tr>
<td>Capacity Bridge method</td>
<td>67</td>
</tr>
<tr>
<td>Heterodyne Beat method</td>
<td>68</td>
</tr>
<tr>
<td>Resonance method</td>
<td>69</td>
</tr>
<tr>
<td>3) Measurement of viscosity</td>
<td>79</td>
</tr>
<tr>
<td>4) Measurement of density</td>
<td>84</td>
</tr>
<tr>
<td>Purification of liquids</td>
<td>85</td>
</tr>
</tbody>
</table>
1. Measurement of complex dielectric constant:

A system for the measurement of the electrical properties of liquids at centimetre wavelengths should have the following essential requirements:

i) The quantity of the liquid required should be moderately small,

ii) Measurement procedure should be rapid, especially as low temperatures will have to be maintained constant during the measurement,

iii) The required constants should be simply related to the quantities measured.

Some of the systems that can be used are the resonant systems, systems in which a standing wave is explored by a travelling probe, and systems in which a fixed detector is used to compare the impedance of the liquid cell with a standard variable impedance.

The present method used at 3.279 cm belongs to the second class, and the method used at 0.847 cm to the third class.

Resonant systems are probably best for the measurement of very low absorption, but become very complicated when a liquid of high absorption is used, because the
amount of liquid in the resonant cavity has to be made very small. They are, however, still capable of yielding results of high accuracy, provided the apparatus itself is accurately made. Standing wave methods in general are affected by the surroundings, and in particular by the position of the observer, because the detectors must have access to the field over a considerable length of the transmission line or waveguide, but with a well designed apparatus the amount of radiation may be made very small and hence this difficulty can be overcome. Fluctuations of input power do not affect the third method, since it is a null method. In the second method they are not serious provided they are very slow since only a ratio of maximum to minimum power is required. Frequency fluctuations are important in the second method as they cause a shift of standing wave pattern and precautions should be taken to maintain the frequency constant. The methods used at both wavelengths allow rapid measurement and simple and direct calculation of the required constants from the measured quantities and neither method requires more than 50 c.c. of the liquid.

Measurement of dielectric constant at 3 cm.

Some of the feasible methods are

1) Variable short circuit method,
2) Roberts and Von Hippel method,
3) Matched line method.

1. **Variable short circuit method:**

Poley has developed this method using rectangular wave guides and involving only the measurement of the standing wave ratio $p$, i.e. the ratio of the field strengths $E_{\text{max}}$ to $E_{\text{min}}$, as a function of the length of a liquid column which is terminated by a short circuit piston, thus avoiding the determination of the phase.

![Diagram](image)

The propagation constant $\gamma_1$ and the wavelength $\lambda_1$ in the air-filled guide are related to the vacuum wavelength $\lambda_v$ and the cut-off wavelength $\lambda_c$, according to

$$\gamma_1 = j\beta_1 = \frac{2\pi j}{\lambda_1} = \frac{2\pi j}{\lambda_v} \sqrt{1 - \left(\frac{\lambda_c}{\lambda_v}\right)^2}$$

Similarly, the propagation constant $\gamma_2$ of the liquid filled guide is given by
\[ \gamma_2 = \alpha_2 + j \beta_2 = \frac{2\pi f \sqrt{\epsilon - \left(\frac{\lambda \nu}{\lambda e}\right)^2}}{\lambda v} \]

and the ratio of the complex intrinsic impedance \( Z_2 \) to that of the air filled guide \( Z_1 \) by

\[ \frac{Z_2}{Z_1} = \frac{\gamma_1}{\gamma_2} = \frac{1 - \left(\frac{\lambda \nu}{\lambda e}\right)^2}{\sqrt{\epsilon - \left(\frac{\lambda \nu}{\lambda e}\right)^2}} \]

The relative complex input impedance \( \frac{Z_2}{Z_1} \) at the mica window (see diagram) for short circuit termination can be shown to be:

\[ Z_o = Z_1 \tan k \gamma_2 d \]

\[ \rho = \frac{E_{\text{max}}}{E_{\text{min}}} = \frac{1 + \left| \frac{Z_o}{Z_1} \right| - 1}{1 - \left| \frac{Z_o}{Z_1} \right| + 1} \]

Solving these equations is extremely difficult, demanding a large number of numerical computations. However, V.S.W.R. can be determined experimentally as a function of the length 'd' of the liquid column, and a curve results which exhibits successive maxima and minima, tending towards a final value \( \rho_{\infty} \) corresponding to a length of liquid column which is electrically infinitely long.
It can be shown that

\[ \frac{p_m}{p_n} = \frac{\tanh(n\pi \tan \frac{\Delta}{2})}{\tanh(m\pi \tan \frac{\Delta}{2})} \quad (1 - C) \]

and

\[ \frac{p_m}{p_\infty} = \frac{1}{\tanh(m\pi \tan \frac{\Delta}{2})} \quad (1 - C_\infty) \]

where \( \tan \frac{\Delta}{2} = \frac{\alpha_k}{p_k} \)

\( p_m \) and \( p_n \) are the standing wave ratios in the \( m \)th and \( n \)th maximums respectively, and \( C \) and \( C_\infty \) are the values of the correction factors which can be neglected with respect to unity, being generally smaller than 1%.

Using the above equations the value of \( \tan \frac{\Delta}{2} \) can be determined and \( \epsilon' \) and \( \epsilon'' \) can now be calculated by the relations:

\[ \epsilon' = \left( \frac{\lambda v}{\lambda_c} \right)^2 + \left( \frac{\lambda v}{\lambda_{kv}} \right)^2 \left( 1 - \tan^2 \frac{\Delta}{2} \right) \]

and

\[ \epsilon'' = 2 \left( \frac{\lambda v}{\lambda_{kv}} \right)^2 \tan \frac{\Delta}{2} \]

Sample calculation is shown on page 40.
\[ 2\pi \tan \frac{A}{2} = \tanh \frac{3.416}{8.000} = 0.835 \quad \tan \frac{A}{2} = 0.1229 \]
\[ 3\pi \tan \frac{A}{2} = \tanh \frac{3.416}{4.125} = 1.1256 \quad \tan \frac{A}{2} = 0.1257 \]
\[ 4\pi \tan \frac{A}{2} = \tanh \frac{3.416}{3.725} = 1.570 \quad \tan \frac{A}{2} = 0.1249 \]
\[ 5\pi \tan \frac{A}{2} = \tanh \frac{3.416}{3.560} = 1.940 \quad \tan \frac{A}{2} = 0.1236 \]

Corrected \( \tan \frac{A}{2} = 0.1279 \)

Thus
\[ \varepsilon' = \left( \frac{\lambda v}{\lambda_c} \right)^2 + \left( \frac{\lambda v}{\lambda_{lw}} \right)^2 \left( 1 - \tan^2 \frac{A}{2} \right) \]
\[ = \left( \frac{3.279}{4.572} \right)^2 + \left( \frac{3.279}{1.314} \right)^2 \left( 1 - 0.1279 \right) = 6.64 \]

and
\[ \varepsilon'' = 2 \left( \frac{\lambda v}{\lambda_{lw}} \right)^2 \tan \frac{A}{2} = 1.59 \]

Graph of \( \rho \) against \( d \) for 1,1-Trichloroethane by variable short circuit method at \( \lambda = 3.279 \) cm.
However, corrections have to be applied due to the losses of the air-filled waveguide (w.g.) section itself. These losses consist of junction (J), wall (W) and termination (T) losses, and add up in the form

\[ \frac{1}{P_{\text{wg}}} = \frac{1}{P_J} + \frac{1}{P_W} + \frac{1}{P_T} \]

Losses due to walls and terminations are negligible compared to junction losses, and so

\[ \frac{1}{P} = \frac{1}{P_{\text{measured}}} - \frac{1}{P_T} \]

Hence to each value of \( P \) in the successive maxima the same correction has to be applied. Application of the correction leads to an increase in consistency in the value of tan \( \frac{A}{2} \) and in fact this correction can be easily found by trial and error.

The V.S.W.R. is determined by using standard techniques and the experiment in itself is very accurate. The error introduced because of the introduction of mica is automatically overcome while applying the correction for tan \( \frac{A}{2} \). The main disadvantage is the time taken to complete one set of readings (at any given temperature) as for liquids with low losses the time may be as much as two hours. At low temperatures maintaining temperature for too long a time proves quite difficult, and for liquids with high losses more than one maximum peak
cannot be obtained, thus making the result very ambiguous.

In the present experiment, the variable short circuit method is used to determine the dielectric constant and the loss factor for suitable liquids (1,1,1 trichloroethane and chlorobenzene) at room temperature and this in turn is used to calculate the correction factor for the apparatus and the method employed. (see "Correction due to mica" - page 55.)

