

MICROWAVE DISPERSION OF SOME POLAR LIQUIDS

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SAMENVATTING

In dit proefschrift wordt een onderzoek beschreven van de dielectrische dispersie en absorptie van een aantal polaire vloeistoffen in het microgolf-gebied. Daar voor vloeistoffen, die bestaan uit polaire moleculen van eenvoudige structuur, de voornaamste absorptie juist in dit golflengte-gebied ligt, biedt een dergelijk onderzoek interessante perspectieven ter verificatie van verschillende dispersie-theorieën en van de modellen, die daaraan ten grondslag liggen.

In de Inleiding wordt een overzicht gegeven van de huidige stand der analyse van dispersiegegevens van polaire vloeistoffen welke kunnen worden beschreven met één relaxatietijd. Voorts wordt de historische ontwikkeling van het experimentele werk op dit gebied geschetst. Hoofdstuk II biedt een vergelijking van verschillende bekende dispersiemodellen. Tevens wordt een nieuwe dispersierelatie voor ellipsoidale moleculen afgeleid. De experimentele gegevens zijn vervat in Hoofdstuk III. Een nieuw ontwikkelde meetmethode maakt de bepaling van ϵ' en ϵ'' met een nauwkeurigheid van 1% in vele gevallen mogelijk. Na een beschrijving van de gebruikte microgolf-apparatuur volgen de eigenlijke meetresultaten, die een golflengte-gebied tot 8 mm bestrijken. Teneinde een theoretische interpretatie van deze resultaten mogelijk te maken is het onderzoek beperkt tot een aantal polaire vloeistoffen waarvan de moleculen zoveel mogelijk corresponderen met de besproken modellen, t.w. een tweetal vrijwel bolvormige moleculen en een reeks mono-gesubstitueerde benzenen. Hieraan zijn metingen aan water en de eenvoudigste alcoholen toegevoegd. Tenslotte is een serie metingen aan oplossingen van enkele dezer vloeistoffen in benzeen verricht. De meetresultaten, die alle zeer goed met een halve cirkel in het ϵ' , ϵ'' -vlak kunnen worden beschreven, wijzen voor de gesubstitueerde benzenen op het bestaan van een tweede dispersiegebied bij mm-golven. In de discussie van deze resultaten in Hoofdstuk IV blijkt, dat dit van dipolaire oorsprong moet zijn. Zulk een verdere dispersie van de dielectrische constante is niet in overeenstemming met het besproken Onsager-model. Zij is echter wel te begrijpen op grond van de veronderstelling dat, tengevolge van de regelmatige rangschikking der moleculen, locale velden werken op een molecule, die mede het dielectrisch gedrag bepalen.

CONTENTS

CHAPTER I. INTRODUCTION

- § 1. The analysis of the dielectric behaviour of polar liquids 1
- § 2. Historical outline of experimental work 5

CHAPTER II. THE ANALYSIS OF DIELECTRIC DISPERSION DATA

- § 3. The formula of Debye 6
- § 4. The formula of Onsager 9
- § 5. Ellipsoidal molecules 11
- § 6. Models with local fields 16

CHAPTER III. EXPERIMENTAL FACTS

- § 7. Principles of measuring method 18
- § 8. Experimental arrangement 24
- § 9. The substances investigated 28
- § 10. Experimental results 29
- § 11. Determination of the atomic polarization 39

CHAPTER IV. INTERPRETATION OF THE EXPERIMENTAL DATA

- § 12. General discussion of the experimental results 40
- § 13. Applicability of various models to the liquids investigated 46

MICROWAVE DISPERSION OF SOME POLAR LIQUIDS

Summary

The chief purpose of the present investigation is the measurement and analysis of the microwave dispersion of some polar liquids. An outline of the problem and a historical survey of experimental work on the dielectric behaviour of polar liquids are given in Chapter I. A number of theoretical expressions for the dielectric constant in the static case and their extension to alternating fields are reviewed in Chapter II. A formula for the dielectric dispersion in liquids composed of ellipsoidal molecules is derived and its consequences are investigated. Chapter III deals with the experimental details of the investigation. A new microwave measuring technique is described, accurate in most cases to about 1% for both the real and imaginary part of ϵ . In order to make the theories applicable, the investigation has been restricted mainly to polar liquids of simple structure, in particular to the mono-substituted benzenes. The results refer to wavelengths down to 0.8 cm. The analysis of our measurements in Chapter IV reveals discrepancies between the dielectric constant ϵ_∞ , extrapolated from the side of cm-waves, and n^2 , the square of the refractive index, extrapolated from measurements in the visible and infrared. This leads to assuming an additional region of dipolar absorption in the neighbourhood of 1 mm. The mechanism to which such an absorption may be due is sought in the strong local fields exerted on a molecule by its immediate neighbours.

CHAPTER I. INTRODUCTION

§ 1. *The analysis of the dielectric behaviour of polar liquids* *). The dispersion and absorption of electromagnetic waves by polar dielectrics have been a subject of investigation for a considerable time. The main purpose of this research is to discuss the behaviour of the dielectric constant $\epsilon = \epsilon' - j\epsilon''$ according to new measure-

*) Throughout this investigation non-rationalized Gauss units are employed, in view of the fact that in this field the use of Giorgi units has as yet made little headway.

ments in the cm-wave region at the hand of various theoretical formulae. The parameters in these investigations in general are the circular frequency ω , the temperature T , and in the case of solutions the concentration.

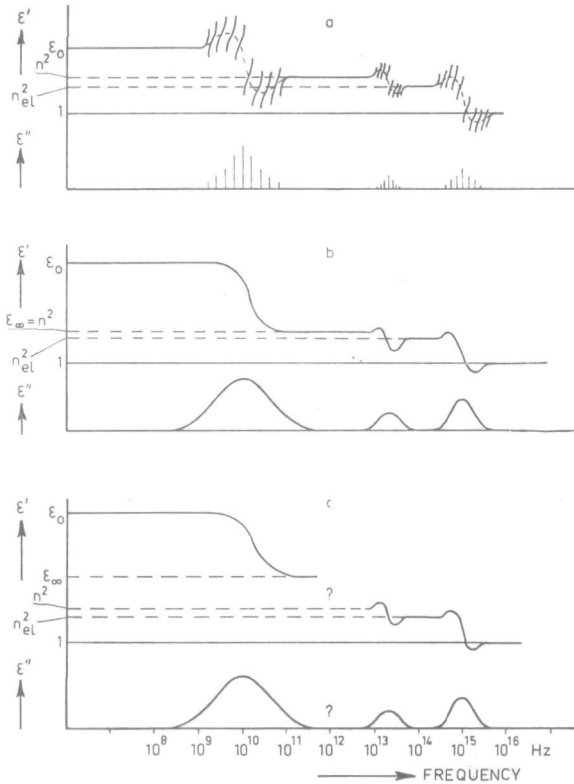


Fig. 1. Qualitative picture of the dispersion and absorption of polar gases and liquids.

a. Gas, *b.* Liquid with $\epsilon_{\infty} = n^2$, *c.* Liquid with $\epsilon_{\infty} \neq n^2$.

The discrete absorption lines observed in polar gases are known to be due molecular rotation, atomic vibration and electronic transitions, located in the frequency scale as sketched roughly in fig. 1*a*. Each spectral line has a width which is dependent on various causes, in particular the vapour pressure, and contributes to ϵ'' . Corresponding to each absorption line a contribution to ϵ' of well-known resonance character arises.

The contribution of the atomic vibrations and electronic trans-

itions to the total polarization in a constant or slowly varying electric field can be determined from measurements of the polarizability α of the molecules in the far infrared where the rotational contribution has decreased to zero. If the gas is sufficiently dilute so that the interaction of the molecules can be neglected, the field acting upon a molecule equals the applied external field E , and the contribution of the molecular rotation amounts to $4\pi N\mu^2 E/3kT$, N being the number of molecules per unit volume, μ the permanent dipole moment and k Boltzmann's constant. All contributions together lead finally to the well-known relation for the dielectric constant ϵ_0 in the static case:

$$\epsilon_0 - 1 = 4\pi N \left(\alpha + \frac{\mu^2}{3kT} \right). \quad (1.1)$$

The strong molecular interaction existing in polar liquids causes radical changes in the situation just discussed. Here a continuous absorption curve describes the behaviour of ϵ'' , while that of ϵ' too no longer shows a discrete structure. This is displayed in fig. 1b. Moreover the interaction between the molecules leads to a considerable difference between the actual field acting on each molecule and the applied external field.

In order to account for the dielectric constant ϵ at low frequencies in terms of α and μ , Debye¹⁾ derived his well-known formula, assuming the field acting on the spherical dipole molecule to be equal to the internal field according to Lorentz-Lorenz. An improvement in the theory was obtained by Onsager²⁾, by taking into account more carefully the interaction between the polarizable molecule and its surroundings. Further refinements were made by Kirkwood³⁾ in his treatment of short-range interaction and by several authors in their extension of Onsager's results for spherical molecules to molecules of ellipsoidal shape. The agreement, however, between the values of μ calculated from liquid data and those determined for the vapour is still disappointing in many cases.

Turning to the analysis of dispersion measurements, it is observed that for dipole molecules of simple shape within the range of the measurements a semi-circular locus in the ϵ' , ϵ'' -plane is obtained, which apparently confirms the theory developed by Debye. The generalization of Onsager's derivation for the case of alter-

nating fields leads to a curve differing markedly from a semi-circle. However, a logical extension to ellipsoidal molecules, as suggested by the author in the first part of this investigation, shows that here too loci approaching more or less a semi-circular form may often be expected.

While the theoretical pictures mentioned seemed to give a consistent account of the dielectric dispersion, our microwave data have provided us with a new topic of investigation in this field. Discrepancies have been revealed, sometimes of substantial magnitude, between the value of the dielectric constant ϵ_∞ , as extrapolated from determinations in the cm-wave region, and the square of the index of refraction n^2 , following from measurements in the far infrared, and representing the effect of atomic vibrations as well as electronic transitions. This is illustrated in fig. 1c. A fair example is provided by nitrobenzene, for which accurate measurements by Cartwright and Errera⁴⁾ have led to $n^2 = 2.43$, whereas our microwave data give $\epsilon_\infty = 4.07$. This suggests a new dispersion region of the dielectric constant between those due to molecular rotation and atomic vibration respectively, which our measurements indicate to be of dipolar origin.

An absorption mechanism which might lead to such a second dipolar dispersion in polar liquids is implicit already in work of Pauling⁵⁾, where the modification of the free rotation of a molecule by a potential is considered. Depending on the strength of this potential two limiting cases can be distinguished. When it is small with respect to kT , the behaviour will lie close to that of a free rotator. When, however, it is large, the molecule will only exert small oscillations around the equilibrium positions determined by the potential. The mathematical treatment by quantum theory shows the possibility of a gradual transition from one extreme to the other, permitting for cases with intermediate strengths of the potential the simultaneous presence of rotation and oscillation dispersion.

The suggestion that an intermolecular field, giving rise to hindered rotation, may play a rôle in the dielectric properties of liquids was first made by Debye⁶⁾ and applied by Debye and Ram⁷⁾ to a discussion of dielectric dispersion. A quantummechanical treatment applicable to the same problem was developed by Gorter and Kronig⁸⁾.

In view of this situation the aim of our present work is twofold. In the first place the nature of the microwave dispersion curve has been established for a number of selected simple polar liquids, satisfying the theoretical assumptions as well as possible. We have chosen for this purpose a series of mono-substituted benzenes where all disturbing effects, such as internal twisting and bending or the presence of intermolecular bonds, can be expected to be relatively unimportant. In the second place we have tried to give a qualitative explanation of the observed dispersion curves in terms of the mechanism just mentioned, for pure liquids as well as for solutions of polar molecules in a non-polar solvent.

§ 2. *Historical outline of experimental work.* Notwithstanding the experimental difficulties a number of short-wavelength data on liquids were obtained before 1940, using mainly free space transmission and reflection techniques.

With damped waves experiments were made some fifty years ago by Lampa⁹⁾ and Drude¹⁰⁾ ¹¹⁾, and some time later by Colley¹²⁾, Eckert¹³⁾, Rubens¹⁴⁾, Rückert¹⁵⁾, Möbius¹⁶⁾, Weichmann¹⁷⁾ ¹⁸⁾ and Tear¹⁹⁾, covering cm- and mm-wavelengths. However during these first pioneering explorations before 1925 were, the results unfortunately turned out to be very unreliable. This was due to the primitive apparatus and detecting devices then available, and to uncertainty as to wavelength and energy distribution. In particular the sharp dispersion regions recorded in data on water and alcohols were later shown to be entirely fictitious.

Meanwhile the development of new types of generators made a gradual advance towards shorter wavelengths possible. Though from 1930 to 1940 most of the authors still used the longer wavelengths between 100 and 1 m (for instance Malsch²⁰⁾, Krause²¹⁾, Schmelzer²²⁾ and Fischer²³⁾), measurements were achieved already in 1926 and 1929 down to 58 cm wavelength by Mizushima²⁴⁾ ²⁵⁾, and in 1930 by Girard and Abadie²⁶⁾ at 40 cm wavelength. During 1933 Seeberger²⁷⁾ reported data on water and alcohols between 24 and 13 cm wavelength. Finally the 10 cm barrier towards the microwaves was overcome in 1937 with the publication of data on the same substances by Esau and Bätz²⁸⁾ and by Kerner²⁹⁾. Here for the first time use was

made of velocity-modulated tubes which in further developments were to conquer the microwave region so successfully. The last pre-war progress was recorded in 1939 in the measurements on water and alcohols at wavelengths between 7 and 1.5 cm published by Keibel³⁰).

The forced development of magnetrons and klystrons and of waveguide measuring-techniques during the last fifteen years has been followed by an avalanche of experimental microwave data on polar liquids. In general these measurements were made at discrete frequencies in the *S*-band (10 cm), *X*-band (3 cm) and *K*-band (1.25 cm), using commercially available oscillators. Not many liquid data are available as yet in the mm-region, where research on energy generation and detection equipment is still going on.

As many data were obtained rather incidentally, however, part of the experimental results is unfortunately either unsuitable for use in fundamental discussions on the dispersion of polar liquids or unreliable due to greater or lesser inaccuracies. Nevertheless, systematic experiments are in progress for instance at Princeton University on organic halides (Smyth c.s.^{31) 32) 33}) and at the Laboratoire de Chimie Physique at Paris on the dispersion of hydrogen-bonding liquids (Magat c.s.³⁴.) The same phenomenon is studied by Hasted c.s. in ionic solutions^{35) 36}), and at the National Physical Laboratory down to 6.2 mm by Saxton and Lane^{37) 38}). Some research on the solvent effect at microwaves has been done by Smyth c.s.³⁹) and by Whiffen and Thompson⁴⁰). The absorption in non-polar liquids has been treated by Whiffen^{41) 42}) and again by Smyth c.s.^{43) 44}). No systematic investigation of our main subject of research, the mono-substituted benzenes, exists as yet.

CHAPTER II

THE ANALYSIS OF DIELECTRIC DISPERSION DATA

§ 3. *The formula of Debye.* As mentioned already in the introduction, the electric polarization P of a substance composed of dipole molecules in an electric field of circular frequency ω can be written as the sum of a contribution due to a partial orientation of the dipoles under the influence of this field and a contribution

from other causes, such as atomic vibrations and electronic transitions. Denoting by \bar{m}_1 the average contribution of non-polar origin to the electric moment of a molecule and by \bar{m}_2 the average dipolar contribution, we have for P and the corresponding complex dielectric constant ϵ at frequency ω

$$4\pi P = (\epsilon - 1)E = 4\pi N(\bar{m}_1 + \bar{m}_2). \quad (2.1)$$

Here N stands for the number of molecules per unit volume.

