MOLECULAR POLARISATION


Thesis presented to the University of London in the Faculty of Science by

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for the Degree of Doctor of Philosophy
An investigation has been made of the molecular polarization of 4-butyl chloride and methyl cyanide in solution in non-polar solvents. The small range of dielectric constants encountered required the accuracy of their determination to be as high as possible and particular attention was given to the design of apparatus and the reduction of experimental errors. The polarization at infinite dilution is independent of the method of extrapolation used provided the accuracy of the experimental results is high but a method which treats the separate physical constants of each solution is preferable to any dependent on a derived function (e.g. molecular polarization). That proposed by Halvorsen and Kurlar is satisfactory and is also very critical of the data examined.

Based on the Debye-Lanczos-Clausius relationship and if the vapour phase data are correct, the apparent molecular polarization of 4-butyl chloride is greater in solution than in the vapour phase while that for methyl cyanide is less. This is the only effect directly attributable to molecular shape and according to the theories of Frisch and Mignolet implies that with 4-butyl chloride the axis of maximum polarisability is at right angles to that of the dipole. However, the results for 4-butyl chloride must be considered anomalous since they do not confirm these authors' predictions that the total molecular polarization at infinite dilution should increase with increasing dielectric constant of the solvent. The apparent specific volumes of the solutes vary from solvent to solvent and although the variations do not correlate with the variations of the polarizations they are similar for each solute, those for methyl cyanide being the greater.

The experimental results have been examined by the application of equations proposed by various authors but in no case are the results correlated for all solvents. All the expressions agree in giving the highest polarizations for solutions in or containing dioxan which is probably due to hydrogen bonding, the exaltation being associated with the orientation polarization only. The normal paraffins are anomalous giving polarizations lower than those found in solvents of higher dielectric constant while mixed solvents give different polarizations from that in a pure solvent with the same dielectric constant.

In general, none of the equations can alone predict the experimental results and it seems probable that each solution must be treated as a separate problem.
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INTRODUCTION
The capacity of a condenser is a function of the medium or "dielectric" between the plates and the ratio of the capacity of the condenser when the medium is present, to that when the space between the plates is evacuated is known as the "specific inductive capacity" of "dielectric constant" of the medium. All substances have a dielectric constant greater than unity and the first accurate explanation of this property was given by Faraday (1).

It is suggested that, in an electric field, particles of matter could come into a constrained condition in which they assume positive or negative parts, i.e. they become electrically polarized by induction, thereby giving rise to a field opposing the applied field. Thus the potential difference between the plates of the condenser is less for a definite charge than it would be in the absence of the dielectric, i.e. the capacity of the condenser is increased.

Now the electrons and nuclei in molecules vibrate about fixed points in space and at any given instant the centres of action of all the positive and all the negative charges may not coincide. The molecules will thereby momentarily possess a "dipole moment" equal to the product of the charge and the instantaneous distance of separation. Under experimental conditions, however, one can observe a dipole moment only if the mean centres of action of the positive and negative charges show a permanent displacement with respect to one another and for rigid molecules with a centre of
symmetry a vanishingly small dipole moment is found and they are said to be non-polar. Most molecules however are polar, i.e. the average dipole moment is finite and therefore the mean positions of the centres of action of the positive and negative charges do not coincide. This permanent dipole moment is a characteristic of the molecule and is given the symbol $\mu$; however, as will be mentioned later, its value can show variations.

If either polar or non-polar molecules are placed in an electric field both the electrons and nuclei will be displaced from their mean positions. Such displacements will correspond to an "induced moment" which will be of two parts - one due to the electrons and the other to the nuclei. This induced moment will be proportional to the applied field since the field strengths used for the determination of dielectric constants are low compared with intramolecular fields.