2. Roberts and Von Hippel method:

A stabilized Klystron oscillator radiates monochromatic waves of a prescribed frequency into one end of a coaxial line or hollow wave guide; they are reflected by a shorting metallic boundary at the other end. Standing waves are set up and can be measured by a probe detector travelling along a narrow slot cut in the guide parallel to the axis. The dielectric is inserted in the closed end of the guide opposite the transmitter. For the short-circuit measurement, the sample is placed in direct contact with the metal short; for the open circuit measurement, it is located a quarter wave length ahead of the termination. It is essential that the sample intimately fits the walls of the guide and the shorting
plate, and that its face be perpendicular to the guide axis. When a wave from the oscillator is propagated along the wave-guide, it is partly reflected and partly transmitted on arrival at the interface. The transmitted part is propagated through the dielectric in a manner dependent upon the propagation constant until it reaches the short circuit, where it is totally reflected and propagated back until it reaches the interface. Again part is transmitted and part is reflected, and the process is continued until, after a certain build up time, the flow of energy in the air filled portion of the guide may be regarded as consisting of two resultant waves moving in opposite directions. The field at the probe depends on the relative magnitudes and phases of the incident and reflected waves, which annul each other at some points and reinforce each other at others, forming a standing wave.

The standing wave is measured in air (medium 1) above the dielectric sample of thickness $d$ (medium 2) and the terminating impedance $Z(0)$ of medium 1 is found by determining the ratio of minimum to maximum electric field strength and the distance $x_o$ of the first minimum from the dielectric boundary. $Z(0)$ can now be expressed in
terms of the directly measurable parameters \( x_0 \), \( \lambda \), and \( E_{\text{min}} \). The function \( \gamma_{ld} \) can be determined from charts of the first minimum from the surface of medium 2; the function \( \gamma_{ld} \) can be determined from charts series approximation of the function.

\[
Z(o) = Z_1 \frac{E_{\text{min}}}{E_{\text{max}}} - j \tan \frac{2\pi x_0}{\lambda v} \left( 1 - j \frac{E_{\text{min}}}{E_{\text{max}}} \tan \frac{2\pi x_0}{\lambda v} \right) + j \tan \frac{2\pi x_0}{\lambda v}
\]

where \( Z_1 \) is the characteristic wave impedance of medium 1.

Using the short circuit method the terminating impedance is

\[
Z(o) = Z_2 \tanh \gamma_2 d
\]

where \( Z_2 \) is the characteristic wave impedance of medium 2 and \( \gamma_2 \) is the propagation function of medium 2.

And since for non-magnetic dielectrics \( Z_1, \gamma_1 = Z_2, \gamma_2 \)

\[
Z(o) = Z_1 \frac{\gamma_1}{\gamma_2} \tanh \gamma_2 d
\]

Using the above equations and also noting that medium 1 is loss free, i.e. \( \gamma_1 = \frac{2\pi}{\lambda_1} \),

\[
\tanh \gamma_2 d = \frac{-i\lambda_1}{2\pi d} \frac{E_{\text{min}}}{E_{\text{max}}} - j \tan \frac{2\pi x_0}{\lambda_1} \left( 1 - j \frac{E_{\text{min}}}{E_{\text{max}}} \tan \frac{2\pi x_0}{\lambda_1} \right) + j \tan \frac{2\pi x_0}{\lambda_1}
\]

\[
C e^{i\phi}
\]

The function \( C e^{i\phi} \) is found by measuring the thickness \( d \) of the sample, the wavelength \( \lambda \), in the airfilled pipe, the inverse V.S.W.R. \( E_{\text{min}}/E_{\text{max}} \), and the distance \( x_0 \).
of the first minimum from the surface of medium 2.

The function $\gamma_2d$ can be determined from charts or from a series approximation of the function,

$$\frac{\tanh Te^{i\Phi}}{Te^{i\Phi}} = Ce^{i\delta}$$

S. Roberts has drawn a survey map, with the argument $\tau$ the ordinate, the absolute value of $T$ the abscissa, whereas $C$ and $\delta$ are parameters of intersecting curves; $T$ and $\delta$ are expressed in degrees. The hyperbolic functions are multivalued so that measurement with a single thickness $d$ of the dielectric may leave the value $\gamma_2$ in doubt, but if two different thicknesses are used, only one set of values $T/d$ and $\tau$ will satisfy both experimental results.

Knowing the characteristic propagation factor $\gamma_2$, the propagation factor $\gamma_2(\gamma_2)$ of the dielectric in free space can be calculated from

$$\gamma_2^2 = \gamma_2^2 + \left(\frac{2\pi}{\lambda_c}\right)^2$$

and the complex dielectric constant of a non-magnetic medium 2 can be expressed

$$\varepsilon_2 = \varepsilon_0 \left(\frac{1}{\lambda_c}\right)^2 - \left(\frac{\gamma_2}{\lambda_{cT}}\right)^2$$

where $\lambda_1$ is the cut-off wavelength and for the lowest
order waves in the customary types of wave guide take the values

Rectangular pipe \( \lambda_c = 2 \times \text{width} \)

Round pipe \( \lambda_c = 1.71 \times \text{diameter} \)

Coaxial line \( \lambda_c = \infty \)

The open circuit method is not very convenient with liquids and also, since the present experiment requires the measurement of dielectric constants at various temperatures, the problem of measuring the thickness of the sample, particularly at low temperatures, will become extremely difficult. As the results are doubtful unless measurements are made at several depths, the experiment proves to be time consuming. The nature of the relation between the measured quantities \( C \) and \( J \) and the required quantities \( \Gamma \) and \( T \) makes it difficult to assess the affect of consistent errors.

3. **Matched line method:**

The specimen is kept in a rectangular waveguide, one end having a plane transverse air-dielectric interface and the other having a long taper with the resultant space in the wave guide filled with an absorbing material. A slotted line carrying a probe measures the standing
wave pattern in the waveguide in front of the interface.

Let the forward wave be \( \exp \left( j(\omega t + k x) \right) \)

Reflected wave \( \gamma e^{j\phi} \exp \left( j(\omega t - k x) \right) \)

where \( x \) is measured from the surface in the direction of the reflected wave and \( \gamma \) is the reflection coefficient.

\[
\text{Signal} \propto \left| \exp \left( j(\omega t + k x) \right) + \gamma e^{j\phi} \exp \left( j(\omega t - k x) \right) \right|^2
\]

\[
= 1 + \gamma^2 + 2\gamma \cos (2kx - \phi)
\]

Minima occur where \( 2kx - \phi = \pm \pi \)

\( \phi = 2\pi x - \pi = 2\theta - \pi \) (say)

The propagation constant \( \beta_2 \) and attenuation \( \alpha_2 \) in the liquid are given by

\[
\frac{Z_1}{Z_2} = \frac{\alpha_2 + j\beta_2}{\alpha_1 + j\beta_1} = \frac{1 - \gamma e^{j\phi}}{1 + \gamma e^{j\phi}}
\]

\[
= \frac{1 - \gamma^2 - j2\gamma \sin\phi}{1 + \gamma^2 + 2\gamma \cos\phi} = \frac{1 - \gamma^2 - j2\gamma \sin\phi}{(1+\gamma)^2 - 4\gamma^2 \sin^2\phi}
\]
On simplifying and expressing \( \gamma \) in terms of the standing wave ratio,

\[
\frac{P_2}{P_1} - j \frac{\alpha_2}{\alpha_1} = \frac{P (1 + \tan^2 \theta)}{1 + P^2 \tan^2 \theta} + j \frac{(P^2 - 1) \tan \theta}{1 + P^2 \tan^2 \theta}
\]

where \( \gamma = \frac{P-1}{P+1} \) and \( P \) is the power standing wave ratio.

\[
\frac{P_2}{P_1} = \frac{P (1 + \tan^2 \theta)}{1 + P^2 \tan^2 \theta}
\]

and \( \frac{\alpha_2}{\alpha_1} = \frac{(P^2 - 1) \tan \theta}{1 + P^2 \tan^2 \theta} \)

\[
= B \text{ (say)}
\]

\[
= A \text{ (say)}
\]

and the real and imaginary parts of the dielectric constants are given by

\[
\varepsilon' = 1 + \left[ \left( \frac{\alpha_2}{\alpha_1} \right)^2 \left( \frac{\lambda_0}{\lambda_c} A^2 \right) \right]
\]

\[
\varepsilon'' = \frac{2 \left( \frac{\alpha_2}{\alpha_1} \right)^2 A \cdot B}{1 + \left( \frac{\alpha_2}{\alpha_1} \right)^2}
\]

where \( \lambda_c \) is cut off wavelength in the air filled guide

\( \lambda_0 \) is the wavelength in the air filled guide.