The best-known formula for ϵ resulting from (2.1) in the case of liquid dielectrics is that of Debye¹:

$$\epsilon - 1 = 4\pi N \left(a + \frac{\mu^2}{3kT} \frac{1}{1 + j\omega\tau} \right) \frac{E_L}{E}, \quad (2.2)$$

where a is the polarizability per molecule, μ the permanent dipole moment, k Boltzmann's constant, T the absolute temperature, τ the molecular relaxation time, and E_L the effective field acting on a molecule.

In deriving (2.2) Debye considered the molecule as a sphere of radius a , suffering viscous resistance when changing its orientation in the medium by which it is surrounded. He was thus led to the relation

$$\tau = \frac{4\pi\eta a^3}{kT} \quad (2.3)$$

between τ and the viscosity η of the medium.

Whatever the mechanism of relaxation, the frequency dependence of the dipolar term given in (2.2) corresponds to the case that a deviation of the distribution of the dipoles over various directions from a uniform distribution would disappear exponentially according to the factor $e^{-t/\tau}$ when left to itself.

E_L was taken by Debye to be equal to the so-called Lorentz-Lorentz field, given by

$$E_L = \frac{\epsilon + 2}{3} E. \quad (2.4)$$

Here the electric action on a given molecule by the surrounding molecules is replaced by their average field.

From (2.2) and (2.4) it follows that

$$\epsilon - 1 = 4\pi N \left(a + \frac{\mu^2}{3kT} \frac{1}{1 + j\omega\tau} \right) \frac{\epsilon + 2}{3}. \quad (2.5)$$

In the limit $\omega = 0$ the quantity ε becomes equal to the static dielectric constant ε_0 , while at sufficiently large values of ω , where the second term in parentheses has practically decreased to zero, ε goes over into the square of the index of refraction n^2 in the far infrared, which involves the contributions from the atomic vibrations and the electronic transitions.

Applying (2.5) to these two limiting cases we can express μ and α in terms of ε_0 and n , obtaining

$$\frac{4\pi N}{9kT} \mu^2 = \frac{3(\varepsilon_0 - n^2)}{(\varepsilon_0 + 2)(n^2 + 2)}, \quad (2.6)$$

$$\frac{4\pi N}{3} \alpha = \frac{n^2 - 1}{n^2 + 2}. \quad (2.7)$$

With (2.6) and (2.7) equation (2.5) may be written as

$$\frac{\varepsilon - n^2}{\varepsilon + 2} = \frac{\varepsilon_0 - n^2}{\varepsilon_0 + 2} \frac{1}{1 + j\omega\tau}, \quad (2.8)$$

which is a linear equation in ε .

Putting the complex quantity ε equal to $\varepsilon' - j\varepsilon''$, we find from (2.8)

$$\varepsilon' = n^2 + \frac{\varepsilon_0 - n^2}{1 + \left(\frac{\varepsilon_0 + 2}{n^2 + 2}\right)^2 \omega^2 \tau^2}, \quad (2.9)$$

$$\varepsilon'' = \frac{\varepsilon_0 - n^2}{1 + \left(\frac{\varepsilon_0 + 2}{n^2 + 2}\right)^2 \omega^2 \tau^2} \frac{\varepsilon_0 + 2}{n^2 + 2} \omega\tau. \quad (2.10)$$

Eliminating the frequency ω from (2.9) and (2.10) it follows that

$$\left(\varepsilon' - \frac{\varepsilon_0 + n^2}{2}\right)^2 + (\varepsilon'')^2 = \left(\frac{\varepsilon_0 - n^2}{2}\right)^2. \quad (2.11)$$

This is the equation of a circle in the complex ε -plane with radius $\frac{1}{2}(\varepsilon_0 - n^2)$ and centre on the real axis at $\varepsilon' = \frac{1}{2}(\varepsilon_0 + n^2)$, as was first shown by Cole and Cole⁴⁵). This representation is hence known as a Cole-Cole-plot. The upper half of this dispersion circle is fully drawn in fig. 2 for $\varepsilon_0 = 12.5$ and $n^2 = 2.5$. As ω

increases from zero to large values, it is described from right to left as indicated by the arrow. From (2.9) and (2.10) it also follows that

$$\omega\tau = \frac{\varepsilon''}{\varepsilon' - n^2} \frac{n^2 + 2}{\varepsilon_0 + 2}, \quad (2.12)$$

permitting τ to be calculated from experimental data.

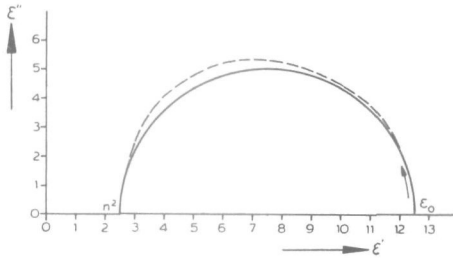


Fig. 2. Dispersion locus for spherical molecules. Full line: according to the Debye equation (2.11). Dashed line: according to the generalized Onsager equation (2.19).

§ 4. *The formula of Onsager.* A more careful study of the interaction between dipole molecules in liquids has been made by Onsager²⁾. He too considers the molecule as a sphere of radius a , surrounded by a medium of dielectric constant ε . a is determined by putting $4\pi a^3/3$ equal to the volume $1/N$ per molecule of the liquid.

According to Onsager (2.2) has to be replaced by

$$\varepsilon - 1 = 4\pi N \left[a + \frac{(2\varepsilon + 1)(n^2 + 2)}{3(2\varepsilon + n^2)} \frac{\mu^2}{3kT} \frac{1}{1 + j\omega\tau} \right] \frac{E_0}{E}, \quad (2.13)$$

where the directing field⁴⁶⁾ E_0 is given by

$$E_0 = \frac{\varepsilon(n^2 + 2)}{2\varepsilon + n^2} E. \quad (2.14)$$

Although in fact (2.13) was given by Onsager only for the case $\omega = 0$, the reduction of the dipolar contribution in (2.13) for increasing frequencies will be effected by the same factor $1/(1 + j\omega\tau)$ as in the model of Debye since the same damping mechanism may be supposed to be acting.

It has been subject of discussion whether this procedure of generalizing the static relation to the case of alternating fields might be open to objections. The model of Onsager, assuming an instantaneous readjustment of the surroundings of the central molecule, might be inadequate at higher frequencies. However, the directing field E_0 has the right magnitude both at very low frequencies and in the far infrared, in the latter case being equal to $E_0 = E_L = \frac{1}{3}(n^2 + 2)E$. Thus there is considerable justification for the use of E_0 also at intermediate frequencies, the time-lag of the readjustment of the surroundings being taken into account by the introduction of the complex dielectric constant in the expression for E_0 . We shall therefore adopt in our following treatment the procedure outlined above, in accordance with analogous approaches of for instance Cole⁴⁷⁾, Fuoss and Kirkwood⁴⁸⁾, Smyth³³⁾, Saxton³⁷⁾ 38) and Bolton⁴⁹⁾, bearing in mind the restrictions possibly adhering to it.

If we now use (2.13) to express μ and a in terms of ϵ_0 and n , we obtain

$$\frac{4\pi N}{9kT} \mu^2 = \frac{(\epsilon_0 - n^2)(2\epsilon_0 + n^2)}{\epsilon_0(n^2 + 2)^2}, \quad (2.15)$$

$$\frac{4\pi N}{3} a = \frac{n^2 - 1}{n^2 + 2}. \quad (2.16)$$

With these expressions for μ and a (2.13) can be written

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon} = \frac{(\epsilon_0 - n^2)(2\epsilon_0 + n^2)}{\epsilon_0} \frac{1}{1 + j\omega\tau}. \quad (2.17)$$

In contrast to (2.8) this is a quadratic equation in ϵ .

Approximate methods for determining the real and imaginary parts of ϵ according to (2.17) have been given by Fischer⁵⁰⁾ in the case where $(\omega\tau)^2 \ll 1$, and by Cole⁴⁷⁾ in the case where $\epsilon_0 \gg n^2$. The limited validity of these approximations is often forgotten. In the experiments to be discussed in Chapter III neither of these conditions is realized. Exact calculations are then required.

The best way, due to Bolton⁴⁹⁾, to achieve these is to separate (2.17) into its real and imaginary parts. Eliminating ω between them and introducing the abbreviations

$$u = \frac{\epsilon'}{n^2}, \quad v = \frac{\epsilon''}{n^2}, \quad \delta = \frac{(\epsilon_0 - n^2)(2\epsilon_0 + n^2)}{\epsilon_0 n^2}, \quad (2.18)$$

it appears that v must satisfy the equation

$$av^4 + bv^2 + c = 0. \quad (2.19)$$

Here

$$\left. \begin{aligned} a &= 4, \\ b &= 8u^2 - (2\delta + 4)u + (\delta + 5), \\ c &= 4u^4 - (2\delta + 4)u^3 + (\delta - 3)u^2 + (\delta + 2)u + 1. \end{aligned} \right\} (2.20)$$

From (2.19) and (2.20) v and hence ε'' can be computed if u , or in other words ε' , is given, leading to the construction of a curve in the complex ε -plane, analogous to the semi-circle in § 3. In fig. 2 this curve is plotted as a dashed line, using again the values $\varepsilon_0 = 12.5$ and $n^2 = 2.5$. It can be shown quite generally, as also appears in fig. 2, that the plot resulting from the relation of Onsager lies everywhere above the semi-circle, the difference being in general much greater than the accuracy of measurement.

From (2.17) one gets

$$\omega\tau = \frac{\varepsilon''[2(\varepsilon'^2 + \varepsilon''^2) + n^4]}{(2\varepsilon' - n^2)(\varepsilon'^2 + \varepsilon''^2) - \varepsilon'n^4}. \quad (2.21)$$

§ 5. *Ellipsoidal molecules.* A generalization of the procedure of Onsager for static fields to the case of molecules of ellipsoidal instead of spherical shape has first been given by Scholte⁵¹). Recently several other relations have been suggested, and it may be profitable to compare these expressions in their practical applicability before choosing one of them as the most suitable basis for extension to the case of alternating fields.

When the permanent dipole moment μ lies along the a_1 -axis of the ellipsoidal molecule, having semi-axes a_1, a_2, a_3 , the static relation replacing (2.13) becomes according to Scholte:

$$\varepsilon_0 - 1 = 4\pi N \left[\frac{1}{3} \sum_i \alpha_i \frac{E_{0i}}{E} + \frac{1}{1 - a_1 f_1} \frac{\mu^2}{3kT} \frac{E_{01}}{E} \right]. \quad (2.22)$$

Here α_i denotes the polarizability of the molecule along the axis a_i . For an ellipsoid of homogeneous and isotropically polarizable material having a refractive index n it is according to Scholte⁵¹) (see his equation (14)) given by

$$\alpha_i = \frac{n^2 - 1}{3[1 + (n^2 - 1)A_i]} a_1 a_2 a_3, \quad (2.23)$$

where

$$A_i = \frac{a_1 a_2 a_3}{2} \int_0^\infty \frac{ds}{(s + a_i^2) \sqrt{(s + a_1^2)(s + a_2^2)(s + a_3^2)}} \quad (2.24)$$

is the depolarization factor along the axis a_i . E_{O_i} is the directing field along the axis a_i , which as shown by Scholtz⁵¹⁾ (see his equation (18)) can be expressed in terms of the electric field E by

$$E_{O_i} = \frac{1}{1 - a_i f_i} \frac{\epsilon_0}{\epsilon_0 - (\epsilon_0 - 1)A_i} E \quad (2.25)$$

with

$$f_i = \frac{3}{a_1 a_2 a_3} \frac{A_i(1 - A_i)(\epsilon_0 - 1)}{\epsilon_0 - (\epsilon_0 - 1)A_i}. \quad (2.26)$$

In analogy with Onsager's theory it is assumed that the volume of the ellipsoid is related to the number of particles per unit volume N by

$$\frac{4\pi}{3} a_1 a_2 a_3 = \frac{1}{N}. \quad (2.27)$$

Eliminating first E_{O_i} from (2.22) by means of (2.25) we find

$$\epsilon_0 - 1 = 4\pi N \left[\frac{1}{3} \sum_i \frac{a_i}{1 - a_i f_i} \frac{\epsilon_0}{\epsilon_0 - (\epsilon_0 - 1)A_i} + \frac{1}{(1 - a_1 f_1)^2} \frac{\epsilon_0}{\epsilon_0 - (\epsilon_0 - 1)A_1} \frac{\mu^2}{3kT} \right] \quad (2.28)$$

Introducing furthermore the a_i from (2.23) and the f_i from (2.26) leads with the aid of (2.27) to

$$\begin{aligned} \epsilon_0 - 1 = & \frac{1}{3} \sum_i \frac{\epsilon_0(n^2 - 1)}{\epsilon_0 - (\epsilon_0 - n^2)A_i} + \\ & + \frac{\epsilon_0[\epsilon_0 - (\epsilon_0 - 1)A_1][1 + (n^2 - 1)A_1]^2}{[\epsilon_0 - (\epsilon_0 - n^2)A_1]^2} \frac{4\pi N}{3kT} \mu^2. \quad (2.29) \end{aligned}$$

The relations (2.28) and (2.29) are suitable for a comparison with expressions proposed by different authors.

For ellipsoids of not too large a deviation from the spherical shape Scholtz⁵²⁾ applied an approximation in the first term on the right-hand side of (2.28) by replacing the directing fields E_{O_i}

in (2.22) by the directing field on a sphere with polarizability

$$\alpha = \frac{1}{3} \sum_i \alpha_i.$$

Since for a sphere $A_i = \frac{1}{3}$, this leads to

$$\epsilon_0 - 1 = 4\pi N \left[\frac{\alpha}{1 - af} \frac{3\epsilon_0}{2\epsilon_0 + 1} + \frac{1}{(1 - \alpha_1 f_1)^2} \frac{\epsilon_0}{\epsilon_0 - (\epsilon_0 - 1)A_1} \frac{\mu^2}{3kT} \right]. \quad (2.30)$$

To give an impression of the error made we have shown in table I the percentage difference of the two terms in question in (2.30) and (2.28) for various ellipsoids of revolution ($a_2 = a_3$) and for two ratios of the quantity ϵ_0/n^2 . It can there be seen that for values of the ratio a_1/a_2 between 0.5 and 3 the errors made are actually not large.