Powles, William and Smyth have used this method. The waveguide was supported vertically so as to keep the air-dielectric interface horizontal. A window was formed in the guide by a thin mica sheet, held between the flanges of two sections of waveguide and made liquid tight.
by a little silicone grease at its edges, and no detectable reflection from the mica sheet was observed. A wedge of glossy material was used to prevent the waves from being reflected into the dielectric medium. The liquid cell was surrounded by a jacket in which the coolant was circulated so as to maintain the temperature in the range of $-80^\circ C$ to $+120^\circ C$. The lower end of the jacket extended to the end of the dielectric, but the waveguide was well insulated for some distance below the interface. The slotted line was maintained close to room temperature, being protected by a length of about 10 cm of the guide and a thermal choke.

The power standing wave ratios were obtained by direct measurement of the maximum and minimum of the standing wave by means of a calibrated attenuator and a microammeter. The shift in the minimum $x_0$ was obtained by comparing the position of the minimum of the standing wave in front of the specimen with that measured in a preliminary experiment in which the specimen was replaced by a short circuit plate.

The apparatus now used is similar to that of Powles, Williams and Smyth and is as shown in the block diagram on page 50.

The signal was modulated at 3 kc/sec and attenuators were introduced between the Klystron and the calibrated
Block diagram of measuring apparatus for 3.279 cm.
variable attenuator to prevent frequency pulling by the oscillator. The Klystron was shielded from stray convection currents of air which improves its stability, and in case of a frequency shift it could always be reset to its previous value by readjusting the resonator potential by observing the signal from the wavemeter, which was displayed on an oscilloscope. The residual noise level of the V.S.W.R. indicator was less than 0.1µv at -10 db with the input open-circuited, and less than 0.03µv with the input short-circuited.

The apparatus was supported horizontally (as this was more convenient than supporting it vertically) except for the liquid cell which was supported vertically using a right angle bend. Mica of uniform thickness 0.0025 cm was used to get a liquid tight seal between the right angle bend and the liquid cell. As using grease is not desirable because the organic liquids dissolve it, the flanges of the right angle bend and the liquid cell were lapped in the workshop so that a clean evenly cut piece of mica, when screwed between these two surfaces, stayed liquid tight. The actual liquid cell itself was surrounded by a jacket in which alcohol could be circulated, the temperature of which could, in turn, be controlled by either heating or cooling it in an adjacent unit. A
range of temperature from +50°C to -75°C was obtained by this method using "Drikold" (solid CO₂) or liquid air with alcohol depending on the temperature needed. The temperature could be maintained at any given value for a time considerably more than was needed to take a set of readings.

A pair of glass vanes coated with nichrome were used in the liquid cell so that all the power was absorbed and none reflected from the top of the liquid cell.

The cross section of the actual temperature control unit is shown in the figure.
Alcohol circulates between the walls of the two concentric cylinders where it is cooled to the required temperature using Drikold and alcohol, or liquid air and alcohol. This unit was kept inside a thermos to prevent heat losses which would be quite appreciable at temperatures below -20°C. A mixture of Drikold and Alcohol was used to go down to -50°C and then liquid air had to be used instead of Drikold. By extending the lower end of the cooling jacket all the way down to the mica sheet, the whole volume of the liquid sample could be maintained at the same temperature. The cooling jacket, the connecting tubes and the pump were all covered with poron (expanded polystyrene) so as to cut down the heat losses.

To get down to lower temperatures merely Drikold or liquid air was added to the mixture in the concentric cylinders, and to actually maintain the temperature either the rate of addition of Drikold was regulated so as to just compensate for the heat losses, or the pump speed was controlled, which in turn controlled the transfer of heat. When the temperature was steady, no difference in temperature was found between the top and the bottom of the cooling jacket, so a sensitive thermometer was used to read the temperatures, a mercury
thermometer to read from +50°C to 0°C and an alcohol thermometer from 0°C to -80°C. For temperatures above room temperature a small piece of copper tubing in the system was directly heated from the outside and the temperature was controlled by adjusting the supply of heat, the circulating liquid still being alcohol.

At temperatures below 0°C ice forms wherever possible and then by itself acts as an insulator. However, if any ice forms on the outer surface of mica (i.e. the surface of mica exposed to air) it gives rise to wrong results. Because of the presence of the slotted line a convection current always sets in, and hence ice always forms on the mica surface unless precautions are taken to prevent this. To avoid this, dry air was blown at the end of the slotted line nearer to the right angle bend, thus preventing moist air from reaching the cold surface of mica or the adjoining guide walls.

As the temperature changes, the right angle bend as well as the liquid cell undergoes a thermal expansion and this slightly shifts the standing wave which in turn alters the position of the minimum. Therefore, the change in the position of the minimum with respect to
temperature is determined for a short circuit, and is taken into account while comparing the position of the minimum of the standing waves for the liquids, with that of the short circuit.

As the weight resting on the right angle bend gives rise to a strain on the bend the total weight, namely that of the cooling jacket and alcohol circulating in the cooling jacket, were kept constant throughout the experiment.

The apparatus is very stable. By properly shielding the Klystron from stray convection currents the frequency could be maintained constant. The position of the minimum could always be accurately reproduced within one part in a hundred. The standing wave ratio could also be accurately reproduced to \( \pm 0.05 \) dB.

**Correction due to mica:**

Introducing a piece of mica of thickness 0.0025 cm between the two flanges gives rise to a gap in the wave guide wall of the same thickness and the effect of this has to be corrected.
Let \( r \) be the reflection coefficient due to mica and the gap in the guide wall; \( t \) be the transmission coefficient; \( R \) be the reflection coefficient of the liquid surface alone.

Where \( r \), \( t \) and \( R \) are all complex quantities.

Consider a wave of unit intensity incident on the mica. \( t \) is transmitted and \( r \) is reflected. The liquid reflects a part of \( t \) equivalent to \( tR \) which is again reflected and transmitted. The diagram shows the affect of multiple reflections and transmissions.

Let \( R^1 \) be the combined reflection due to mica and the liquid surface

\[
\therefore R^1 = r + t^2R + t^2R^2r + t^2R^3r^2 + \ldots
\]
\[
= r + t^2R(1 + Rr + R^2r^2 + \ldots)
\]
\[
= r + \frac{t^2R}{1 - Rr}
\]

\[
\therefore R = \frac{R^1 - r}{t^2 + (R^1 - r)r}
\]
or \[
t^2R = (R^1 - r)(1 - Rr)
\]
Using a match, \( R = 0 \) as all the waves are absorbed and we have \( R = r \) which ideally should be zero. There should, therefore, be no standing wave in this case. However, because of the reflection due to mica and the gap a small signal variation could be detected. The position of the minima and the standing wave ratio of this standing wave were found. These were found to be almost constant in the temperature range \(+50^\circ C\) to \(-75^\circ C\).

Similarly, using a short, \( R = 1 \) as all the waves are reflected, and hence \( t^2 \) can be found out in principle.

When a liquid is used instead, the match was used in the liquid as well, to make sure that there were no reflections from the liquid cell other than that due to the liquid itself. So, knowing \( R^l \), \( R \) can be calculated.

\[
R = \frac{t^2}{t^2 + R( R^l - r )} \quad \text{which is a complex quantity.}
\]

\[
= X + jY \quad \text{(say)}
\]

From this the dielectric constant and the loss factors are calculated by the relations,

\[
\rho = \frac{1 + |r|}{1 - |r|} \quad \text{where} \quad |r| = \sqrt{X^2 + Y^2}
\]

and \( \tan \theta = -\frac{Y}{X} \)

Thus, knowing \( A \) and \( B \), \( \varepsilon' \) and \( \varepsilon'' \) are calculated.

However, in practice an experimental determination of the reflection coefficient for a short circuit is
extremely difficult to obtain because of the very high value of the standing wave ratio. This was easily overcome by determining the dielectric constant and the loss factor for a suitable liquid (1,1,1 Trichloroethane) by the variable short circuit method, and then at the same temperature by finding out the power standing wave ratio and the shift in the minimum of the wave form from that of the minimum of the standing wave for a short circuit, $t^2$ was calculated. This value of $t^2$ was used in all further calculations involving the piece of mica for which this correction term was worked out.

Thus, with any liquid the only two readings necessary are the position of the minimum in the standing wave and the power standing wave ratio. As the position of the minimum is not very sharp it was not possible to read it directly. Hence, points on either side of the minima at which the signal was equal were found. This was done by adjusting the indicator needle to a particular position by moving the probe. This probe position was noted and then the probe was moved so that the signal went through the minimum and rose again to the same strength as before. The average of these two probe position readings gave the position of the minimum. The P.S.W.R. was obtained by knowing the setting of the
calibrated attenuator (usually 2.30 mm) and finding the minimum reading on the indicator. The probe was then moved until the indicator denoted a maximum signal when the attenuation of the calibrated attenuator was increased to bring the signal back to the original minimum value, and the reading of the attenuator noted. By knowing these two readings the P.S.W.R. was calculated from the calibration graphs.
Measurement of dielectric constant at 0.847 cm.

The 'Bridge method' was used to measure the dielectric constant and loss factor of the sample. The total length of the waveguide is made roughly the same as that of the arm, i.e., the arm containing the liquid under test and the arm containing the variable impedance, insensitive to the second frequency condition for white light fringes. Identical calibrated attenuators were used in both arms and phase shifts were introduced in each arm.

The amplitude $r$ and phase $\phi$ of the reflection coefficient are measured directly from the attenuator setting and the setting of the short circuit respectively. If $r$ is the reflection coefficient, $r = \frac{1 - k}{1 + k}$, where $k$ and $r$ are defined previously.
Measurement of dielectric constant at 0.847 cm.

Bridge method:

The 'Bridge method' used to measure the dielectric constant and loss factor at 0.847 cm is as shown in the block diagram.* The total length of the wave guide is made roughly the same in both the arms, i.e. the arm containing the liquid under test and the arm containing the variable impedance, thus making the method frequency insensitive. (Analogous to the Michelson interferometer condition for white light fringes). Identical calibrated attenuators (with rotary vanes) are used in both the arms thus introducing the same amount of insertion loss and phase shift in both arms.

The amplitude $\gamma$ and phase $\phi$ of the reflection coefficient are measured directly from the attenuator setting and the setting of the short circuit respectively.

If $\gamma e^{i\phi}$ is the reflection coefficient,

$$\gamma e^{i\phi} = \frac{Z_2/z_1}{Z_2/z_1 + i} = \frac{j\beta_i}{\alpha_2 + j\beta_2}$$

where $Z_2$ and $Z_1$ are defined as previously.

* Page 60.
Solving for $\frac{\sqrt{A}}{p}$ and $\frac{\sqrt{B}}{p}$,

$$A = \frac{\sqrt{A}}{p} = \frac{1 - \gamma^2}{1 + \gamma^2 + 2\gamma \cos \phi}$$

and

$$B = \frac{\sqrt{B}}{p} = \frac{2\gamma \sin \phi}{1 + \gamma^2 + 2\gamma \cos \phi}$$

and the values of $\varepsilon'$ and $\varepsilon''$ then follow as in the previous method.

Firstly, with a fixed short instead of the liquid cell the setting of the variable short and the reading on the calibrated attenuators are found for a zero signal. This is done by alternately adjusting the variable short and the calibrated attenuator. Since the fixed short had a greater reflection coefficient than the variable short, the calibrated attenuator in the variable short arm was kept at zero while the other one was varied. Secondly, the piece of mica later to be used to seal the liquid cell was used with the short and the experiment repeated. From these two results the transmission coefficient of the piece of mica used can be found. Thirdly, the short circuit was replaced by the empty liquid cell and match (the liquid cell being sealed with the piece of mica) and the new setting of the variable short and the new reading of the calibrated attenuator, for a zero signal found. From this the reflection coefficient of mica can
be calculated, which allows the correction to be applied for the presence of mica. Lastly, the experiment is repeated with the liquid in the liquid cell, thus determining the reflection due to the liquid. In the third and the last part of the experiment the calibrated attenuator in the liquid cell arm was kept at zero while the other calibrated attenuator was varied.

The phase change $\phi$ on reflection at the liquid surface and the amplitude reflection coefficient $r$ are found from

$$\begin{align*}
\text{change in the position of the variable short circuit } X & \times X \times 2\pi \\
\text{phase change} &= \frac{\lambda g}{\text{short circuit } X \times 2\pi} + \pi \\
\text{reflection coefficient} &= \cos \phi \times \cos \phi' \\
\end{align*}$$

where $\theta$ is the angle of attenuator in the test arm and $\theta'$ that of the attenuator in the reference arm.

The setting of the variable short, for short circuit only, varied with temperature for a zero signal, and this has to be taken into consideration while determining the shift in its position. The variation was found to be linear with temperature. No appreciable variation in the position of the calibrated attenuator with temperature was observable in the case of match and mica. No phase shift with change of attenuator setting was observable.

The temperature was controlled by using the same techniques as before.
2. **Measurement of static dielectric constant:**

The unit of electrostatic charge is defined as such that if two unit point charges, in a vacuum, are one centimetre apart, the force exerted by one on the other is one dyne. As the inverse square law holds, it follows that charges $e_1$ and $e_2$, in a vacuum and $r$ cm apart, will repel one another with a force of $\frac{e_1 e_2}{r^2}$ dynes. If, however, the charges are separated by a uniform dielectric medium - gaseous, liquid or solid, the force exerted between them is less than when they are the same distance apart in a vacuum, and is given by $\frac{e_1 e_2}{\varepsilon r}$ dynes, $\varepsilon$ being the dielectric constant of the medium.

The dielectric constant of a medium can also be defined as the ratio of the capacity of an ideal condenser with the medium filling the space between its plates to its capacity with the space evacuated, and the usual methods for determining dielectric constants are based on the measurement of this ratio. This view of the matter implies that the quantity of charge required to raise the potential difference between the two plates of a condenser to a specified value is greater when there is a dielectric material between
the plates than when there is none. The ratio of the quantities of charge required in the two cases is the dielectric constant of the medium.

The measurements actually required, therefore, are the capacity changes, and these are usually made with reference to a standard condenser of as high precision as possible.

The dielectric constant of a liquid measured at a frequency as high as a megacycle is equal to the static dielectric constant for liquids whose dispersion region is in the microwave range.

Several methods of determining static dielectric constant are:
1. Substitution method.
2. Capacity Bridge method.
4. Resonance method.

1. Substitution method.

C, is a variable condenser of a stable, but not necessarily precision type. D is the dielectric cell and S is a standard condenser. The
connections are arranged as shown so that the dielectric cell and the standard condenser can be brought alternately into the circuit. With the dielectric cell in the circuit the condenser, $C$, is adjusted until the total capacity in the circuit has a definite value, and then keeping this setting unchanged, the dielectric cell is replaced in the circuit by the standard variable condenser, which is then adjusted to give the same total capacity in the circuit. At this particular setting, therefore, the capacity of the standard condenser, plus that of its leads, is equal to that of the dielectric cell and its leads. Hence the change in the capacity of the dielectric cell when one medium is replaced by another is measured by the change in setting of the standard condenser which gives an equal capacity change.

In this method comparisons of the capacities of the dielectric cell and of the standard condenser can be made within a second of one another, thus eliminating errors which tend to arise due to slight drift in frequency of the alternating current used.
2. Capacity Bridge method

If the four arms of a bridge network of the form shown in the figure contain ideal condensers $C_1$, $C_2$, $C_3$, and $C_4$, and the bridge is fed from a source of alternating current, the potential difference between X and Y will change, and hence the current through the detecting instrument D will change as the capacity of the condenser $C_1$ is varied.

When the balance point is reached, i.e. when the current is zero in D,

$$C_1 : C_2 = C_3 : C_4$$

If condenser $C_2$ is the dielectric cell and condenser $C_1$ is a standard variable condenser, the capacitance $C_2$ can be calculated given $C_3$ and $C_4$ or by knowing the ratio to one another.

If, however, the medium in the dielectric cell is such that it has a slight conductivity, the cell behaves as a condenser with a resistance in parallel. In order to obtain complete balance, with zero current passing through D, it is necessary to introduce a
variable resistance across condenser $C_1$. Balance is then attained by adjusting the condenser and resistance alternately.

The accuracy of this method depends critically upon the constancy of the capacities $C_2$ and $C_4$ and on the resistances in the circuit. Stray capacities also play a very important part and it is essential to keep these as low as possible. However, it has the advantage that, provided all the equivalent series resistances in the circuit are low, it does not depend critically upon the constancy of the frequency fed to the bridge.

3. The Heterodyne Beat method

This is based upon the principle that, if two circuits oscillating with nearly the same frequency, are each loosely coupled to a third circuit, there is produced in the last circuit a beat frequency corresponding with the difference of the two inducing oscillators.