TABLE I

Error made by introduction of approximation of Scholte			
a_1/a_2	A_1	Error in %	
		$\epsilon_0/n^2 = 2.5$	$\epsilon_0/n^2 = 5.0$
3.3	0.1	1.5	3
1.7	0.2	0.5	1
1.12	0.3	0.1	0.1
0.78	0.4	0.15	0.2
0.54	0.5	0.9	2
0.37	0.6	2.4	5.3

In (2.29) the same approximation comes down to replacing A_i by $\frac{1}{3}$ in the first term on the right hand side. Then (2.29) can be rewritten as⁵³⁾

$$\frac{4\pi N}{3kT} \mu^2 = \frac{(\epsilon_0 - n^2)(2\epsilon_0 + 1) [\epsilon_0 - (\epsilon_0 - n^2)A_1]^2}{\epsilon_0(2\epsilon_0 + n^2) [\epsilon_0 - (\epsilon_0 - 1)A_1] [1 + (n^2 - 1)A_1]^2}. \quad (2.31)$$

Another formula has been proposed by Abbott and Bolton⁵⁴⁾. Assuming the polarizability to be isotropic and taking the total induced dipole moment to have the direction of the permanent moment, they get instead of (2.28)

$$\epsilon_0 - 1 = 4\pi N \left[\frac{1}{3} \sum_i \frac{\alpha}{(1 - af_1)} \frac{\epsilon_0}{\epsilon_0 - (\epsilon_0 - 1)A_i} + \frac{1}{(1 - af_1)^2} \frac{\epsilon_0}{\epsilon_0 - (\epsilon_0 - 1)A_1} \frac{\mu^2}{3kT} \right]. \quad (2.32)$$

Buckingham⁵⁵⁾ rightly criticizes these assumptions. By

taking into account a correction suggested by Kirkwood³), he finds instead of (2.29)

$$\varepsilon_0 - 1 = \frac{1}{9} \sum_i \frac{\varepsilon_0(n^2 - 1)}{\varepsilon_0 - (\varepsilon_0 - n^2)A_i} \frac{2\varepsilon_0 + 1}{\varepsilon_0 - (\varepsilon_0 - 1)A_i} + \frac{\varepsilon_0(2\varepsilon_0 + 1) [1 + (n^2 - 1)A_1]^2}{[\varepsilon_0 - (\varepsilon_0 - n^2)A_1]^2} \frac{4\pi N}{9kT} \mu^2. \quad (2.33)$$

In a second paper Buckingham⁵⁶) introduces in addition an approximation analogous to that of Scholte, finding ultimately instead of (2.31)

$$\frac{4\pi N}{3kT} \mu^2 = \frac{3(\varepsilon_0 - n^2) [\varepsilon_0 - (\varepsilon_0 - n^2)A_1]^2}{\varepsilon_0(2\varepsilon_0 + n^2) [1 + (n^2 - 1)A_1]^2}. \quad (2.34)$$

To investigate the practical applicability of the different formulae the author has computed for a number of liquids, listed in table II, the value of μ_i resulting from them. The experimental data used have been taken from the references quoted there. The depolarization factors for CH_3Cl , CH_3Br , CH_3I and CH_3CN have been given by Abbott and Bolton⁵⁴), for CHCl_3 and CHBr_3 by Scholte⁵²), while for the mono-substituted benzenes we have determined them from the graphs of Osborne⁵⁷), using data on the ellipticity given by le Fèvre and le Fèvre⁵⁸). The values for n^2 of the mono-substituted benzenes have been taken equal to n_D^2 (n_D being the index of refraction for the

TABLE II

Comparison of μ -values in Debye-units, computed according to several suggested relations									
Substance	T °K	ε_0	n^2	μ_g	μ				
					(2.15)	(2.32)	(2.33)	(2.34)	(2.31)
CH_3Cl	223	14.88 ⁵⁴)	2.42 ⁵⁴)	1.86 ⁵⁴)	1.54 ⁵⁴)	1.78 ⁵⁴)	1.82 ⁵⁵)	1.95	1.72
CH_3Br	223	12.63 ⁵⁴)	2.79 ⁵⁴)	1.78 ⁵⁴)	1.33 ⁵⁴)	1.55 ⁵⁴)	1.57 ⁵⁵)	1.74	1.50
CH_3I	293	7.00 ⁵⁴)	2.34 ⁵⁴)	1.64 ⁵⁴)	1.31 ⁵⁴)	1.38 ⁵⁴)	1.44 ⁵⁵)	1.59	1.38
CH_3CN	293	37.5 ⁵⁴)	1.84 ⁵⁴)	3.94 ⁵⁴)	3.32 ⁵⁴)	3.53 ⁵⁴)	4.33 ⁵⁵)	4.69	4.04
CHCl_3	292	4.80 ⁵²)	2.10 ⁵²)	1.02 ⁵²)	1.22	1.10	1.08	1.12	1.07 ⁵²)
CHBr_3	299	4.29 ⁵²)	2.54 ⁵²)	1.00 ⁵²)	0.97	0.80	0.82	0.87	0.88 ⁵²)
$\text{C}_6\text{H}_5\text{F}$	294	5.44 ⁶⁰)	2.15 ⁵⁹)	1.61 ⁶¹)	1.43	1.72	1.76	1.80	1.67
$\text{C}_6\text{H}_5\text{Cl}$	295	5.69 ⁵²)	2.33 ⁵⁹)	1.70 ⁶²)	1.45	1.81	1.83	1.87	1.73
$\text{C}_6\text{H}_5\text{Br}$	295	5.43 ⁴⁸)	2.43 ⁵⁹)	1.73 ⁶³) ⁶⁴)	1.37	1.72	1.72	1.75	1.63
$\text{C}_6\text{H}_5\text{I}$	294	4.64 ⁶⁰)	2.63 ⁵⁹)	1.67 ⁶⁴)	1.13	1.61	1.35	1.43	1.34
$\text{C}_6\text{H}_5\text{NO}_2$	293	35.7 ⁶⁵)	2.43 ⁴)	4.21 ⁶²) ⁶³)	4.13	5.56	5.86	5.92	5.34
$\text{C}_6\text{H}_5\text{CN}$	294	25.6 ⁶⁶)	2.34 ⁵⁹)	4.14 ⁶⁷)	3.55	4.87	5.21	5.26	4.69

sodium *D*-lines). The justification of this procedure is given in Chapter III, § 11.

From this table it is observed that the agreement between the computed values for μ_l in the liquid and those for the vapour μ_g is generally rather poor. The applicability of a certain formula seems to depend mainly on the ratio ϵ_0/n^2 involved. No pronounced preference for one of the suggested relations can be arrived at, although at least for the substances under investigation our expression (2.31) leads on the average to the best results. We shall therefore restrict the further discussion where the ellipsoidal shape is involved to the use of (2.31).

No attempts have been made up to now to extend the foregoing static considerations to the case of dispersion for ellipsoidal molecules, although the actual molecular shape will hardly ever be spherical. In order to complete the basis for analysis of our dielectric measurements we generalized the relation (2.31) for ellipsoidal molecules to alternating fields in a way completely analogous to that followed in the case of the formulae of *Debye* and *Onsager*. We have then as the expression determining the dielectric constant ϵ :

$$\frac{(\epsilon - n^2)(2\epsilon + 1)[\epsilon - (\epsilon - n^2)A_1]^2}{\epsilon(2\epsilon + n^2)[\epsilon - (\epsilon - 1)A_1]} = \frac{(\epsilon_0 - n^2)(2\epsilon_0 + 1)[\epsilon_0 - (\epsilon_0 - n^2)A_1]^2}{\epsilon_0(2\epsilon_0 + n^2)[\epsilon_0 - (\epsilon_0 - 1)A_1]} \frac{1}{1 + j\omega\tau} \quad (2.35)$$

As this is a fourth degree equation in ϵ , it can best be solved by numerical methods.

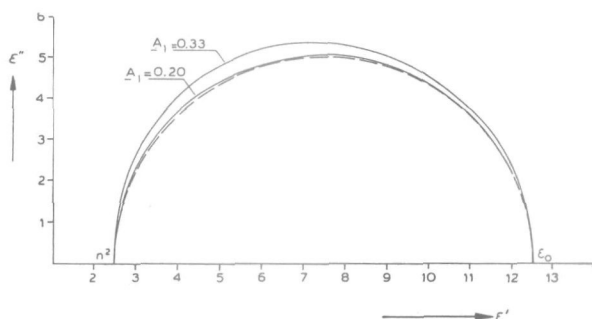


Fig. 3. Dispersion locus for ellipsoidal molecules, for various values of A_1 . The semi-circular locus is inserted as a dashed line.

We have established the locus of (2.35) in the ϵ' , ϵ'' -plane as a function of A_1 , analogous to the representation of (2.11) and (2.19)⁵³). The computations have been made at assumed values of $\omega\tau$ of 0.5, 1.0, 2.0 and 4.0, for a value of $A_1 = 0.20$ and 0.33, representing a case of medium eccentricity with the axis ratio $a_1/a_2 = 1.7$ and that of a sphere respectively. We have collected the results in fig. 3. The locus of a Debye dispersion, i.e. a semi-circle, is indicated there by a dashed line. From this picture the important fact is manifest that the Onsager reaction field combined with suitable eccentricity may lead to a dispersion curve which can hardly be distinguished from a semi-circle.

§ 6. *Models with local fields.* In order to account for the discrepancies between the values of μ found in the gaseous and liquid state from his formula Debye⁶)⁶⁸) suggested a modification of his model by assuming that the dipole molecule, even in the absence of an applied electric field, is subject to a local field E' , arising from the surrounding dipoles. He took this field to be homogeneous over the region occupied by the molecule and of arbitrary direction. In consequence the average dipolar contribution to the electric moment per molecule is reduced from the value $\mu^2 E_L / 3kT$ as given in (1.1) to the value

$$\bar{m}_2 = \frac{\mu^2}{3kT} [1 - L^2(y)] E_L \quad (2.36)$$

with

$$L(y) = \coth y - \frac{1}{y}, \quad y = \frac{\mu E'}{kT}. \quad (2.37)$$

The same model was applied by Debye and Ram⁷) to the case of alternating fields. In particular formulae were derived by them for the limiting cases $y \ll 1$ and $y \gg 1$.

For $y \ll 1$, where the model approaches that of the free rotator, it was shown that the dipolar contribution is additively composed of a series of terms with the frequency dependence

$$\frac{A_n}{1 + j\omega\tau_n}.$$

The relaxation times τ_n characterizing them are given by

$$\tau_n = \frac{8\pi\eta a^3}{\lambda_n kT}, \quad (2.38)$$

the λ_n being eigenvalues of a differential equation which in the limit $y \rightarrow 0$ approach the values $n(n+1)$. In this limit τ_1 goes over in (2.3), while only A_1 remains then different from zero so that the results of § 3 are reobtained.

For $y \gg 1$, where the dipole never deviates much from the position of minimum potential energy in which it is aligned with the direction of the local field, there results as dipolar contribution to the electric moment

$$\bar{m}_2 = \frac{\mu^2 E_L}{\frac{3}{2} \mu E'} \frac{1}{1 + j \omega \tau'} \quad (2.39)$$

with a single relaxation time given by

$$\tau' = \frac{8\pi\eta a^3}{\mu E'}. \quad (2.40)$$

By Gorter and Kronig⁸⁾ ⁶⁹⁾ a general approach on a quantummechanical basis has been developed for computing the polarization due to atoms or molecules, simultaneously subjected to a time-independent field, such as would originate from the surroundings of a given atom or molecule, and an alternating field. In addition to these agencies an intermolecular coupling to the thermal motion is assumed to be present that gives rise to transitions between the various stationary states of the atomic systems. If in particular only two stationary states 1 and 2 with energy difference small compared with kT are involved, for which the electric moment in the direction of the alternating field has diagonal matrix elements M_1 and M_2 , then there results for the polarization

$$P = \pi N \frac{(\overline{M_1 - M_2})^2}{kT} \frac{1}{1 + j \omega \tau} E_L, \quad (2.41)$$

the relaxation time τ being related to the transition probabilities A_{12} and A_{21} between the states 1 and 2 by

$$\tau = \frac{1}{A_{12} + A_{21}}. \quad (2.42)$$

The situation just described would arise for example if a strong local field were not of the type considered by Debye, but had a plane of symmetry, tending to align the dipole in either one of two opposite directions. The dipole, caught in the lowest vibrational state of the

two troughs of potential energy, would have $M_1 = \mu \cos \vartheta$, $M_2 = -\mu \cos \vartheta$, ϑ being the angle between the direction in which the potential energy has the troughs and the direction of the alternating field. The averaging in (2.41) over the factor $\cos^2 \vartheta$ leads then back to the usual formula. As shown by Kronig⁷⁰⁾, the presence of more than two stationary states gives rise to the occurrence of a number of terms of the type given in (2.41) with different relaxation times. Also the influence of non-diagonal matrix-elements of the moment was discussed by him, be it for the analogous magnetic case. The considerations of Kronig and Gorter were later repeated by Fröhlich^{71) 72)} at the hand of a classical model when discussing the behaviour of solid dielectrics.

CHAPTER III. EXPERIMENTAL FACTS

§ 7. *Principles of measuring method.* The common microwave measuring technique consists in determining the input impedance of a liquid-filled waveguide section from the phase and amplitude of the standing-wave pattern in front of a separating mica window (see fig. 4). This, however, leads to inaccuracies increasing with the value of the complex dielectric constant, which are mainly due to the uncertainties in the phase determination.

We have therefore developed a measuring technique involving only measurement of the standing-wave ratio η , i.e. the ratio of the field strengths E_{max} and E_{min} , as a function of the length d of a liquid column which is terminated by a short-circuit piston⁷³⁾. Thus the determination of the phase has been avoided. An analogous

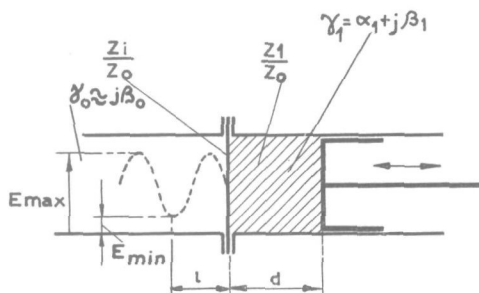


Fig. 4. Schematic drawing of liquid section.

technique described by Crouch⁷⁴) uses an open-circuit terminating-piston and in consequence is dependent upon the frequency. In the measurements rectangular waveguides have been used, operating in the TE_{01} (i.e. H_{01}) mode. The propagation constant γ_0 and the wavelength λ_{0g} in the air-filled guide are related to the vacuum wavelength λ_v and the cut-off wavelength λ_c , equal to twice the width of the guide, according to

$$\gamma_0 \approx j\beta_0 = \frac{2\pi j}{\lambda_{0g}} = \frac{2\pi j}{\lambda_v} \sqrt{1 - (\lambda_v/\lambda_c)^2}. \quad (3.1)$$

The propagation constant of the liquid-filled guide is given by

$$\gamma_1 = \alpha_1 + j\beta_1 = \frac{2\pi j}{\lambda_v} \sqrt{\epsilon - (\lambda_v/\lambda_c)^2}, \quad (3.2)$$

and the ratio of its complex intrinsic impedance Z_1 to that of the air-filled guide Z_0 by

$$\frac{Z_1}{Z_0} = \frac{\gamma_0}{\gamma_1} = \frac{\sqrt{1 - (\lambda_v/\lambda_c)^2}}{\sqrt{\epsilon - (\lambda_v/\lambda_c)^2}}. \quad (3.3)$$

The relative complex input impedance Z_i/Z_0 at the mica window for short-circuit termination follows from common transmission line theory according to

$$\frac{Z_i}{Z_0} = \frac{Z_1}{Z_0} \tanh \gamma_1 d \quad (3.4)$$

and is related to the standing-wave ratio $\eta = E_{max}/E_{min}$ by

$$\eta = \frac{1 + \left| \frac{Z_i/Z_0 - 1}{Z_i/Z_0 + 1} \right|}{1 - \left| \frac{Z_i/Z_0 - 1}{Z_i/Z_0 + 1} \right|}. \quad (3.5)$$

When the standing-wave ratio is determined as a function of the length d of the liquid column, a curve results which exhibits successive maxima and minima, tending towards a final value η_∞ for a length of liquid column which is electrically infinitely long. An example is shown in fig. 5. The mathematical expression for this curve, resulting after introduction of (3.4) in (3.5), is transcen-

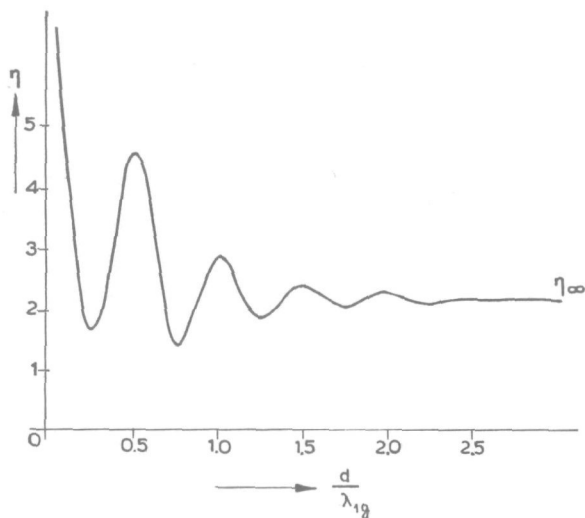


Fig. 5. Dependence of η on liquid column length for a liquid with $\epsilon' = 3.68$ and $\tan \frac{1}{2}\Delta = 0.155$.

dental and leads to equations for the extrema which cannot be evaluated without a large amount of numerical computation. It is, however, not so difficult to deduce the wavelength in the liquid-filled waveguide λ_{1g} as well as the loss-factor of the liquid from this curve.