If the frequency of the oscillator A is kept constant, while the frequency of the oscillator B is
varied by changing the capacity C, the beat note heard in the telephone T will change, and can be brought to a definite value. If the inductance in the circuit B is kept constant the beat frequency will be the same whenever the total capacity in this circuit has a certain value. If, therefore, this comprises a variable condenser in parallel with the dielectric cell, changes in the capacity of the latter can be followed, as in the other methods by determining the change in the capacity of the variable condenser required to maintain the same beat note.

4. Resonance method

When an inductance L, a capacity C, and a resistance R are arranged in series in a circuit, the impedance of the circuit is given by

$$Z = \sqrt{R^2 + \left(2\pi\nu L - \frac{1}{2\pi\nu C}\right)^2}$$

where $\omega$ is the frequency of the current passing in the circuit. This impedance is a minimum, and hence for a fixed e.m.f. the current flowing is a maximum when

$$2\pi\nu L = \frac{i}{2\pi\nu C}$$

is zero, i.e. $\nu L C = 1$. If this condition holds the circuit is said to be in a state of
resonance, and if $R$ is small the current will rise to very high values when an e.m.f. of frequency $\nu$ is induced in the circuit.

If a constant frequency is used, therefore, and the inductance of the circuit is kept constant, resonance occurs when the capacity $C$ has a definite value. Hence if a variable condenser is arranged in parallel with the dielectric cell, resonance to a constant induced frequency will occur when the former is set to such a value that the sum of the capacities of the variable condenser and dielectric cell has this required value. Consequently, changes in the capacity of the dielectric cell brought about by changing the medium in it are reflected in changes in the variable condenser required to maintain the state of resonance.

Oscillations are induced by means of a very stable oscillator. To detect resonance in the circuit, the circuit is loosely coupled to a subsidiary circuit containing a rectifier, such as a crystal, and a galvanometer. Alternatively, a valve voltmeter can be
can be connected across the condenser, so as to determine the setting at which the voltage across it is a maximum.

In the present experiment the resonance method is used with the frequency of the alternating current in the circuit at about 20 Kc/s. A cathode ray oscilloscope is used as a detector and observing the signal on the oscilloscope the resonance position is easily and accurately set. The method by itself is simple and straightforward and the circuit can be set up with as few connecting leads as possible, and the resonance position can be adjusted and checked within about twenty seconds or so, making it possible to obtain the static dielectric constant of the liquids at any required temperature.

The capacity of the empty dielectric cell is found out by the substitution method. It can also be measured by the resonance method, using a standard liquid like benzene whose value of the static dielectric constant is known. The measurements by both methods give the same results as long as the total length of the leads in either case is kept constant. As the dielectric cell is silvered it attains temperature
equilibrium very rapidly and then maintaining the
temperature for a minute at a time is sufficient to
set the apparatus for resonance. The experiment is
carried out for a range of temperature from +50°C to
-80°C. As the temperature is varied the static
dielectric constant changes, thus changing the state
of resonance, and to maintain this resonance state the
capacitance of the variable condenser is changed.
Knowing the change in the capacitance, the "static"
dielectric constant is calculated, according to:

\[
\text{Static dielectric constant of the medium} = \frac{\text{Capacity of the condenser filled with the medium}}{\text{Capacity of the condenser filled with air}}
\]

The dielectric cell

One of the most important problems with a
dielectric cell for use with solutions is that the
trapping of air bubbles during filling must be avoided.
The filling and emptying of the cell must also be as
easy as possible. Hence, designs which incorporate
blocks or wedges of insulating material to separate
the plates may give rise to difficulties owing to the
The construction of a recent apparatus which avoids the trouble just mentioned is based on the design of a cell introduced by A. A. van Biesbroeck. It consists of two concentric glass tubes, the inner tube being closed at its lower end, and the outer tube having its upper end sealed to the outer tube. Access to the inner space thus formed is provided by a capillary tube sealed to the bottom of the outer tube and to the side of the inner tube at the top of the capillary, respectively. The inner surface of the capillary tube and the outer surface of the inner tube are covered over the lower three-quarters of their lengths, whereby giving two condenser plates, contact to which is afforded by platinum wires sealed through the bottom of the inner tube and through the wall of the outer tube, respectively. The latter contact is protected by a glass tube, sealed to the wall of the outer tube and bent vertically upwards. Mercury can be introduced into this latter and into the space of the inner tube in order to make contact.
fact that there are capillary interstices which may or may not become filled with liquid. Further, when a solution has once been introduced into such interstices it may be difficult to remove it by washing.

The condenser used in the present experiment which avoids these difficulties is based on the design introduced by Sayce and Briscoe. It comprises two concentric glass tubes, the inner tube being closed at its lower end, whilst its upper end is sealed to the outer tube. Access to the annular space thus formed is provided by narrower tubes sealed to the bottom of the outer tube and to the side of the outer tube at the top of the annular space, respectively. The inner surface of the outer tube, and the outer surface of the inner tube are silvered over the lower three-quarters of their length, thereby giving two condenser plates, contact to which is effected by platinum wires sealed through the bottom of the inner tube and through the wall of the outer tube, respectively. The latter contact is protected by a glass tube, sealed to the wall of the outer tube and bent vertically upwards. Mercury can be introduced into this member and into the inside of the inner tube in order to make contact
between the leads from the measuring circuit and the platinum contact wires.

The inner tube is extended upwards so as to permit the whole of the portion of the cell which contains liquid to be immersed in a thermostat. Tie bars linking the central tubes with the filling tubes and the tube carrying the contact to the outer plate make the structure much more rigid and thereby avoiding variations in capacity due to strain, as well as making the cell less fragile. The filling tubes are of short capillary tube with about 2 mm bore, which facilitate the introduction and removal of solutions by air pressure without the introduction of bubbles. The capacity to earth of the lead to the central electrode is minimized and made more nearly constant by bringing the platinum wire, which is sealed through the bottom of the inner tube, vertically through the length of this tube, where it is held taut by being sealed at the upper end into a glass cup, integral with the top of the cell. With the same purpose in view the diameter of the central tube is fairly large at the top. In order to minimize the capacity between the leads to the two plates the arm carrying the lead to the outer
plate is spaced at least 3 to 4 cm from the main tube.

This cell has the advantage that no material other than the dielectric under test is introduced between the plates, and one plate is almost completely surrounded in all directions by the second plate. Thus it is as near as possible to an "ideal" condenser, i.e. one for which the capacity is proportional to the dielectric constant of the medium introduced.

For silvering the cell the solution recommended by Sugden is used, which is made up as follows:

(a) 8 gms. of glucose are dissolved in 150 c.c. of water containing 0.5 c.c. of nitric acid, and the solution boiled for two minutes. After cooling 150 c.c. of alcohol are added. This solution is stored.

(b) 6 gms. of silver nitrate are dissolved in 100 c.c. of water, and ammonia solution is added until the precipitate first formed just redissolves; 70 c.c. of 3 per cent sodium hydroxide solution is then added, after which the solution is just cleared by addition of ammonia. It is made up to 500 c.c. with distilled water. This solution is always freshly prepared as required.

After cleaning with a hot mixture of chromic and nitric acids the cell is washed well with distilled water
and dried. One part of solution (a) is mixed with ten parts of solution (b) and introduced into the cell through the tube leading to the bottom of the annular space. When deposition of the film is complete (about half an hour) the solution is withdrawn by suction through the same tube. After about three such layers have been deposited, the inside of the cell is washed thoroughly with distilled water and dried. As the film is not very stable in dry state, the cell is kept filled with dry benzene when not in use.

The capacity of the cell, with air as the medium, changes with temperature and hence the change of capacity with respect to temperature is determined by an independent experiment. It is found that the capacity of the cell changes linearly with temperature.

As the silver coating is not very stable, the dielectric cell cannot be cleaned very effectively without destroying part of the silver coating. So, for every liquid used the dielectric cell was freshly silvered, calibrated with a known liquid (benzene) and used.

The lower three quarters length of the cell only was silvered and care was taken to see that the dielectric
covered the whole silvered portion all the time. This was easily achieved by filling the dielectric cell completely at room temperature and in no case did the level of the liquid go below the silvered surface due to thermal contraction.