As Crouch⁷⁴⁾ has shown for an open circuit termination, the distances between the minima equal to a very high degree of accuracy the value $\frac{1}{2}\lambda_{1g}$. This also applies to our short-circuit termination. Introducing furthermore

$$\tan \Delta = \frac{\epsilon''}{\epsilon' - (\lambda_v/\lambda_c)^2} \quad (3.6)$$

as a waveguide loss tangent⁷⁵⁾, analogous to the free space loss tangent $\delta = \epsilon''/\epsilon'$, it is possible to deduce the value of $\tan \frac{1}{2}\Delta = \alpha_1/\beta_1$ from the ratios of the η -values in the successive maxima, using the fact that the values of η change only slowly near the maxima (at values of $d \approx \frac{1}{2}m\lambda_{1g}$). Denoting the standing-wave ratio in the m -th maximum by η_m , we obtain

$$\frac{\eta_m}{\eta_n} = \frac{\tanh(n\pi \tan \frac{1}{2}\Delta)}{\tanh(m\pi \tan \frac{1}{2}\Delta)} (1 - C) \quad (3.7)$$

and

$$\frac{\eta_m}{\eta_\infty} = \frac{1}{\tanh(m\pi \tan \frac{1}{2}\Delta)} (1 - C_\infty) \quad (3.8)$$

respectively for the ratios of the m -th and n -th maximum, and the m -th maximum and η_∞ . The values of the correction-factors are given by

$$C = 4 \sin^2 \frac{1}{4}\Delta [\tanh^2(m\pi \tan \frac{1}{2}\Delta) - \tanh^2(m\pi \tan \frac{1}{2}\Delta)] \cdot \frac{|Z_1/Z_0|^2}{(1 - |Z_{im}/Z_0|^2)(1 - |Z_{in}/Z_0|^2)}, \quad (3.9)$$

$$C_\infty = 4 \sin^2 \frac{1}{4}\Delta [1 - \tanh^2(m\pi \tan \frac{1}{2}\Delta)] \cdot \frac{|Z_1/Z_0|^2}{(1 - |Z_{im}/Z_0|^2)(1 - |Z_{i\infty}/Z_0|^2)}. \quad (3.10)$$

In practically all our measurements C or C_∞ can be neglected with respect to unity, being generally smaller than 1%. This can be shown with the aid of table III, C being expressible in terms of the functions f_1 and f_2 tabulated there by

$$C = f_1(\tan \frac{1}{2}\Delta) \cdot f_2(\varepsilon', \tan \Delta) \cdot [1 - (\lambda_v/\lambda_c)^2].$$

TABLE III

Correction factor in eq. (3.7)		Correction factor in eq. (3.7)				
tan $\frac{1}{2}\Delta$ $f_1(\tan \frac{1}{2}\Delta)$		$f_2(\varepsilon', \tan \Delta)$				
		tan $\Delta \backslash \varepsilon'$	2	5	10	20
$1/16$	0.0004	0.62	0.37	0.107	0.049	0.024
$\frac{1}{8}$	0.0043	0.41	0.89	0.193	0.082	0.038
$\frac{1}{4}$	0.0245	0.24	1.45	0.263	0.099	0.048
$\frac{1}{2}$	0.032	0.00	2.00	0.31	0.123	0.055

Thus we are justified in using in our measurements the relations

$$\frac{\eta_m}{\eta_n} = \frac{\tanh(n\pi \tan \frac{1}{2}\Delta)}{\tanh(m\pi \tan \frac{1}{2}\Delta)} \quad (3.11)$$

and

$$\frac{\eta_m}{\eta_\infty} = \frac{1}{\tanh(m\pi \tan \frac{1}{2}\Delta)}. \quad (3.12)$$

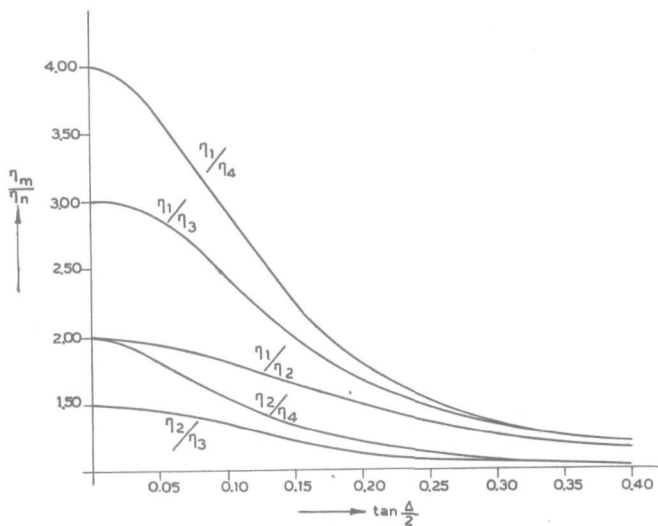


Fig. 6. Graph of the functions $\eta_m/\eta_n = f(\tan \frac{1}{2}\Delta)$.

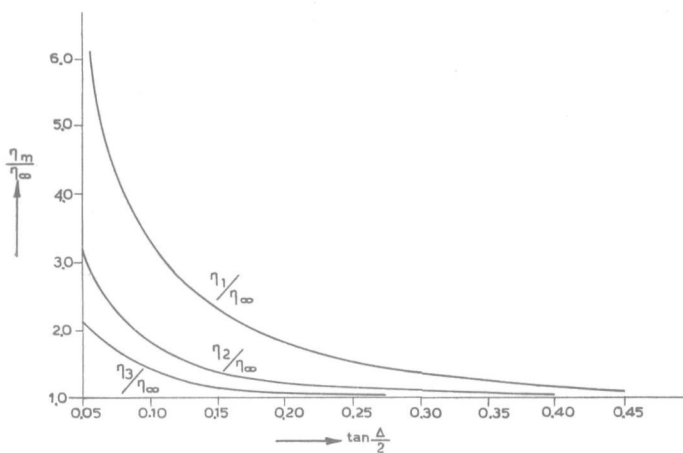


Fig. 7. Graph of the functions $\eta_m/\eta_\infty = f(\tan \frac{1}{2}\Delta)$.

The η_m having been measured, the value for $\tan \frac{1}{2}\Delta$ can be determined from graphs which we have plotted according to (3.11) and (3.12), giving η_m/η_n and η_m/η_∞ as a function of $\tan \frac{1}{2}\Delta$. These graphs are reproduced in figs 6 and 7.

With the data for $\frac{1}{2}\lambda_{1g}$ and $\tan \frac{1}{2}\Delta$ the required values for ϵ' and

ε'' follow in a straightforward manner from (3.2):

$$\varepsilon' = \left(\frac{\lambda_v}{\lambda_c}\right)^2 + \left(\frac{\lambda_v}{\lambda_{1g}}\right)^2 (1 - \tan^2 \frac{1}{2}\Delta), \quad (3.13)$$

$$\varepsilon'' = 2 \left(\frac{\lambda_v}{\lambda_{1g}}\right)^2 \tan \frac{1}{2}\Delta. \quad (3.14)$$

Corrections have to be applied due to the losses of the air-filled waveguide section itself. These losses consist of junction, wall and termination losses. When the standing-wave ratios involved are sufficiently large, the separate contributions simply add according to the relation

$$\frac{1}{\eta_{wg}} = \frac{1}{\eta_j} + \frac{1}{\eta_w} + \frac{1}{\eta_t}. \quad (3.15)$$

By a number of careful experiments it could be shown that wall and termination losses could be neglected with respect to the junction loss, thus reducing the final corrected standing-wave ratio to

$$\frac{1}{\eta} = \frac{1}{\eta_{meas}} - \frac{1}{\eta_j}. \quad (3.16)$$

This tallies with data from other publications⁷⁶). Our computational procedure requires only values of η at column lengths $d = \frac{1}{2}m\lambda_{1g}$. Thus to each value of η in the successive maxima the same correction has to be applied. This correction is determined easily for $m = 0$. Application of this correction leads to an increase in accuracy in the value of $\tan \frac{1}{2}\Delta$, as appears from the probable errors given in table IV.

Care has also to be taken to see if the rectifying characteristic of the crystal is quadratic. In case the rectification takes place

TABLE IV

Decrease of the probable error by introduction of waveguide loss corrections		
Solution	$\tan \frac{1}{2}\Delta$	
	uncorrected	corrected
0.05 C ₆ H ₅ NO ₂ 0.95 C ₆ H ₆	0.116 ± 0.018	0.104 ± 0.001
0.15 C ₆ H ₅ NO ₂ 0.85 C ₆ H ₆	0.212 ± 0.010	0.205 ± 0.002

according to the k -th power of the electric field strength E , we have for the measured deflections D :

$$\frac{D_{max}}{D_{min}} = \left(\frac{E_{max}}{E_{min}} \right)^k = \eta^k. \quad (3.17)$$

Deviations from the normal value $k = 2$ must be corrected for. Actually such corrections had to be applied only at $\lambda_v = 0.8$ cm, where our detecting apparatus had a value of $k = 1.9$.

The final accuracy of ϵ' and ϵ'' resulting from our method is fairly high; in both cases the errors generally do not exceed about 1%. The accuracy of the loss factor is higher than is encountered usually in microwave practice, due to the fact that the value of $\tan \frac{1}{2}\Delta$, obtained as an average from a number of ratios η_m/η_n , has a much higher accuracy than the value taken from a single determination. Although the degree of accuracy lies close to the possible limits for microwave detection apparatus, it cannot compete with the accuracy obtained at lower frequencies, where the value of the dielectric constant can be determined with an accuracy far within 1%.

§ 8. *Experimental arrangement.* The general set-up for our microwave measurements consisted of the elements shown in the block diagram reproduced in fig. 8. Some details about these elements and their actual operation are given in the following sections. A view of the apparatus for 1.25 cm wavelength is shown in fig. 9.

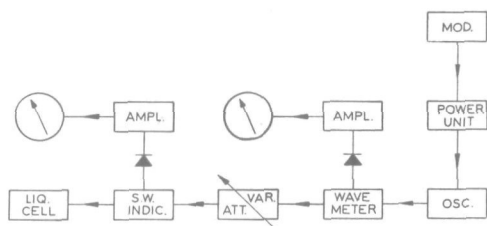


Fig. 8. Block diagram of measuring-apparatus.

8.1. The generators used to provide the microwave energy at the wavelengths of operation consisted of the following

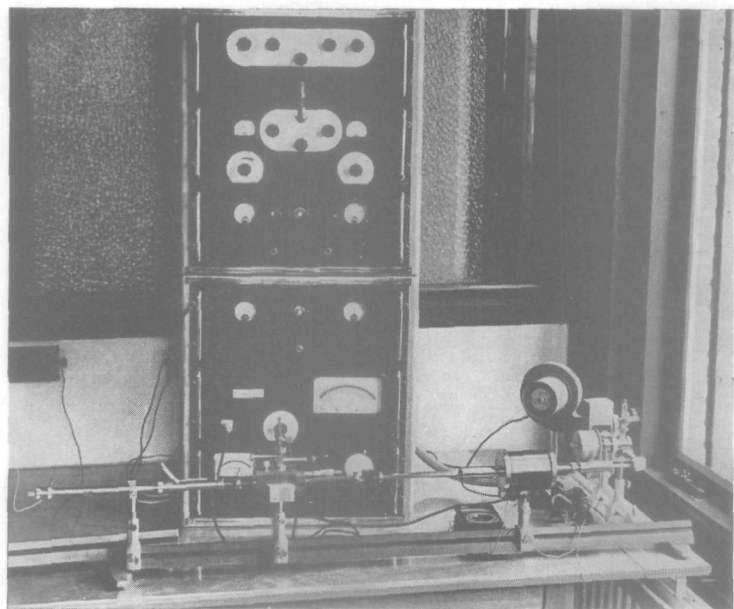


Fig. 9. View of the apparatus and electronic equipment for 1.25 cm wavelength.

types of klystrons:

wavelength cm	frequency MHz	type	manufacturer
3.99	7.520	2K44	Raytheon
3.55	8.451	2K39	Raytheon
3.20	9.375	CV 129	?
1.25	24.000	2K33	Raytheon
0.80	37.500	VX 357	R.R.E.

In all our measurements square-wave reflector modulation at a rate of 1000 Hz was applied to the generator.

8.2. The wavemeters for the discrete frequencies, of the resonant-cavity type (Q -factor $> 10^4$), were used for the indication of the frequency as well as to check the stability of the frequency. It can be shown that maximum sensitivity with respect to frequency variations exists at deflections of about $\frac{3}{4}$ times maximum deflection in resonance condition. The frequency of operation can thus be

maintained constant within $1 : 10^4$ à 10^5 , excluding frequency instability as a source of errors.

Apart from the wavemeter for 0.8 cm wavelength, which was provided by Hilger and Watts (London), all the wavemeters which were used were constructed and machined at the precision workshop of our laboratory, after the design of Ir M. L. Toppinga. Details may be found for instance in ⁷⁷⁾.

8.3. Variable attenuators are generally used to decouple the measuring-section from the oscillator to prevent pulling of the oscillator by changes in the terminating impedance. In all the arrangements except the 1.25 cm apparatus the common type of attenuator, using strips of absorbing material, has been used. In practice an attenuation of about 16 db resulted in sufficient decoupling.

In the 1.25 cm apparatus the decoupling was achieved by making use of the gyrator, a new electromagnetic circuit element, described at length by van Trier in his thesis ⁷⁸⁾. The advantage of this new type of decoupler is that almost no energy is lost in it, nearly all the energy produced by the oscillator being available in the measuring-section.

8.4. Standing-wave detector. The detection at all wavelengths of operation was obtained using a precision standing-wave detector, consisting of a slide-mounted tunable probe which could be moved through a narrow slot in the waveguide to sample the standing-wave pattern. The energy detected after rectification by a suitable crystal was amplified by a selective amplifier and applied to a tube voltmeter.

Precautions have been taken to avoid errors in the standing-wave detection due to deviations from a quadratic crystal rectifying-characteristic, due to non-linearity of the amplifiers and due to field disturbance by excessive probe penetration.

The following specification applies to the detectors:

wavelength cm	type, design	crystal-type
3.99	B.T.H.type V	1N21
3.55		
3.20		
1.25	Phys. Lab. NDRC	1N26
0.80	Hilger & Watts	VX 3136 G.E.C.

W 870

8.5. Liquid section. At each wavelength of operation a liquid cell is used of the same general design. While the waveguide is terminated at one end by a thin mica-window, a non-contacting movable aluminium piston constitutes the required short-circuit at the other. The following window thicknesses have been used:

wavelength	thickness
cm	cm
3-4	0.0025
1.25	0.0015
0.8	0.0015

The piston is mounted in a liquid-tight waveguide section, to make the movement of the short-circuit by external drive possible. The displacement of the piston could be determined with an accuracy of about 0.0005 cm when necessary. The liquid is allowed to pass along the piston by some small savings in it. Details of this mounting are shown in fig. 10. With this design a reproduction of observed meter readings at a certain piston setting was obtained within $\frac{1}{2}\%$.

For the wavelengths of operation of 3.99, 3.55 and 3.20 cm the same liquid cell could be used, due to the frequency insensitivity of our measuring-method. For the measurements on tertiary butyl chloride and methyl chloroform a copper short-circuiting piston has

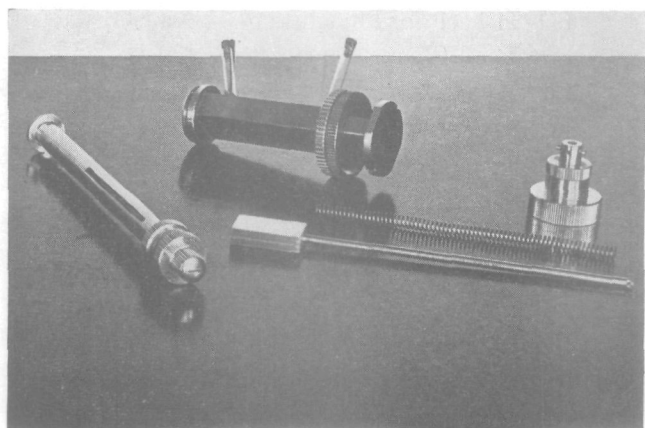


Fig. 10. Details of liquid section.

been used to avoid a chemical reaction between the liquid under investigation and the movable piston. All the liquid-sections were designed and constructed in the precision-workshop of our laboratory.

As our measuring cells are not yet equipped with provisions for temperature variation, all our measurements have been made at room temperature. Precautions have been taken to keep this temperature constant within $\pm 0.5^\circ\text{C}$ during the measurements. The actual temperature has been given together with the other data.

§ 9. *The substances investigated.* The substances chosen for investigation should permit structural interpretation of the measured data. Therefore dipole molecules of simple shape were chosen with fairly rigid binding between the component parts and having no intermolecular bonds.

The following specification applies to the series of substances which has been investigated:

Substance	Origin	Purification	Dried with	Boiling-point $^\circ\text{C}$
$(\text{CH}_3)\text{CCl}_3$	Kodak	Lab. Phys. Chem.	Na_2SO_4	73.8
$(\text{CH}_3)_3\text{CCl}$	B.D.H.	Lab. Phys. Chem.	Na_2SO_4	50.8
$\text{C}_6\text{H}_5\text{F}$	B.D.H.	Lab. Phys. Chem.	CaCl_2	84.5
$\text{C}_6\text{H}_5\text{Cl}$	B.D.H.	Lab. Phys. Chem.	CaCl_2	131
$\text{C}_6\text{H}_5\text{Br}$	B.D.H.	Chem. Dept.	CaCl_2	156
$\text{C}_6\text{H}_5\text{I}$	B.D.H.	Lab. Phys. Chem.	Na_2SO_4	188
$\text{C}_6\text{H}_5\text{NO}_2$	Merck	Chem. Dept.	CaCl_2	210.5
$\text{C}_6\text{H}_5\text{CN}$	Fluka	Chem. Dept.	CaCl_2	191
C_6H_6	Merck	Lab. Phys. Chem.	CaCl_2	78.1
H_2O	Waalsdorp dunes	Chem. Dept.		100
CH_3OH	Merck	Chem. Dept.		64.5
$\text{C}_2\text{H}_5\text{OH}$	B.D.H.	Chem. Dept.		78.3

Lab. Phys. Chem. = Laboratory for Physical Chemistry, University of Leyden.

Chem. Dept. = Chemical Department of the Physical Laboratory N.D.R.C., Waalsdorp.

Grateful acknowledgement is made for this aid in purification.

A number of measurements on the almost spherical molecules $(\text{CH}_3)\text{CCl}_3$ and $(\text{CH}_3)_3\text{CCl}$ have been included to test the differences between diverse dispersion relations (cf. Chapt. II, § 4). We have further restricted the discussion mainly to a number of mono-substituted benzenes. These molecules might be approximated in shape by an ellipsoidal model with a dipole-moment which is bound rigidly to the longest axis of the ellipsoid. Finally some data on simple associating liquids, H_2O , CH_3OH and $\text{C}_2\text{H}_5\text{OH}$, are given.

§ 10. Experimental results.

10.1. Pure liquids. Data for the static dielectric constant of several substances have been supplied by the Laboratory for Physical Chemistry of the University of Leyden, as well as by Ir G. P. de L o o r (Physical Laboratory N.D.R.C.) from precision measurements at frequencies of about 1 MHz. The permission to quote these unpublished data is gratefully acknowledged here.

10.1.1. Spherical molecules. Care has been taken in the measurements to avoid errors due to decomposition of the substances used, especially in the case of $(\text{CH}_3)_3\text{CCl}$. The measurements

TABLE V

Microwave dispersion of methyl chloroform		
CH_3CCl_3 ; $T = 293^\circ\text{K}$ $\epsilon_0 = 7.20$ ⁷⁹⁾ ; $n^2 = 2.07$ ⁵⁹⁾		
own meas.		
λ , cm	ϵ'	ϵ''
3.20	6.64	1.59
1.25	5.20	2.42
0.802	4.02	2.44

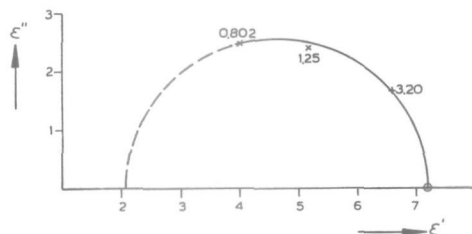


Fig. 11. Microwave dispersion of methyl chloroform, $(\text{CH}_3)\text{CCl}_3$, at $T = 293^\circ\text{K}$.
 × own measuring data; ○ ref. ⁷⁹⁾.

have been carried out immediately after an intensive drying and distillation process at the Laboratory for Physical Chemistry, Leyden. The experimental data are given in tables V and VI and in the corresponding figs 11 and 12.

TABLE VI

Microwave dispersion of tertiary butyl chloride						
$(\text{CH}_3)_3\text{CCl}$; $T = 293^\circ\text{K}$; $\epsilon_0 = 9.90^{79}$; $n^2 = 1.92^{59}$						
own meas.			literature			
λ_v cm	ϵ'	ϵ''	λ_v cm	ϵ'	ϵ''	ref.
3.20	9.34	2.31	10.10	10.06	0.70	44)
1.25	7.50	3.64	3.22	9.48	2.00	44)
0.802	6.07	3.97	1.25	7.17	4.12	44)

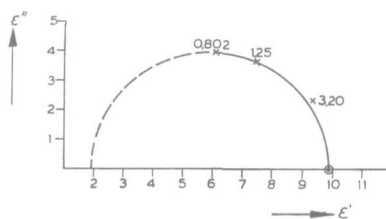


Fig. 12. Microwave dispersion of tertiary butyl chloride, $(\text{CH}_3)_3\text{CCl}$, at $T = 293^\circ\text{K}$.
 × own measuring data; ○ ref. ⁷⁹).

10.1.2. Mono-substituted benzenes. The experiments have been carried out on a series of six mono-substituted benzenes: $\text{C}_6\text{H}_5\text{F}$, $\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_6\text{H}_5\text{Br}$, $\text{C}_6\text{H}_5\text{I}$, $\text{C}_6\text{H}_5\text{NO}_2$ and $\text{C}_6\text{H}_5\text{CN}$. The data obtained are given in tables VII to XII and are plotted in the corresponding figs 13 to 18. Some data obtained by other investigators have been included in the tables and the graphs.

TABLE VII

Microwave dispersion of fluorobenzene		
$\text{C}_6\text{H}_5\text{F}$; $T = 294^\circ\text{K}$; $\epsilon_0 = 5.44^{60}$; $n^2 = 2.15^{59}$		
own meas.		
λ_v cm	ϵ'	ϵ''
3.99	5.22	0.71
3.20	5.09	0.95
1.25	4.15	1.54
0.802	3.43	1.48

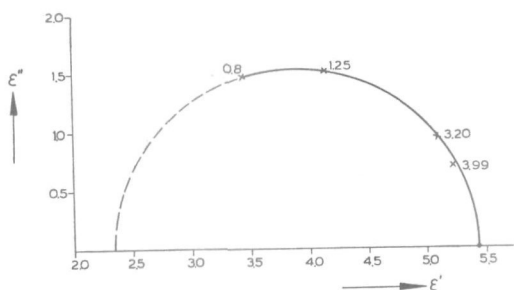


Fig. 13. Microwave dispersion of fluorobenzene, C_6H_5F , at $T = 294^\circ K$.
 × own measuring data; . ref. ⁶⁰).

TABLE VIII

Microwave dispersion of chlorobenzene C_6H_5Cl ; $T = 295^\circ K$; $\epsilon_0 = 5.69$ ⁵²); $n^2 = 2.33$ ⁵⁹)						
own meas.			literature			
λ_v cm	ϵ'	ϵ''	λ_v cm	ϵ'	ϵ''	ref.
3.99	4.93	1.32	10.0	5.54	0.67	³³)
3.55	4.79	1.42	3.22	4.62	1.43	³¹)
3.20	4.59	1.49	1.27	3.43	1.34	³²)
1.25	3.37	1.39				
0.802	2.96	1.06				

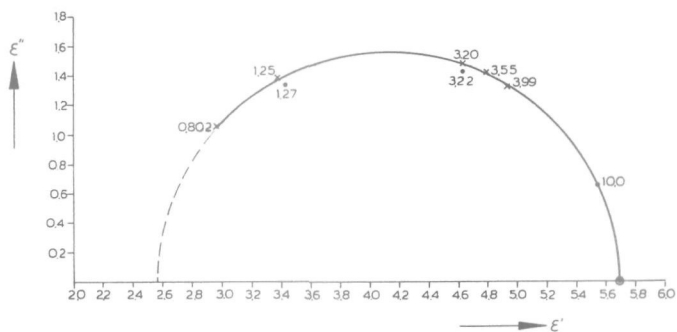


Fig. 14. Microwave dispersion of chlorobenzene, C_6H_5Cl , at $T = 295^\circ K$.
 × own measuring data.
 . ref. ³¹), ³²), ³³); ○ ref. ⁵²).

TABLE IX

Microwave dispersion of bromobenzene C_6H_5Br ; $T = 295^\circ K$; $\epsilon_0 = 5.43^{43)}$; $n^2 = 2.43^{59)}$						
own meas.			literature			
λ_v cm	ϵ'	ϵ''	λ_v cm	ϵ'	ϵ''	ref.
3.99	4.32	1.36	10.0	5.09 ⁵	0.80	33)
3.55	4.16	1.42	3.22	3.88	1.34	31)
3.20	4.06	1.40				
1.25	3.00	0.98				
0.802	2.82	0.71				

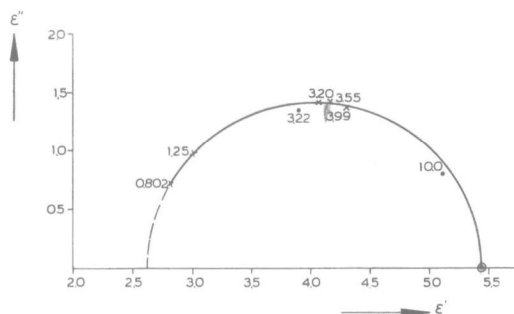


Fig. 15. Microwave dispersion of bromobenzene, C_6H_5Br , at $T = 295^\circ K$.
 \times own measuring data; \cdot ref. 31), 33); \circ ref. 43).

TABLE X

Microwave dispersion of iodobenzene C_6H_5I ; $T = 294^\circ K$; $\epsilon_0 = 4.64^{60)}$; $n^2 = 2.63^{59)}$		
own meas.		
λ_v cm	ϵ'	ϵ''
3.99	3.44	0.92
3.20	3.31	0.875
1.25	2.88	0.47
0.802	2.80	0.36

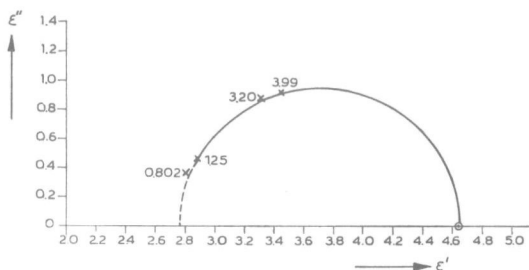


Fig. 16. Microwave dispersion of iodobenzene, C_6H_5I , at $T = 294^\circ K$.
 \times own measuring data; \circ ref. 60).

TABLE XI

Microwave dispersion of nitrobenzene $C_6H_5NO_2$; $T = 293^{\circ}K$; $\epsilon_0 = 35.7^{65}$; $n_D^2 = 2.40^{59}$; $n_{ir}^2 = 2.43^4$)						
own meas.			literature			
λ_w , cm	ϵ'	ϵ''	λ_w , cm	ϵ'	ϵ''	ref.
3.99	10.15	12.36	10.0	22.8	15.9	⁸⁰⁾
3.55	8.53	10.91				
3.20	7.45	9.51				
1.25	4.73 ⁵	4.58				
0.802	4.05	3.26				

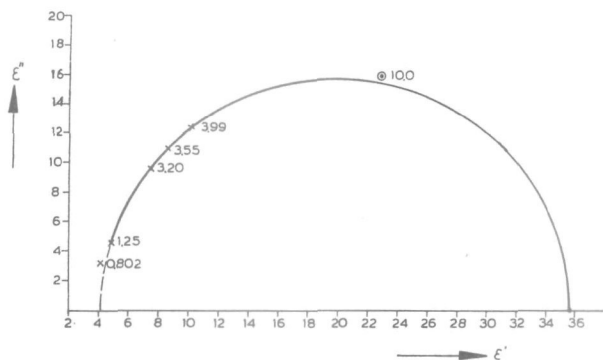


Fig. 17. Microwave dispersion of nitrobenzene, $C_6H_5NO_2$, at $T = 293^{\circ}K$.
 × own measuring data; . ref. ⁶⁵⁾; ○ ref. ⁸⁰⁾.

TABLE XII

Microwave dispersion of benzotrile C_6H_5CN ; $T = 294^{\circ}K$; $\epsilon_0 = 25.6^{66}$; $n^2 = 2.34^{59}$)		
own meas.		
λ_w , cm	ϵ'	ϵ''
3.99	9.39	9.65
3.20	7.17	7.98
1.25	4.64	4.29
0.802	3.99	3.07

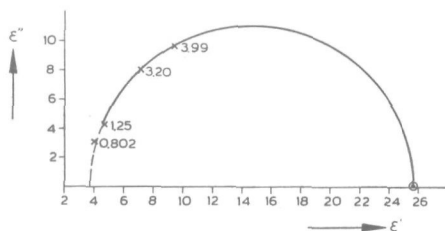


Fig. 18. Microwave dispersion of benzonitrile, C_6H_5CN , at $T = 294^\circ K$.
 × own measuring data; ○ ref. ⁶⁶⁾.

10.1.3. Associating liquids. Some measurements have been made on water and on pure methyl and ethyl alcohol, the latter as part of the investigation on the dispersion of solutions of polar molecules, to be recorded in the following section. The results on the pure liquids are given in tables XIII to XV and are plotted in the figs 19 to 22.