The results are very stable and reproducible, and the following table shows a comparison of some of the present results with other published results.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Temperature</th>
<th>Present Experimental Value</th>
<th>Published Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-xylene</td>
<td>20°C</td>
<td>2.36</td>
<td>2.27</td>
</tr>
<tr>
<td>Thiophen</td>
<td>20°C</td>
<td>2.764</td>
<td>2.769</td>
</tr>
<tr>
<td></td>
<td>1°C</td>
<td>2.832</td>
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<tr>
<td>0-xylene</td>
<td>21°C</td>
<td>2.517</td>
<td>2.515</td>
</tr>
<tr>
<td>1,1,1 Trichloro-ethane</td>
<td>20°C</td>
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<td>7.18</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>25°C</td>
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<td>5.58</td>
</tr>
<tr>
<td>Iodobenzene</td>
<td>21°C</td>
<td>4.59</td>
<td>4.69</td>
</tr>
</tbody>
</table>
3. **Measurement of Viscosity:**

An ideal fluid is not capable of sustaining shearing stresses. However, in real fluids shearing stresses occur when different parts of the fluid move with different velocities and the fluids are then said to possess viscosity. This is attributed to internal frictional forces occurring between the fluid particles, the force $F$ per unit area required to maintain a constant velocity gradient $\frac{dv}{dx}$ in the liquid

$$F = \eta A \frac{dv}{dx}$$

where $\eta$ is the coefficient of dynamic viscosity.

For homogeneous fluids $\eta$ is a characteristic constant for each fluid for a given temperature and pressure; its dimensions are $M^{-1} L^{-1} T^{-1}$ and the unit is the poise. The ratio $\eta/P$ where $P$ is the fluid density, is known as the kinematic viscosity and this is measured in stokes.

Relative measurements of viscosity are easily made using U-tube viscometers.

A typical U-tube viscometer is shown in the figure. Suppose a constant volume of the liquid in
the left hand limb is allowed to flow down through the tube. Then the flow may be considered to be caused by an average head $H$, which is constant, since the volume of the liquid used is constant. The average pressure is therefore proportional to $Hg$ so that for a liquid of dynamic viscosity $\eta$, and density $\rho$,

$$\nu = \frac{\eta}{\rho} = \frac{\eta Hg a^4}{8L V} t,$$

where $L$ = length of the capillary tube.

$t_1$ = time taken for the volume $V$ to flow through.

$a$ = radius of the capillary tube.

Similarly for a different liquid,

$$\nu_2 = \frac{\eta_2}{\rho_2} = \frac{\eta_2 Hg a^4}{8L V} t_2$$

therefore

$$\frac{\nu_1}{\nu_2} = \frac{\nu_1}{\nu_2} \frac{t_1}{t_2} \text{ where } \alpha = \frac{\eta Hg a^4}{8L V}$$

from which a comparison can be made.
However, after applying corrections because some of the pressure difference between the two ends of the tube is used to communicating kinetic energy to the liquid, and because there is an expenditure of energy due to differences of velocity between adjacent line of flow as the liquid converges on the tube, it can be shown that

\[
\frac{\eta}{\rho} = At - \frac{B}{t}
\]

where \(A\) and \(B\) are constants for a given viscometer.

Thus

\[
\frac{\nu_1}{\nu_2} = \frac{At_1 - \frac{B}{t_1}}{At_2 - \frac{B}{t_2}}
\]

\(A\) and \(B\) are found by measurements of liquids having known kinematic viscosities. Thus, knowing the constants, the kinematic viscosity can be calculated by experimentally observing the time of flow.

In the present experiment, the two free ends of the viscometer were rigidly fixed to a metal holder which in turn could be screwed on to a rigid support thereby ensuring exactly the same position every time. Benzene and cyclohexane were used to determine the constants \(A\) and \(B\), both the experiments being carried out at 18°C. The viscometer was immersed in the
constant temperature bath to such a depth that the highest level of the liquid in the viscometer always was below the level of the bath liquid. Care was taken to see that only clean dry air entered the viscometer, thus avoiding formation of ice inside the viscometer at low temperatures. This was easily accomplished with the help of two tubes filled with anhydrous calcium chloride connected to the two open limbs of the viscometer. The level of the liquid inside the viscometer was always adjusted to the level g so that at every temperature the volume of liquid used was the same. This was done as shown in the diagram. As the liquid contracts with decrease in temperature the level is brought up to g by carefully dropping the liquid from the funnel. As it always takes a long time to reach temperature equilibrium, it was desirable to blow the liquid up to the mark b and allow it to fall through the capillary tube a couple of times before taking the
actual reading. The time taken for the liquid to fall from b to C was determined within an accuracy of \( \pm 0.01 \) sec and throughout the experiment the temperature was controlled to \( \pm 0.1^\circ C \).

The greatest care has to be taken in cleaning the viscometer so that not even a single particle of dust remains in it. This was done by cleaning with a mixture of nitric acid and alcohol, the two liquids to be mixed in the viscometer and not outside. It was then thoroughly cleaned with distilled water and dried with clean dry air.

Two types of viscometers were used throughout the experiments, Viscometer C for liquids with high viscosity, like Nitro Benzene, and viscometer B 188 for like chlorobenzene, etc.

The following shows a comparison of some of the present results with the other published results.

<table>
<thead>
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<th>Liquid</th>
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<td>565</td>
<td>547</td>
</tr>
<tr>
<td>p-xylene</td>
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<td>568</td>
<td>561</td>
</tr>
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<td>Quinoline</td>
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<td>Bromobenzene</td>
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<td>1,1,1 Trichloro-ethane</td>
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<td>725</td>
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<tr>
<td>Chloroform</td>
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<tr>
<td>Isoquinoline</td>
<td>30°C</td>
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</table>
4. **Measurement of Density:**

An ordinary pyknometer was used to determine the density of the liquids in the temperature range + 50°C to - 50°C.

Unlike the other measurements the experiment was done starting from lower temperatures. It was convenient to do this way as the liquids expand on increasing the temperature and hence the difficult task of keeping the volume of the liquid inside the pyknometer constant was overcome. A very accurate balance was used (reading to four figures) to do the weighings and benzene was used as a standard liquid to determine the volume of the pyknometer.

The results are accurate to about one part in a thousand, and the following gives a comparison of some of the present experimental results with those previously published.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Temperature</th>
<th>$\rho$(present experiment) gm/c.c.</th>
<th>$\rho$(published) gm/c.c.</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.864</td>
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<tr>
<td></td>
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<td>P-xylene</td>
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<td>0.861</td>
</tr>
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<td>Quinoline</td>
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<tr>
<td></td>
<td>20°C</td>
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<td>1.094</td>
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<tr>
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<td>0°C</td>
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Purification of liquids

All the liquids were bought from the commercial agents. They were all fractionally distilled and dried with the appropriate drying agents. Before making measurements on any liquid, it was checked for its dryness. This was easily done by cooling the liquid to near its freezing point in a glass U tube (initially filled with dry air). The presence of even the slightest quantity of water shows itself in the separation of ice, which could be easily seen. Some liquids, however, did not show any presence of water after fractional distillation. This was generally true of those liquids with boiling points not in the neighbourhood of water. However, as all the liquids had to be stored for some time they were all kept with the appropriate drying agents.

Before the liquids were actually used they were filtered to get rid of the drying agents, taking care to see that the filter paper was absolutely dry. This was done by warming the filter paper with hot air and keeping it in a desicator containing anhydrous calcium chloride.
The following shows the B.P. and the F.P. of all the liquids along with the drying agents used.

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<th>F.P.</th>
<th>Drying agent</th>
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<tr>
<td>Iodobenzene</td>
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<td>CaO₂</td>
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<td>74°C</td>
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<td>Chloroform</td>
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<td>51°C</td>
<td>-25°C</td>
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<td>+13°C</td>
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<td>MgSO₄</td>
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CHAPTER 3.

Experimental results:

Variation of $\gamma$ of the liquids with temperature 88
Variation of $\eta$ of the liquids with temperature 89
Variation of $\varepsilon_\infty$ of the liquids with temperature 90
Variation of $\varepsilon'$ and $\varepsilon''$ of the liquids with temperature
at $3.279$ cm and $0.347$ cm wavelengths 91-100
at $29.89$ cm and $19.88$ cm wavelengths 97-98
Variation of $\varepsilon_\infty$ of the liquids with temperature 102
Variation of $\alpha$ of the liquids with temperature 103

$\frac{\Delta b}{b}$ % of the liquids 104
<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Bromobenzene</th>
<th>Iodobenzene</th>
<th>1,1,1 Trichloro-ethane</th>
<th>Chloroform</th>
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<th>2-chloro-2-methyl propane</th>
<th>Chlorobenzene</th>
<th>p-xylene</th>
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Table showing the variation of density (gm/c.c) of the liquids with temperature.
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<th>Chloroform</th>
<th>Nitrobenzene</th>
<th>2-chloro-2-methyl propane</th>
<th>Chlorobenzene</th>
<th>p-xylene</th>
<th>o-xylene</th>
<th>Methyl alcohol</th>
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Table showing the variation of viscosity (10 poise) of the liquids with temperature.
<table>
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<th>Temperature °C</th>
<th>Bromobenzene</th>
<th>Iodobenzene</th>
<th>1,1,1-Trichloroethane</th>
<th>Chloroform</th>
<th>2-chloro-2-methyl propane</th>
<th>Chlorobenzene</th>
<th>p-xylene</th>
<th>o-xylene</th>
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<th>Isoquinoline</th>
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Table showing the variation of static dielectric constant of the liquids with temperature
## Bromobenzene

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<th>$\varepsilon''$</th>
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<th>$\lambda = 0.847$ cm</th>
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### P-xylene

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<th>Temp. °C</th>
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<th>$\varepsilon''$</th>
<th>$\lambda = 3.279 \text{ cm.}$</th>
<th>$\lambda = 0.847 \text{ cm.}$</th>
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### O-xylene

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<tr>
<th>Temp. °C</th>
<th>$\varepsilon_0$</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
<th>$\lambda = 3.279 \text{ cm.}$</th>
<th>$\lambda = 0.847 \text{ cm.}$</th>
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Thiophen

\[ \lambda = 3.279 \text{ cm} \quad \lambda = 0.847 \text{ cm} \]

<table>
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<tr>
<th>Temp. (^\circ\text{C})</th>
<th>(\varepsilon_0)</th>
<th>(\varepsilon')</th>
<th>(\varepsilon'')</th>
<th>(\varepsilon')</th>
<th>(\varepsilon'')</th>
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### QUINOLINE

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<th>Published results.</th>
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<tr>
<td></td>
<td>λ</td>
<td>29.89</td>
</tr>
<tr>
<td>at 40° C</td>
<td>cm</td>
<td>λ&lt;sub&gt;c&lt;/sub&gt;</td>
</tr>
<tr>
<td>at 20° C</td>
<td>cm</td>
<td>8.17</td>
</tr>
<tr>
<td>at 0° C</td>
<td>cm</td>
<td>10.95</td>
</tr>
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### IODOBENZENE

|       | λ | 29.89 | 19.88 | 3.279 | 0.847 | 3.99 | 3.22 | 1.25 | 0.80 |
|-------| cm | λ<sub>c</sub> | 4.39 | 5.17 | 5.80 | 4.86 | 5.20 | 4.86 | 4.68 | 4.10 |
| at 21° C | cm | | | | | | | | |

Table showing λ<sub>c</sub> of all the liquids at various temperatures.
<table>
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<th>Compound</th>
<th>50°C</th>
<th>40°C</th>
<th>30°C</th>
<th>20°C</th>
<th>10°C</th>
<th>0°C</th>
<th>-10°C</th>
<th>-20°C</th>
<th>-30°C</th>
<th>-40°C</th>
<th>-50°C</th>
<th>-60°C</th>
<th>-70°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1'-Dichloro-2,4,4-trimethylpentane</td>
<td>3.13</td>
<td>3.11</td>
<td>3.06</td>
<td>3.00</td>
<td>2.95</td>
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<td>2.72</td>
<td>2.67</td>
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<td>2.59</td>
<td>2.58</td>
<td>2.57</td>
<td>2.56</td>
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<td>2.63</td>
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<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
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Table showing specific volume of all the liquids at various temperatures.
<table>
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<th>Temperature C</th>
<th>Bromobenzene</th>
<th>Iodobenzene</th>
<th>1,1,1-Trichloroethane</th>
<th>Chloroform</th>
<th>Nitrobenzene</th>
<th>2 chloro 2 methyl propane</th>
<th>Chlorobenzene</th>
<th>Quinoline</th>
<th>iso quinoline</th>
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<td>-.07</td>
<td>-.05</td>
<td>.13</td>
<td>.07</td>
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<td>-.02</td>
<td>-.04</td>
<td>-.22</td>
<td>.28</td>
<td>-.01</td>
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<td>-.02</td>
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<td>-30</td>
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</table>

Table showing the variation of $\alpha$ of the liquids with temperature.
<table>
<thead>
<tr>
<th>Liquid</th>
<th>b</th>
<th>b'</th>
<th>Δb%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromobenzene</td>
<td>0.62</td>
<td>0.60</td>
<td>3.2</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.58</td>
<td>0.53</td>
<td>8.6</td>
</tr>
<tr>
<td>1,1,1 Trichloroethane</td>
<td>0.69</td>
<td>0.65</td>
<td>5.8</td>
</tr>
<tr>
<td>2-chloro-2 methyl propane</td>
<td>1.06</td>
<td>1.00</td>
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<tr>
<td>Chlorobenzene</td>
<td>0.83</td>
<td>0.80</td>
<td>3.6</td>
</tr>
</tbody>
</table>
CHAPTER 4.

Experimental accuracy:

Complex dielectric constant 106
Static dielectric constant 107
Relaxation time 107
Viscosity and density 107

At 0.567 cm the reflection coefficient depends on the fourth power of the cosine of the angle of the calibrated attenuator and this is reproducible to 0.05%. Hence the error in T is extremely small of the order of 0.2%.
Experimental accuracy.

1) The complex dielectric constant.

As mentioned before, at 3.279 cm, \( x_c \) is reproducible to 1% and \( \phi \) to better than 0.05 \( \text{deg} \).

Thus to a first approximation,

\[
B = \frac{\beta^2}{\rho^2} = \rho \quad \text{and} \quad A = \frac{\alpha^2}{\rho^2} = (\rho^2 - 1) \frac{1 + \frac{\pi}{\rho}}{\rho}
\]

Typically \( \rho^2 \sim 7 = 8.45 \text{ dB} \). An error of 0.05 dB amounts to 1% in \( \rho^2 \). The error in \( B^2 \) is therefore about 1% and that in \( A^2 \) about 2%.

\[
\varepsilon' = \frac{1 + \left( \frac{\alpha}{\pi} \right)^2 (B^2 - A^2)}{1 + \left( \frac{\alpha}{\pi} \right)^2} \approx \frac{1 + \left( \frac{\alpha}{\pi} \right)^2 B^2}{1 + \left( \frac{\alpha}{\pi} \right)^2}
\]

and \( \varepsilon'' = \frac{2 \left( \frac{\alpha}{\pi} \right)^2 B A}{1 + \left( \frac{\alpha}{\pi} \right)^2} \)

Since \( \left( \frac{\alpha}{\pi} \right)^2 \sim 1 \), the error in \( \varepsilon' \) is about \( \pm 0.01 \) while that in \( \varepsilon'' \) is \( \pm 0.02 \).

At 0.847 cm the reflection coefficient depends on the fourth power of the cosine of the angle of the calibrated attenuator and this is reproducible to 0.05%. Hence the error in \( \phi \) is extremely small of the order of 0.2%.

\[
B = \frac{2 \gamma S \cos \phi}{1 + \gamma^2 + 2 \gamma \cos \phi} \quad \text{and} \quad A = \frac{1 - \gamma^2}{1 + \gamma^2 + 2 \gamma \cos \phi}
\]
 depends on the shift in the minimum and this is reproducible to about 0.002 \mu m. The actual calculations of \( \varepsilon' \) and \( \varepsilon'' \) on the basis of the above reproducibility gives a maximum random error of \( \pm 0.01 \) for both \( \varepsilon' \) and \( \varepsilon'' \) which are independent of the actual values of \( \varepsilon' \) and \( \varepsilon'' \).

2) The static dielectric constant.

The error in this is considerably less than 1% and is negligible compared with the error of \( \varepsilon' \).

3) The relaxation time.

This is effectively calculated from \( \frac{\lambda_c}{\lambda} = \frac{\varepsilon'' - \varepsilon'}{\varepsilon''} \) or \( \frac{\varepsilon''}{\varepsilon' - \varepsilon_\infty} \). Typically \( \varepsilon' - \varepsilon' \) or \( \varepsilon' - \varepsilon_\infty \) is of the order 2 while the uncertainty of \( \varepsilon' \) is \( \pm 0.03 \). The uncertainty in \( \varepsilon_\varepsilon - \varepsilon' \) is of the order 1.5%. The error in \( \lambda_c \) is therefore of the order 4% although the error in the relative values at different temperatures is appreciably less. In most cases the values of \( \lambda_c \) calculated from the two different wavelengths agree within these limits. The cases in which this is not so are discussed further in the next section.

4) Viscosity and density.

The densities are accurate to \( \pm 0.1\% \).

Flow times are measured to 0.1 sec. in total times of the order 200 sec. or more. Since \( \gamma \sim \rho \), \( \gamma \) is accurate to 0.15%.
The temperature was held constant to 0.1°C. A temperature change of 0.1°C corresponds typically to a change of 0.15% in $\gamma$. The scatter of the experimental points about the straight line in the graphs of $\frac{1}{\gamma}$ vs V corresponds in extreme cases to a variation in $\gamma$ of the order 1% or in V of the order 0.2%.
CHAPTER 5.