TABLE XIII

Microwave dispersion of water						
H_2O ; $T = 293^\circ K$; $\epsilon_0 = 80.0$ ³⁷⁾ ; $n_{tr}^2 = 2.82$ ⁴⁾						
own meas.			literature			
λ_v cm	ϵ'	ϵ''	λ_v cm	ϵ'	ϵ''	ref.
3.99	70.1	24.6	10.00	77.7	13.0	⁸¹⁾
3.55	67.7	27.1	6.48	74.0	18.8	⁸¹⁾
3.20	61.8	32.0	3.19 ⁵⁾	61.5	31.6	⁸¹⁾
1.25	31.5	35.5	1.58	43.9	37.1	³⁷⁾
0.802	21.34	29.6	1.26	31.0	35.0	⁸¹⁾

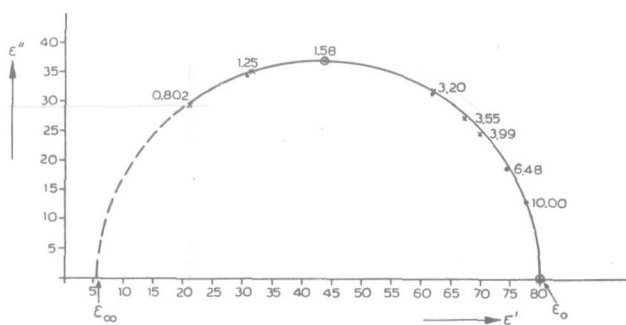


Fig. 19. Microwave dispersion of water, at $T = 293^\circ K$.
 × own measuring data.
 . ref. ⁸¹⁾; ○ ref. ³⁷⁾.

TABLE XIV

Microwave dispersion of methyl alcohol CH_3OH ; $T = 293^\circ\text{K}$; $\epsilon_0 = 32.2^{82)}$; $n^2 = 1.99^4)$						
own meas.			literature			
λ_{ν} cm	ϵ'	ϵ''	λ_{ν} cm	ϵ'	ϵ''	ref.
3.99	9.72	10.20	3.21	8.36	8.20	87)
3.51	8.68	9.14	1.24	6.88	4.76	88)
3.20	7.78	7.69	0.62	6.04	3.15	89)
1.25	5.98	4.48				
0.802	5.68	3.23				
CH_3OH ; $T = 298^\circ\text{K}$; $\epsilon_0 = 31.0^{83)}$						
own meas.			literature			
λ_{ν} cm	ϵ'	ϵ''	λ_{ν} cm	ϵ'	ϵ''	ref.
3.20	8.18	8.00	3.21	8.70	8.53	87)
1.25	6.04	4.13	1.24	6.90	4.94	88)
			0.62	6.04	3.22	89)

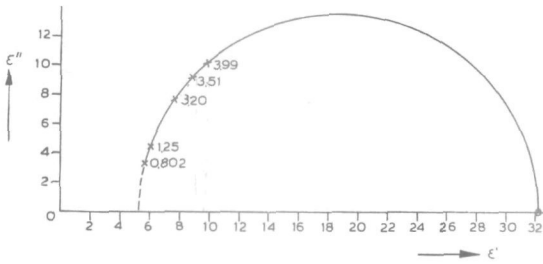


Fig. 20. Microwave dispersion of methyl alcohol, CH_3OH , at $T = 293^\circ\text{K}$.
 × own measuring data; ○ ref. 82).

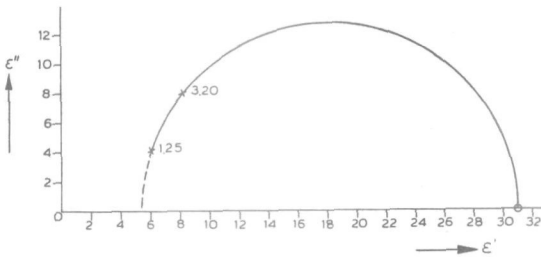


Fig. 21. Microwave dispersion of methyl alcohol, CH_3OH , at $T = 298^\circ\text{K}$.
 × own measuring data; ○ ref. 83).

TABLE XV

Microwave dispersion of ethyl alcohol C_2H_5OH ; $T = 294^\circ K$; $\epsilon_0 = 24.1^{82)}$; $n^2 = 2.16^4)$						
own meas.			literature			
λ_v , cm	ϵ'	ϵ''	λ_v , cm	ϵ'	ϵ''	ref.
3.99	4.84	2.91	3.21	4.54	2.28	³⁷⁾
3.55	4.75	2.77	1.24	4.23	1.56	³⁸⁾
3.20	4.59	2.50	0.62	3.47	1.11	³⁸⁾
1.25	4.13	1.42				
0.802	3.89	1.30				

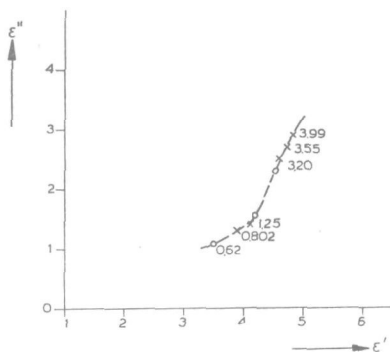


Fig. 22. Microwave dispersion of ethyl alcohol, C_2H_5OH , at $T = 294^\circ K$.
 × own measuring data; ○ ref. ³⁷⁾ ³⁸⁾.

10.2 Measurements on solutions. In order to provide some information on the behaviour of the relaxation time as a function of concentration a series of measurements at several wavelengths was made on solutions of nitrobenzene in benzene as well as on solutions of the associating liquids methyl and ethyl alcohol in benzene.

The dielectric constant of the solvent benzene at microwaves has been determined using the normal impedance measuring method according to von Hippel⁸⁴⁾, leading to $\epsilon' = 2.28 \pm 0.01$ at a wavelength of 3.20 cm. The dielectric loss appeared to be too small to be measured with sufficient accuracy.

The results on these solutions are assembled in the tables XVI, XVII and XVIII. Some examples of ϵ' , ϵ'' -diagrams for a given concentration as obtained by interpolation from these tables, are

shown in figs 23 to 25. A further discussion of these data is given in the following chapter.

TABLE XVI

Microwave dispersion of solutions of $C_6H_5NO_2$ in C_6H_6 ; $T = 293^\circ K$; own meas.								
$\lambda_v = 1.25$ cm.			$\lambda_v = 3.20$ cm.			$\lambda_v = 3.99$ cm.		
conc. v_1 %	ϵ'	ϵ''	conc. v_1 %	ϵ'	ϵ''	conc. v_1 %	ϵ'	ϵ''
0	2.28	—	0	2.28	—	0	2.28	—
15.0	2.97	1.01	4.98	2.87	0.50	10.0	3.72	0.912
30.0	3.42 ^s	1.88	14.97	3.97	1.49	19.8	4.82	1.88
44.9	3.79	2.64	24.9	4.87	2.58	33.1	6.40	3.51
59.6	4.12	3.42 ^s	34.6	5.59	3.71	49.7	7.78	5.64
79.8	4.48	4.13	49.6	6.50	5.40	65.0	8.69	7.70
100	4.73 ^s	4.58	65.0	7.07	7.18	76.8	9.23	9.30
			80.0	7.40	8.73	100	10.15	12.36
			100	7.45	9.51			

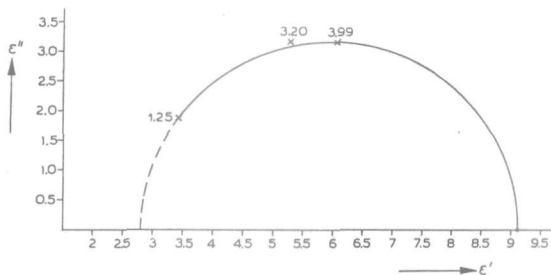


Fig. 23. Microwave dispersion of solution of 30% $C_6H_5NO_2$ in C_6H_6 , following from interpolated experimental data. $T = 293^\circ K$.

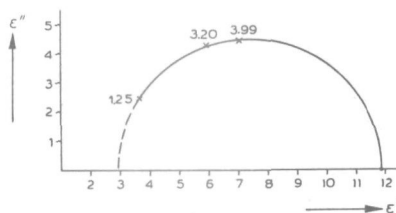


Fig. 24. Microwave dispersion of solution of 40% $C_6H_5NO_2$ in C_6H_6 , following from interpolated experimental data. $T = 293^\circ K$.

TABLE XVII

Microwave dispersion of solutions of CH ₃ OH in C ₆ H ₆ ; T = 298°K; own meas.				
conc. v ₁ %	$\lambda_U = 1.25$ cm		$\lambda_U = 3.20$ cm	
	ϵ'	ϵ''	ϵ'	ϵ''
10	2.73	0.266	2.90	0.402
25	3.20	0.69	3.51	1.16
40	3.63	1.18	4.20	2.16
55	4.17	1.76	4.96	3.39
70	4.69	2.42	5.74	4.84
85	5.25	3.16	7.06	6.42
100	6.04	4.13	8.18	8.00

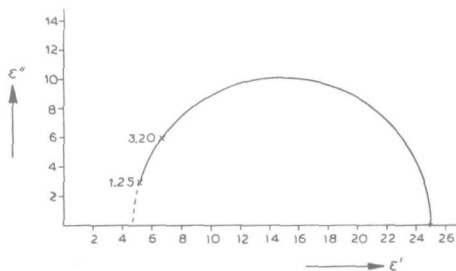
Fig. 25. Microwave dispersion of solution of 80% CH₃OH in C₆H₆, following from interpolated experimental data. T = 298°K.

TABLE XVIII

Microwave dispersion of solutions of C ₂ H ₅ OH in C ₆ H ₆ ; T = 294°K; own meas.						
conc. v ₁ %	$\lambda_U = 1.25$ cm		$\lambda_U = 3.20$ cm		$\lambda_U = 3.99$ cm	
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
0	2.28	—	2.28	—	2.28	—
10	2.54	0.16?	2.67	0.25?	2.77	0.22
20	2.77	0.31 ⁵ ?	2.99	0.50	3.09	0.51
30	2.98	0.47	3.25	0.75	3.34	0.83
40	3.16	0.62	3.46	1.00	3.55 ⁵	1.14
50	3.34	0.77	3.66	1.25	3.75	1.45
60	3.51	0.91	3.84	1.50	3.96	1.76
70	3.68	1.05	4.02 ⁵	1.75	4.16	2.07
80	3.83	1.19 ⁵	4.20	2.00	4.38	2.39
90	3.97	1.33	4.37	2.25	4.61	2.69
100	4.12	1.42	4.59	2.50	4.84	2.91

§ 11. *Determination of the atomic polarization.* The proper way of determining the value of the refractive index n in the formulae of Chapter II would be the measurement of this quantity at wavelengths longer than those where absorptions due to atomic vibrations occur and yet short enough so that the dipolar effects do not contribute to the total polarization any more. Such wavelengths would lie between 100 and 500 μm , as the atomic vibrations most frequently occur between wavelengths of 3 and 30 μm . As the former wavelength-region, however, is still almost inaccessible, other methods for determining n have to be found.

One procedure is to plot the static dielectric constant ϵ_0 for the vapour as function of the temperature and to determine the value which it approaches as T goes to infinity. This limit can be identified with n^2 , the dipolar contribution to ϵ_0 decreasing as $1/T$. Such an extrapolation, of course, is not very accurate.

One can also make use of the empirical knowledge that in general n , in passing from the lower visible part of the spectrum to the further infrared in those substances in which measurements are available, changes only very slightly. We have checked this in particular for a number of substances which are quite similar in chemical structure to the mono-substituted benzenes. Experimental values n_{ir} in the extreme infrared, at wavelengths between 52 and 152 μm , are here available from a publication of Cartwright and Errera⁴⁾. The values for the index of refraction at the sodium D -lines n_D have been taken from Timmermans' handbook⁵⁹⁾. A comparison is given in table XIX. It is seen that the values n_{ir} and n_D do not differ noticeably.

TABLE XIX

Comparison of the values for n_D and n_{ir} for several substances		
Substance	n_D	n_{ir}
C_6H_6	1.501	1.49
$\text{C}_6\text{H}_5\text{CH}_3$	1.497	1.49
$\text{C}_6\text{H}_5\text{NO}_2$	1.552	1.56
$\text{C}_5\text{H}_5\text{N}$	1.510	1.52
$\alpha\text{-CH}_3\text{-C}_6\text{H}_4\text{N}$	1.501	1.51
CCl_4	1.460	1.47

We shall hence proceed in the present investigation by assuming that for the mono-substituted benzenes the quantity n in our formulae can be replaced with an accuracy of about 1% by the value n_D for these substances.

CHAPTER IV

INTERPRETATION OF THE EXPERIMENTAL DATA

§ 12. *General discussion of the experimental results.*

12.1. *Spherical molecules.* In the measurements on molecules of approximately spherical shape, viz. $(\text{CH}_3)_3\text{CCl}_3$ and $(\text{CH}_3)_3\text{CCl}$, the experimental data can quite well be represented by semi-circles in the ϵ' , ϵ'' -plane through ϵ_0 and n^2 (see figs 11 and 12). However, as the available measuring frequencies cover only half of the dispersion region, no definite conclusions can be drawn as yet, as to which of the two relations (2.11) and (2.19), corresponding respectively to the treatment of Debye and Onsager, gives the better fit.

The curve representing our data for $(\text{CH}_3)_3\text{CCl}$ deviates from the curve through the points of Smyth c.s.⁴⁴), which are located above the semi-circle through ϵ_0 and n^2 . As Prof. Smyth kindly has informed us, these deviations can be ascribed to decomposition of the substance under investigation.

The deviation of our measuring point at $\lambda_v = 3.20$ cm from the semi-circular locus may perhaps too be attributed to the onset of decomposition.

12.2. *Mono-substituted benzenes.* The data obtained on the series of mono-substituted benzenes can be represented very well by semi-circles in the ϵ' , ϵ'' -plane (see figs 13 to 18). Here a large part of the dispersion region is covered by the points determined. It then appears that the intersections ϵ_∞ of these semi-circles with the ϵ' -axis at the high frequency end, which can be extrapolated with an error of about 1%, differ markedly from the values n^2 obtained from infrared and optical data according to § 11. The relevant figures are collected in the upper part of table XX, where also the values of $\delta = \epsilon_\infty - n^2$ and of the square of the dipole moment in the gaseous state μ_p^2

TABLE XX

Difference δ between ϵ_∞ and n^2 for several substances. Values of μ_g are given in D e b i j e-units						
Substance	$T^\circ\text{K}$	n^2	ϵ_∞	δ	μ_g^2	δ/μ_g^2
$\text{C}_6\text{H}_5\text{F}$	294	2.15	2.33	0.18	2.6	0.07
$\text{C}_6\text{H}_5\text{Cl}$	295	2.33	2.56	0.23	2.9	0.08
$\text{C}_6\text{H}_5\text{Br}$	295	2.43	2.62	0.19	3.0	0.06
$\text{C}_6\text{H}_5\text{I}$	294	2.63	2.76	0.13	2.8	0.05
$\text{C}_6\text{H}_5\text{NO}_2$	293	2.43	4.07	1.64	17.6	0.09
$\text{C}_6\text{H}_5\text{CN}$	294	2.34	3.85	1.51	17.1	0.09
HOH	293	2.8	5.5	2.7	3.3	0.82
CH_3OH	293	2.0	5.3	3.3	2.9	1.14
$\text{C}_2\text{H}_5\text{OH}$	294	2.2	4.0?	1.8	2.9	0.62

are given. There is a striking parallelism between δ and μ_g^2 , the ratio δ/μ_g^2 , as set out in the last column, being roughly the same for all the substances in question notwithstanding the wide range of μ -values involved. The difference δ can only mean that between the cm-waves and the ordinary infrared there must lie an additional region of absorption and dispersion. The parallelism between δ and μ_g^2 suggests that we are dealing here with a phenomenon of dipolar origin⁸⁵). Indeed, in view of the considerations of Chapt. III, § 11, atomic vibrations give only rather small contributions to the dielectric constant and could hardly be held responsible for the observed differences.

The beginning of a new region of absorption is actually indicated by our data for the heaviest molecules $\text{C}_6\text{H}_5\text{I}$, $\text{C}_6\text{H}_5\text{NO}_2$, $\text{C}_6\text{H}_5\text{CN}$ at a wavelength of 0.802 cm, the ϵ' , ϵ'' -data beginning to depart from a D e b i j e-circle there. Further evidence might be expected from an extension of the measurements towards still smaller wavelengths.