Conclusion:

Viscosity measurements

Dispersion measurements
110

CONCLUSION

1. Viscosity measurements:

The present viscosity measurements allow investigation of the dependence of viscosity on temperature over much greater range than has been done before. Graphs (pages 116 to 127) show \( \eta \) plotted against the specific volume of the liquids. In every case except Quinoline the graph is a straight line. Thus, the temperature dependence of the viscosity at normal pressure of a large number of liquids can be described successfully by Batschinskis relation

\[
\eta = \frac{A}{V - b}
\]

where \( A \) and \( b \) are constants and \( V \) is the specific volume.

Graphs on page 128 are plotted based on the exponential relationship \( \eta = A e^{\frac{b}{V}} \) which as can be seen does not account for the temperature dependence adequately for any of these liquids.

The relation \( \eta V^\frac{1}{3} = c e^{\frac{23}{V}} \) suggested by Andrade shows no appreciable improvement over the simple exponential relationship. (Page 129)

Viscosity measurements at low temperatures and in particular at supercooled liquid states has made it possible to uphold Batschinskis relation \( \eta = \frac{A}{V - b} \) rather than the exponential relation \( \eta = A e^{\frac{b}{V}} \). No discontinuity is apparent between the ordinary liquid and supercooled states.
2 Dispersion measurements:

The graphs (pages 130 to 147) show the variation of $\varepsilon$, $\varepsilon'$ and $\varepsilon''$ with temperature at wavelengths of 3.279 cm and 0.847 cm.

The results were first fitted to the equation

$$\frac{\varepsilon - \varepsilon_0}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{1}{(1 - i\omega \tau)\alpha}$$

but this leads to negative values of $\alpha$ in some cases. The variation of $\alpha$ of all the liquids with temperature is shown on page 103. In all cases $\alpha$ is more negative at higher temperatures tending towards zero or positive as its freezing point is approached. In all cases other than Bromobenzene and Chloroform $\alpha$ is not less than -0.13 at 50°C but in the above two cases it is as low as -0.30 at 50°C or less. Nitrobenzene whose B.P. is +210.8°C gives a value of $\alpha$ of +0.31 at 2°C and +0.04 at 50°C, thus tending towards a negative value of $\alpha$ at still higher temperatures.

The tendency of $\alpha$ to become negative at higher temperatures is observable also in other results in the literature. However, as a negative value of $\alpha$ has no physical significance, in all such cases $\alpha$ was taken as zero and the equation

$$\frac{\varepsilon - \varepsilon_0}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{1}{1 + i\omega \tau} = \frac{1}{1 + \frac{i\omega \tau}{\lambda_c^2}}$$

used to calculate the critical wavelength $\lambda_c = 2\pi c \tau$.

Results (pages 91 to 98) show reasonably consistent values of $\lambda_c$ from the two experimental wavelengths except for Nitrobenzene, Iodobenzene, Quinoline and iso-quinoline.
The dielectric constants of o-xylene, p-xylene and Thiophen (pages 99 to 100) give values of \( \varepsilon' \) so close to that of \( \varepsilon_0 \) that no significant inference can be drawn as \( \varepsilon_0 - \varepsilon' \) is zero within experimental error.

Graphs (pages 153 to 157) show \( \frac{1}{\varepsilon_0} \) plotted against specific volume and these can all be fitted into straight lines within the experimental error except for 2-chloro-2 methyl propane. The estimated error in \( \lambda_c \) depends on \( \varepsilon_0 - \varepsilon' \) and \( \varepsilon'' \). The error in \( \varepsilon' \) and \( \varepsilon'' \) is estimated to be \( \pm 0.01 \) and \( \pm 0.02 \) respectively at 3.279 cm and \( \pm 0.01 \) at 0.847 cm the error being the same in both the quantities, the error in \( \varepsilon_0 \) being negligible in comparison. The error in \( \lambda_c \) depends on the relative values of \( \lambda \) and \( \lambda_c \) but is typically about 5%.

The weighted mean of \( \lambda_c \) from the two wavelengths was calculated by

\[
\lambda_c \text{ (weighted mean)} = \frac{\left( \varepsilon_0 - \varepsilon' \right) \lambda_c}{a_b \sigma_{3.279 \text{ cm}}} + \frac{\left( \varepsilon_0 - \varepsilon' \right) \lambda_c}{a_{-0.847 \text{ cm}}}.
\]

\( b' \) was calculated from \( \frac{1}{\varepsilon_0} = A(\nu - b') \) and \( b \) from the viscosity measurements namely \( \eta = \frac{A}{\nu - b} \). The percentage difference \( \frac{b - b'}{b} \times 100 \) gives a measure of deviation from Debye theory, i.e. \( \frac{1}{\varepsilon_0} \approx \frac{1}{\eta} \). In all cases this quantity \( \Delta b \) is non zero but there is a tendency for it to be smaller the greater the molecular assymmetry, i.e. the more difficult for the molecule to turn without
displacing its neighbours. The results of $\frac{\Delta b}{b} \times 100$ are shown on page 104.

The fact that $b'$ is always smaller than $b$ suggests that less free volume is required for molecular rotation than for viscous flow so that $\lambda_c$ varies less rapidly with temperature than $\gamma$ does. The class II substances which show dipole rotation in the solid state thus differ from the Class I liquids in degree rather than in kind.

The discrepancies between the values of $\lambda_c$ found at different wavelengths in the cases of Iodobenzene, Quinolone and iso-quinolone (pages 97 to 98) are also observable in the hitherto published results, (page: 101) and suggest breakdown of any law of the kind,

$$\frac{\varepsilon - \varepsilon_\infty}{\varepsilon_\infty} = \frac{1}{(1 + i\omega \tau)^{1-\lambda}}$$

The measurements done for these three liquids at wavelengths of 29.89 cm and 19.88 cm (results on pages 97 to 98) suggest that there may be a second dispersion region leading to abnormally high values of $\varepsilon''$ at the shorter wavelengths. However, no definite conclusion can be reached unless the values of $\varepsilon'$ and $\varepsilon''$ for these liquids are found out covering a wide range of frequencies.
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Graphs of the experimental results:

$\frac{1}{\eta}$ against specific volume, according to $\eta = \frac{A}{V-b}$  

Log($\eta \times 10^5$) against $\frac{1}{T} \times 10^4$, according to $\eta = A e^{\frac{B}{T}}$ 128

Log($\eta \times 10^5 \times V^\frac{1}{3}$) against $\frac{1}{\sqrt[3]{V}}$, according to $\eta V^\frac{1}{3} = C e^{\frac{S}{T}}$ 129

$\epsilon_0$, $\epsilon'$, and $\epsilon''$ with respect to temperature at wavelengths of 3.279 cm and 0.847 cm 130-147

$\frac{1}{\lambda \epsilon T} \times 10^4$ against specific volume 148-152
Bromobenzene
1,1,1, Trichloroethane
Chloroform
Nitrobenzene
2-chloro-2-methyl propane
Chlorobenzene
p-xylene
Methyl-alcohol
1. Quinoline
2. Iodobenzene
3. Bromobenzene
4. 1,1,1 Trichloroethane
5. Chlorobenzene
6. Methyl alcohol
7. Chloroform
1. Methyl alcohol
2. Chlorobenzene
3. Iodobenzene
4. Chloroform
Bromobenzene
F. P.: -31°C
λ: 3,279 cm
Poley, Smyth et al.
Bromobenzene
F.P.: -31°C
λ = 0.847 cm
Poley J.P.²⁴
1,1,1-Trichloroethane
F.P.: -32°C
λ = 0.847 cm
Poley J. P. 24
Chloroform
F.P. : -63°C
λ = 0.847 cm
2 Chloro-2 Methyl propane
F.P.: -25.5°C
λ = 0.847 cm
Nitrobenzene
F.P.: +6°C
λ = 3.279 cm

Poley J.P. 24
Quinoline

F.P.: -15°C

$\lambda = 3.279$ cm

$\varepsilon_0 = 9.0$

$\varepsilon = 8.0$

- HOLLAND R.S. and SMYTH C.P.
Quinoline
E.P.: -15°C
\(\lambda = 0.847 \text{ cm}\)
Isoquinoline
F.P. : +26.5°С
λ = 3.279 cm

Holland R.S. and Smyth C.P.
Isoquinoline
F.P. : +26.5°C
λ = 0.847 cm
Iodobenzene
F.P.: −31°C
λ = 0.847 cm
Poley J.P.
Trichloroethane

Poley J.D.

Smyth et al.
2-chloro-2-methyl propane

\[ \frac{1}{\lambda T} \times 10^3 \]

\* POLEY J.P. 24

\* SMYTH et al. 13
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