In addition to inquiring whether the points representing our measurements in the ϵ' , ϵ'' -plane lie on a circle, one may ask if they are located on such a circle in agreement with one of the formulae proposed in Chapt. II. This can best be verified by computing a relaxation time τ from them and by noting if the values thus resulting are the same at different wavelengths.

One will in the first place try the simple D e b i j e equation (2.12) in which n^2 has been replaced by the quantity ϵ_∞ resulting from the measurements. This has been done in table XXI. It

TABLE XXI

Values of the relaxation time τ according to (2.12) with ϵ_∞ replacing n^2 , computed from the experimental data given in tables VII to XII, at the wavelengths indicated								
Substance	T °K	$\tau \times 10^{10}$ s						$\tau_{av} \times 10^{10}$ s
		λ_v 10.00 cm	λ_v 3.99 cm	λ_v 3.55 cm	λ_v 3.20 cm	λ_v 1.25 cm	λ_v 0.802 cm	
C ₆ H ₅ F	294		0.031		0.034	0.033	0.034	0.033
C ₆ H ₅ Cl	295	0.071	0.070	0.071	0.074	0.068	0.067	0.070
C ₆ H ₅ Br	295	0.112	0.106	0.109	0.104 ^b	0.110	0.099	0.107
C ₆ H ₅ I	294		0.205		0.194	0.186	×	0.195
C ₆ H ₅ NO ₂	293	0.073	0.069	0.074	0.077	0.073	×	0.073
C ₆ H ₅ CN	294		0.078		0.087	0.076	×	0.080

× values not computed due to the presence of the second dispersion region.

appears that the values of τ thus obtained are practically constant for the whole range of wavelengths. In the places marked × no τ -values have been computed, as here the new region of dispersion mentioned above is already coming into play. The values of τ show a steady increase with increasing size of the molecule.

One might furthermore try to obtain τ from our equation (2.35) for ellipsoidal molecules, since it too gives an approximately semi-circular dispersion locus for ellipticities such as we are here dealing with. It would then seem most reasonable to let n^2 stand in the terms involving the depolarization factor A_1 , i.e. in the terms $[\epsilon - (\epsilon - n^2)A_1]$ and $[1 + (n^2 - 1)A_1]$, since these factors arise from the internal polarization of the molecule involving nothing but the electronic transitions and atomic vibrations, and only to replace n^2 by ϵ_∞ elsewhere. If this is done, it is found that the constancy of τ with changing wavelength is markedly inferior to that realized in table XXI, the extreme variation resulting for instance in the case of C₆H₅Cl being about 18%. We shall, indeed, see in § 13 that the application of (2.35) to molecules where ϵ_∞ and n^2 differ noticeably must be rejected also for theoretical reasons.

One may finally compare the values of τ given in table XXI with the values resulting according to (2.3) if we there replace $4\pi a^3/3$ by $1/N$, the volume per molecule. It is found that the values thus computed are by about a factor 8 larger than those of table XXI. To this point we also shall return in § 13.

12.3. Associating liquids. The data for the associating liquids H_2O , CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ (see figs 19 to 22) show that for the first two liquids the points in the ϵ' , ϵ'' -plane lie on semi-circles, while for the third all the reliable points available lie near the high frequency end. For this last molecule a beginning of a second region of absorption is clearly apparent. As the structure of these liquids is very complicated due to the presence of strong hydrogen bonds, one may question whether a dipolar mechanism may serve to explain the discrepancy between ϵ_∞ and n^2 resulting also here. In fact no proportionality of δ with μ_g^2 is found, as is shown in the lower half of table XX. The formal application of (2.12) to the computation of τ , again with n^2 replaced by ϵ_∞ , leads to the results shown in table XXII.

TABLE XXII

Values of the relaxation time τ according to (2.12) with ϵ_∞ replacing n^2 , computed from experimental data given in tables XIII and XIV, at the wavelengths indicated										
Substance	T °K	$\tau \times 10^{10}$ s								$\tau_{av} \times 10^{10}$ s
		λ_v 10.00 cm	λ_v 6.48 cm	λ_v 3.99 cm	λ_v 3.55 cm	λ_v 3.20 cm	λ_v 1.58 cm	λ_v 1.25 cm	λ_v 0.802 cm	
H_2O	293	0.0088	0.0086	0.0074	0.0075	0.0088	0.0074	0.0083	0.0073	0.008
CH_3OH	293			0.104	0.107*)	0.112		0.093	0.077	0.10

*) at $\lambda_v = 3.51$ cm.

12.4. Solutions of polar molecules in a non-polar solvent. The data obtained on solutions can be analysed in an analogous way. From this analysis, however, the data in which the presence of a second dipolar dispersion makes itself felt should be excluded. Furthermore, in order to increase the number of available data, the results of static measurements on these solutions can be taken from literature.

Displaying the results in the ϵ' , ϵ'' -plane, it is observed that for instance for $\text{C}_6\text{H}_5\text{NO}_2$ in C_6H_6 and for CH_3OH in C_6H_6 the data for a given concentration can again quite well be fitted by semi-circles. Some examples were given in fig. 23 and fig. 24 for volume concentrations v_1 of 30% and 40% $\text{C}_6\text{H}_5\text{NO}_2$ in C_6H_6 respectively, and in fig. 25 for 80% CH_3OH in C_6H_6 . The values of ϵ' and ϵ'' for various concentrations, determined graphically by inter-

polation, are tabulated in table XXIII and table XXIV respectively, together with the corresponding static data and the values for ϵ_{∞} following from semi-circular extrapolation at the concentrations considered. The static results for the solution of $C_6H_5NO_2$ in C_6H_6 have been interpolated from the measurements of Piekara⁸⁶⁾ and of the National Physical Laboratory⁶⁵⁾. The static data for the solution of CH_3OH in C_6H_6 have been deduced from data of Filippov⁸⁷⁾ and of the M.I.T. Tables of Dielectric Materials⁸³⁾.

TABLE XXIII

Interpolated data for the dielectric constant of solutions of $C_6H_5NO_2$ in C_6H_6 . $T = 293^{\circ}K$								
v_1 %	$\lambda_v = 3.99$ cm		$\lambda_v = 3.20$ cm		$\lambda_v = 1.25$ cm		ϵ_0	ϵ_{∞}
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''		
0	2.28	—	2.28	—	2.28	—	2.28	2.28
10	3.72	0.92	3.45	1.00	2.76	0.70	4.26	2.46
20	4.92	2.00	4.46	2.09	3.12	1.33	6.57	2.63
30	6.03	3.13	5.27	3.17	3.42	1.88	9.10	2.79
40	7.04	4.38	5.94	4.28	3.68	2.42	11.76	2.96
50	7.81	5.71	6.52	5.47	3.91	2.90	14.60	3.13
60	8.39	7.03	6.91	6.62	4.11	3.34	17.95	3.29
70	8.93	8.36	7.20	7.69	4.28	3.77	21.6	3.47
80	9.36	9.73	7.40	8.70	4.46	4.13	26.0	3.65
90	9.77	11.04	7.48	9.28	4.60	4.40	30.6	3.87
100	10.15	12.36	7.45	9.51	4.74	4.58	35.7	4.07

TABLE XXIV

Interpolated data for the dielectric constant of solutions of CH_3OH in C_6H_6 . $T = 298^{\circ}K$						
v_0 %	$\lambda_v = 3.20$ cm		$\lambda_v = 1.25$ cm		ϵ_0	ϵ_{∞}
	ϵ'	ϵ''	ϵ'	ϵ''		
0	2.28	—	2.28	—	2.28	2.28
10	2.72	0.41	2.68	0.24	4.8	2.66
20	3.20	0.90	3.04	0.54	7.5	3.00
30	3.69	1.48	3.34	0.83	10.2	3.30
40	4.22	2.14	3.68	1.16	13.1	3.62
50	4.74	2.94	4.00	1.54	15.9	3.91
60	5.30	3.82	4.33	1.97	18.8	4.18
70	5.92	4.84	4.68	2.40	21.8	4.48
80	6.65	5.88	5.05	2.89	24.9	4.70
90	7.39	6.95	5.48	3.46	27.9	5.01
100	8.18	8.00	6.04	4.13	31.0	5.30

The dependence of the values of ϵ_{∞} and n^2 on concentration is shown in fig. 26 and 27 respectively. Between the known values

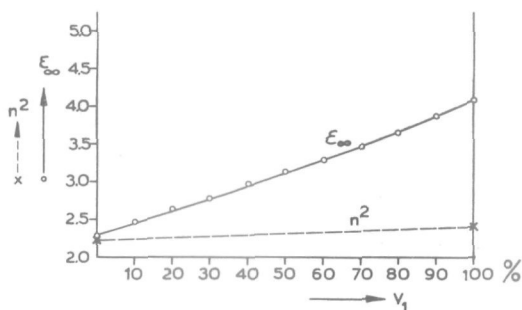


Fig. 26 Dependence of ϵ_∞ and n^2 on the concentration for a solution of $C_6H_5NO_2$ in C_6H_6 . $T = 293^\circ K$.

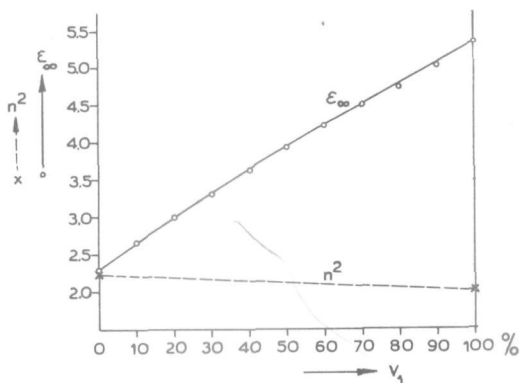


Fig. 27 Dependence of ϵ_∞ and n^2 on the concentration for a solution of CH_3OH in C_6H_6 . $T = 298^\circ K$.

of n^2 at 0% and 100% a straight line has been drawn, no values at intermediate concentrations being available. From other similar cases of mixtures an approximately linear behaviour may be expected. Again the inequality of ϵ_∞ and n^2 is evident at once. It is observed that the difference $\delta = \epsilon_\infty - n^2$ increases with the concentration, suggesting that the origin of this difference must be sought in the presence of the dipolar component.

In table XXV we have given the values of the relaxation time, calculated according to (2.12), for solutions of $C_6H_5NO_2$ in C_6H_6 at several wavelengths. It is seen that just as for pure $C_6H_5NO_2$ these values are practically independent of wavelength and decrease gradually for increasing concentration v_1 , as shown also in fig. 28. For solutions of CH_3OH in C_6H_6 no consistent values of τ at different

TABLE XXV

Values of the relaxation time $\tau \times 10^{10}$ s according to (2.12), with ϵ_∞ replacing n^2 , for solutions of $C_6H_5NO_2$ in C_6H_6 as a function of the concentration v_1 at several wavelengths										
v_1 %	10	20	30	40	50	60	70	80	90	100
λ_{cm}										
3.99	0.110	0.100	0.088	0.083	0.080	0.077	0.075	0.073	0.071	0.069
3.20	0.122	0.105	0.094	0.088	0.085	0.082	0.080	0.079	0.079	0.077
1.25	0.110	0.097	0.085	0.080	0.076	0.072	0.072	0.068	0.072	0.074
τ_{av}	0.114	0.101	0.089	0.084	0.082	0.078	0.076	0.074	0.074	0.073

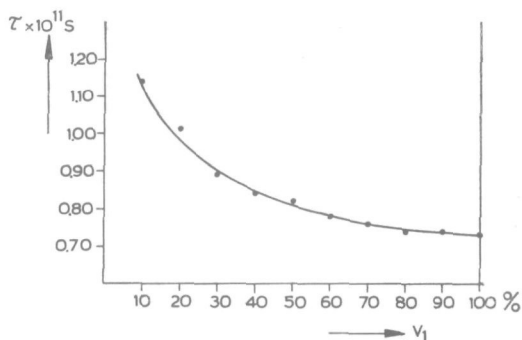


Fig. 28 Dependence of the relaxation time computed according to (2.12) on the concentration for a solution of $C_6H_5NO_2$ in C_6H_6 . $T = 293$ °K.

wavelengths could be obtained. At low concentrations the unavoidable inaccuracy in the measurements makes reliable conclusions impossible, while at high concentrations the associating character of the solute probably comes into play.

It may be noted in passing that the extrapolated value of τ for infinite dilution of nitrobenzene in benzene ($\tau \approx 0.13 \times 10^{10}$ s) has approximately the same magnitude as the corresponding values for chloro- and bromo-benzene⁴⁰), indicating the absence of predominant influences due to the dipole-moment.

§ 13. *Applicability of various models to the liquids investigated.* For the mono-substituted benzenes and their solutions in benzene we are now in a position to draw some definite conclusions regarding the possibility of interpreting the experimental results of Chapter III at the hand of the models discussed in Chapter II. As mentioned already in § 12.1 the data in the case of the spherical molecules

$(\text{CH}_3)\text{CCl}_3$ and $(\text{CH}_3)_3\text{CCl}$ are still too incomplete for this purpose, while in the case of the associating liquids their complicated structural properties make it improbable already beforehand that their dielectric behaviour can be explained in simple terms.

The most striking experimental result found for the mono-substituted benzenes and their solutions is the difference between ϵ_∞ and n^2 . Neither the original model of Debye, discussed in § 3, nor that of Onsager, discussed in § 4, nor the generalizations of the latter to ellipsoidal molecules, discussed in § 5, show this feature. For the models with local fields mentioned in § 6, on the other hand, such a difference is just what would be expected, as we shall illustrate in greater detail presently.

Local fields may arise from the existence of a quasi-crystalline structure in the liquid. The presence of a more or less regular arrangement of the neighbours of a molecule can be argued theoretically from steric as well as energy considerations. Even for molecules of essentially spherical shape effects of closest packing will result in the preponderance of certain intermolecular distances, and if the molecules are oblong or disk-shaped, a tendency towards mutual alignment is plausible on a purely geometrical basis. For molecules of the type of benzene such a tendency will, moreover, be favored by van der Waals forces (see e.g. J. H. de Boer⁸⁸). But quite aside from theoretical arguments direct experimental evidence is afforded by X-ray diffraction measurements, showing a pronounced preference for parallel orientation^{89, 90}, while experiments on nuclear relaxation support this conclusion⁹¹.

If the effect on a given dipole molecule of the more or less aligned dipole molecules in its neighbourhood may be represented in first approximation by a constant field, then we have the situation considered in the model of Debye and Ramo⁷), mentioned in § 6. We saw there that the first region of dipolar dispersion may be followed by others with smaller relaxation times.

On the other hand, in view of the fact that the molecules in question have symmetry elements, it seems more likely that the potential energy of orientation, considered as a function of suitable polar angles, has two or more minima. If the corresponding troughs of potential energy are sufficiently deep, the molecule, caught in the lowest stationary states of vibrational motion about the minima, will have non-vanishing diagonal matrix-elements of its

electric moment, and the treatment of G o r t e r and K r o n i g⁸⁾, discussed in § 6, can advantageously be applied. The diagonal matrix-elements will have practically the value μ_g in the direction of the minima. If the troughs are less pronounced, the zero-point vibrational motion will reduce this value somewhat, while transitions to the first excited vibrational levels become possible and give rise to additional absorption and dispersion at shorter wavelengths.

Both in the treatment of D e b i j e and R a m m and in that of G o r t e r and K r o n i g the influence of the immediate surroundings on a given dipole is represented by the local field introduced. To make use of a reaction field of the sort suggested by O n s a g e r would appear to be taking into account twice this same influence. The use of the L o r e n t z-L o r e n z field therefore seems to us to be appropriate and leads then, indeed, in both cases for pure liquids as for solutions to the semi-circular plots through ϵ_0 and ϵ_∞ which practically all our measurements confirm.

That as mentioned in § 12, the values of the relaxation time τ , as experimentally determined, generally are smaller by a considerable factor than those following from the expression (2.3), working with the viscosity, is not surprising either. In the treatment of G o r t e r and K r o n i g τ is a measure of the time between transitions of the molecule from one minimum of its potential energy of orientation to another. That the strong local interactions might bring about such transitions much more frequently than the general interaction incorporated in the macroscopic viscosity is altogether plausible.

In particular our determinations of τ for the solution of $C_6H_5NO_2$ in C_6H_6 , represented in fig. 28, illustrate our view-point. Suggestions in this direction also form the basis of a theory recently published by Miss H i l l⁹²⁾, leading to values of τ roughly five times as small as the D e b i j e values.

REFERENCES

- 1) D e b i j e, P., Polare Molekeln, 1st ed. Leipzig, 1929, Chapter V.
- 2) O n s a g e r, L., J. Am. Chem. Soc. **58** (1936) 1486.
- 3) K i r k w o o d, J. G., J. Chem. Phys. **7** (1939) 911.
- 4) C a r t w r i g h t, C. H. and E r r e r a, J., Proc. Roy. Soc. **154 A** (1936) 183.
- 5) P a u l i n g, L., Phys. Rev. **36** (1930) 430.
- 6) D e b i j e, P., Phys. Z. **36** (1935) 100, 193.

- 7) Debije, P. and Ramm, W., Ann. Phys. Lpz. **28** (1937) 28.
- 8) Gorter, C. J. and Kronig, R., Physica **3** (1936) 1009.
- 9) Lampa, A., Wied. Ann. **61** (1897) 79.
- 10) Drude, P., Ann. Phys. Lpz. **61** (1897) 466.
- 11) Drude, P., Ann. Phys. Lpz. **8** (1902) 336; **16** (1905) 116.
- 12) Colley, A. R., Phys. Z. **11** (1910) 324.
- 13) Eckert, F., Verh. dtsh. Phys. Ges. **15** (1913) 307.
- 14) Rubens, H., Verh. dtsh. Phys. Ges. **17** (1915) 315.
- 15) Rückert, E., Ann. Phys. Lpz. **55** (1918) 151.
- 16) Möbius, W., Ann. Phys. Lpz. **62** (1920) 293, 307.
- 17) Weichmann, R., Phys. Z. **22** (1921) 535.
- 18) Weichmann, R., Ann. Phys. Lpz. **66** (1921) 501.
- 19) Tear, J. D., Phys. Rev. **21** (1923) 611.
- 20) Malsch, J., Ann. Phys. Lpz. **12** (1932) 865.
- 21) Krause, K., Phys. Z. **35** (1934) 687.
- 22) Schmelzer, W., Ann. Phys. Lpz. **28** (1937) 35.
- 23) Fischer, E., Phys. Z. **21** (1939) 645.
- 24) Mizushima, S., Bull. Chem. Soc. Japan **1** (1926) 47, 163.
- 25) Mizushima, S., Proc. Imp. Ac. Tokyo **5** (1929) 15.
- 26) Girard, P. and Abadie, P., C. R. Acad. Sci., Paris, **191** (1930) 1300; **195** (1932) 119, 217.
- 27) Seeberger, A., Ann. Phys. Lpz. **16** (1933) 77.
- 28) Esau, A. and Bätz, G., Phys. Z. **38** (1937) 774.
- 29) Knerr, H. W., Phys. Rev. **52** (1937) 1054.
- 30) Kebbel, W., Hochfreq. Techn. u. Elektro Akustik **53** (1939) 81.
- 31) Heston, W. M., Smyth, Ch. P. a.o., J. Amer. Chem. Soc. **70** (1948) 4093, 4102.
- 32) Laquer, H. and Smyth, Ch. P., J. Amer. Chem. Soc. **70** (1948) 4097.
- 33) Branin, F. H. and Smyth, Ch. P., J. Chem. Phys. **20** (1952) 1121.
- 34) Brot, C., Magat, M. and Reinisch, L., Kolloid Z. **134** (1953) 101.
- 35) Haggis, G. H., Hasted, J. B. and Buchanan, T. J., J. Chem. Phys. **20** (1952) 1452.
- 36) Hasted, J. B. and El Sabeh, S. H. M., Trans. Faraday Soc. **49** (1953) 1003.
- 37) Lane, J. A. and Saxton, J. A., Metereological factors in Radiowave Propagation, 1946, p. 292.
- 38) Lane, J. A. and Saxton, J. A., Proc. Roy. Soc. **213 A** (1952) 400, 473.
- 39) Heston, W. M., Smyth, Ch. P. a.o., J. Amer. Chem. Soc. **72** (1950) 3443, 3447.
- 40) Whiffen, D. H. and Thompson, H. W., Trans. Faraday Soc. **42 A** (1946) 114, 122.
- 41) Whiffen, D. H., J. Amer. Chem. Soc. **70** (1948) 2452.
- 42) Whiffen, D. H., Trans. Faraday Soc. **46** (1950) 124.
- 43) Heston, W. M., Smyth, Ch. P. a.o., J. Amer. Chem. Soc. **72** (1950) 2071, 3443.
- 44) Curtis, A. J., Smyth, Ch. P. a.o., J. Amer. Chem. Soc. **74** (1952) 644.
- 45) Cole, K. S. and Cole, R. H., J. Chem. Phys. **9** (1941) 341.
- 46) Böttcher, C. J. F., Physica **5** (1938) 635.
- 47) Cole, R. H., J. Chem. Phys. **6** (1938) 385.
- 48) Fuoss, R. M. and Kirkwood, J. G., J. Amer. Chem. Soc. **63** (1941) 385.
- 49) Bolton, H. C., J. Chem. Phys. **16** (1948) 486.
- 50) Fischer, E., Ann. Phys. Lpz. **6** (1949) 117.
- 51) Scholte, Th. G., Physica **15** (1949) 437.
- 52) Scholte, Th. G., Thesis Leyden 1950.
- 53) Poley, J. Ph., J. Chem. Phys. **22** (1954) 1466.

- 54) Abbott, J. A. and Bolton, H. C., *Trans. Faraday Soc.* **48** (1952) 422.
- 55) Buckingham, A. D., *Trans. Faraday Soc.* **49** (1953) 881.
- 56) Buckingham, A. D., *Austr. J. Chem.* **6** (1953) 93.
- 57) Osborne, J. A., *Phys. Rev.* **67** (1945) 351.
- 58) Le Fèvre, R. J. W. and Le Fèvre, C. G., *Austr. J. Chem.* **7** (1954) 33.
- 59) Timmermans, J., *Phys. Chem. Constants of pure Organic Compounds 1st ed.*, Amsterdam 1950.
- 60) Lab. for Phys. Chemistry, Univ. of Leyden, unpublished measurements.
- 61) Moore, E. M. and Hobbs, M. E., *J. Amer. Chem. Soc.* **71** (1949) 411.
- 62) McAlpine, K. B. and Smyth, C. H. P., *J. Chem. Phys.* **3** (1935) 55.
- 63) Groves, L. G. and Sugden, S., *J. Chem. Soc.* (1934, II) 1094.
- 64) Hurdis, E. C. and Smyth, C. H. P., *J. Amer. Chem. Soc.* **64** (1942) 2212.
- 65) National Physical Laboratory, Teddington, England.
- 66) Ball, A. O., *J. Chem. Soc.* (1930) 570.
- 67) Lide, D. R., *J. Chem. Phys.* **22** (1954) 1577.
- 68) Debije, P., *Chem. Rev.* **19** (1936) 171.
- 69) Kronig, R., *Z. techn. Phys.* **19** (1938) 509.
- 70) Kronig, R., *Physica* **5** (1938) 65.
- 71) Fröhlich, H., *J. Instn. Elect. Engrs* **91 I** (1944) 456.
- 72) Fröhlich, H., *Theory of Dielectrics*, 1st ed. Oxford 1949.
- 73) Poley, J. Ph., *l'Onde Electrique*, to be published.
- 74) Crouch, G. E., *J. Chem. Phys.* **16** (1948) 364.
- 75) Poley, J. Ph., *Communication U.R.S.I.-conference*, Sydney, 1952.
- 76) Dakin, T. W. and Works, C. W., *J. Appl. Phys.* **18** (1947) 789.
- 77) Toppinga, M. L., *Tijdschr. Ned. Radiogenoot.* **16** (1951) 185.
- 78) Trier, A. A. Th. M. van, *Appl. Sci. Res.* **B 3** (1953) 305.
- 79) Loor, G. P. de, unpublished measurements.
- 80) Hill, Nora E., Bedford College, London, private communication.
- 81) Roberts, J. E. and Cook, H. F., *Brit. J. Appl. Phys.* **3** (1952) 33.
- 82) Mecke, R. and Reuter, A., *Z. Naturforsch.* **4 A** (1949) 368.
- 83) M.I.T. Tables of Dielectric Materials, published in "Dielectric Materials and applications", New York, 1954.
- 84) Roberts, S. and Hippel, A. von, *J. Appl. Phys.* **17** (1946) 610.
- 85) Poley, J. Ph., *J. Chem. Phys.* **23** (1955) 405.
- 86) Piekara, A., *Bull. Int. Acad. Polon. Sc.* (1939) 168.
- 87) Filippov, M. I., *J. of Phys. U.S.S.R.* **1** (1939) 479.
- 88) Boer, J. H. de, *Ned. T. Natuurk.* **15** (1949) 205.
- 89) Kortüm, G., *Z. angew. Chem.* **64** (1952) 4.
- 90) Selman, J., *Thesis Amsterdam 1932*, p. 105.
- 91) Giulotto, L. a.o., *J. Chem. Phys.* **22** (1954) 1143.
- 92) Hill, Nora E., *Proc. Phys. Soc.* **67 B** (1954) 149.

CURRICULUM VITAE

Johannes Philippus Poley, geboren 28 Juni 1924 te Bandoeng, behaalde in 1942 het eindexamen H.B.S.-B aan het Chr. Lyceum te Haarlem. Na eerste inschrijving in datzelfde jaar aan de T.H. te Delft, kon hij de studie aldaar in 1945 hervatten, waarna hij in 1948 het diploma van natuurkundig ingenieur verkreeg. Sinds 1947 is hij, met een onderbreking voor militaire dienst, verbonden aan het Fysisch Laboratorium der Rijksverdedigings Organisatie - T.N.O., waar hij per 1 Januari 1953 werd benoemd tot hoofdingenieur.

STELLINGEN

I

Op grond van verschillende modellen voor de wisselwerking tussen moleculen in een dipoolvloeistof mag een dielectrische dispersie verwacht worden, welke in het ϵ' , ϵ'' -vlak kan worden beschreven door een halve cirkel. Indien experimenteel zulk een halve cirkel wordt gevonden, mag dit dus op zichzelf geen bewijs worden genoemd voor de juistheid van één dezer modellen.

Debije, P., *Polare Molekeln*, Leipzig, 1929, Hfdst. V.
Gorter, C. J. en R. Kronig, *Physica*, **3** (1936) 1009.
Fröhlich, H., *J.I.E.E.*, **91 I** (1944) 456.
Poley, J. Ph., *J. Chem. Phys.*, **22** (1954) 1466.

II

In de theorie der dielectrische dispersie dient te worden onderscheiden tussen een moleculaire relaxatietijd, zoals bv. gebruikt in dit proefschrift, en relaxatietijden, welke formeel kunnen worden toegekend aan macroscopische functies van de dielectrische constante, zoals bv. de polarisatie. Verwaarlozing van dit onderscheid leidt soms tot onjuiste resultaten.

Mandel, M., *Bull. Soc. Chim. Belg.*, **60** (1951) 301.

III

Ten onrechte merkt Jaynes op, dat de theorie van het inwendige veld in dielectrica volgens Onsager het optreden van spontane polarisatie uitsluit.

Jaynes, E. T., *Ferroelectricity*, Princeton, 1953, 9.
Pirene, J., *Helv. Phys. Acta*, **22** (1949) 479.

IV

Bij de berekeningen van de complexe dielectrische constante uit microgolf impedantie metingen kan met voordeel gebruik worden gemaakt van de door Benoit ingevoerde methode.

Benoit, J., *Ann. d. Téléc.*, **4** (1949) 27.
Poley, J. Ph., *Appl. Sci. Res.*, **4** (1954) 173.

V

De functie, welke Granier voorstelt voor de mathematische beschrijving van experimentele dispersie-gegevens, is identiek met de reeds in 1941 door Fuoss en Kirkwood aangenomen functie.

Granier, J., *Comptes Rendus Acad. Sc.*, **226** (1948) 1354.
Fuoss, R. M. en J. G. Kirkwood, *J. Am. Chem. Soc.*, **63** (1941) 385.

VI

De dielectrische constante van telluriet-glazen bedraagt bij microgolven omstreeks 26, terwijl de verliezen verwaarloosbaar zijn. Verdere ontsluiting van het mm-golf gebied biedt interessante perspectieven voor een voortgezet onderzoek naar de samenhang van de electromagnetische eigenschappen met de structuur dezer glazen.

Stanworth, J. E., *J. Soc. Glass Techn.*, **36** (1952) 217.
Poley, J. Ph., *Nature*, **174** (1954) 268.

VII

Bij de studie van de electromagnetische eigenschappen van halfgeleiders verdient het aanbeveling de door M. en R. Freymann ontwikkelde methode toe te passen.

Freymann, M. en R. Freymann, *J. Phys. Rad.*, **13** (1952) 589; *J. Chem. Phys.*, **20** (1952) 1970.

VIII

Het onderzoek met microgolven levert nieuwe en zeer nauwkeurige gegevens ter bepaling van diverse fysische grootheden, zoals bv. het dipoolmoment van polaire moleculen, de massaverhouding van isotopen en de magnetische momenten der kernen.

Townes, C. H., *Physica*, **17** (1951) 354.
Gordy, W. et al., *Microwave Spectroscopy*, New York, 1953.

IX

In het golflengte-gebied, dat begrensd wordt enerzijds door de microgolven en anderzijds door het langgolvig infrarood, is het niet mogelijk op rendabele wijze electromagnetische energie van redelijke intensiteit op te wekken. Dit gegeven mag worden gezien als een principiële beperking van groot belang voor het voortbestaan van het leven, daar vele moleculen, die essentieel voor het fysisch onderhoud der levensverschijnselen zijn, in dit golflengte-gebied absorptiebanden hebben.

Klumb, H., *Zs. f. Phys.*, **116** (1940) 321.
Franz, R., *Radiotechnik*, (1947) 165.
Eder, F. X., *Funk und Ton*, (1948) 491.

X

De betekenis, welke de Reformatie heeft gehad voor de ontwikkeling der natuurwetenschap, wordt veelal sterk onderschat.

Pelseneer, J., o.a. in: *Geloof en Wetenschap*, **47**
(1949) 21.
Hooykaas, R., *Proceedings Research Scientists' Christian Fellowship Conference, London, 1953.*

XI

In de Kerkenordening der Gereformeerde Kerken in Nederland dient de eigensoortigheid van het gezag, dat aan de Generale Synode toekomt, tot uitdrukking te worden gebracht. Voorts dient in de plaatselijke kerkelijke praktijk het sociale aspect van het kerkelijk levensverband in toenemende mate tot zijn recht te komen.

XII

De bezwaren ingebracht tegen het Mandement der Bisschoppen gaan veelal voorbij aan het recht, dat aan de Kerk gegeven is, de levenspraktijk van haar lidmaten te toetsen aan de Heilige Schrift en daartoe ideologieën en hun uitingsvormen te beoordelen, c.q. te veroordelen. Dit recht is niet afhankelijk van een specifieke kerkbeschouwing.