We may write therefore
\[
\bar{m} = \alpha F = (\alpha_E + \alpha_A) F
\]
where $F$ is the applied field; $\bar{m}$ the average moment taken over all the molecules; $\alpha_E$ and $\alpha_A$ the electronic and atomic (nuclear) proportionality constants or "polarisabilities". It should be noted that $\alpha_E$ and $\alpha_A$ are the values obtained in the direction of the applied field and for anisotropic molecules depend on the orientation of the molecule. If, however, the number of molecules is large and they do not exhibit preferred orientation then $\alpha_E$ and $\alpha_A$ will be mean values.
when a molecule possessing a permanent dipole is placed in an electric field it will tend to orient itself so that its potential energy is a minimum. In a polar liquid this action of the field will be opposed by thermal agitation which alone would produce random orientation; as a consequence a dynamic equilibrium is reached in which a slight excess of molecules have a component of their own field antiparallel to the applied field.

This will correspond effectively to a further moment whose average value \( \overline{m} \) will be a function of the permanent moment and was first deduced by P. Debye (2).

\[
\begin{align*}
\text{A molecule possessing a permanent moment } \mu, \text{ when placed in an electric field of intensity } F \text{ such that its axis makes an angle } \Theta \text{ with the direction of the field, will have a potential energy } u \text{ given by } u = -\mu F \omega \Theta \text{ and a permanent moment in the direction of the field of } \mu \omega \Theta. \text{ Neglecting for the present the presence of an induced moment, and assuming that there is no molecular interaction, the Maxwell-Boltzmann distribution law may be applied. The number of molecules with their dipole arms within a solid angle } \delta \omega \text{ at any instant is } A e^{-\overline{m} F} \delta \omega \text{ where } A \text{ is determined by the total number of molecules present and } \overline{m} \text{ is }
\end{align*}
\]

Page 7
the Boltzmann constant. The total number of molecules will be
found by integrating this expression over all directions in space:

Total number of molecules = \( \int_0^{2\pi} \int_0^\pi A e^{-\frac{\mu_0}{kT}} \sin \theta \, d\omega \)

Now the total moment in the direction of the field within the solid
angle \( \delta \omega \) is \( A e^{-\frac{\mu_0}{kT}} \mu \cos \theta \delta \omega \) and the resultant moment for all
the molecules can be found by integrating this expression between
\( 0 \) and \( 2\pi \). Hence the mean moment of one molecule in the direction
of the field is

\[
\overline{m}_o = \frac{\int_0^{2\pi} \int_0^\pi A e^{-\frac{\mu_0}{kT}} \mu \cos \theta \, d\omega}{\int_0^{2\pi} \int_0^\pi A e^{-\frac{\mu_0}{kT}} \, d\omega}
\]

which reduces to

\[
\frac{\overline{m}_o}{\mu} = \frac{e^x - e^{-x}}{e^x + e^{-x}} - \frac{1}{x} = \cot \theta \tan x - \frac{1}{x}
\]

If \( x \) is small, a condition obtaining when the field strength is
low and saturation effects do not arise, the expression approximates
to \( \frac{x^2}{3} \)

\[
\overline{m}_o = \frac{\mu x}{3} = \frac{\mu^2}{3kT} F
\]

To obtain the total moment per molecule in the direction of the
field \( \overline{m}_o \) must be added to the induced moment \( \overline{m} \) giving

\[
m = (\overline{m}_E + \overline{m}_A) F + \frac{\mu^2}{3kT} F \quad \text{......................... (I)}
\]

It is now necessary to eliminate \( m \) and \( F \) from this equation and the
method below is that due to Rosotti and Clausius but other methods of
interpreting \( m \) and \( F \) in terms of measurable quantities have been
proposed.
It can be readily shown that for a dielectric between the plates of a condenser

\[ E_o = E + 4 \pi I \quad \text{or} \quad (\varepsilon - 1) E = 4 \pi I \quad \ldots \ldots \quad (II) \]

where \( E_0 \) is the field strength between the plates of the condenser in the absence of the dielectric,

\( E \) is the field strength between the plates of the condenser with the dielectric; sometimes called the 'electrical induction',

\( \varepsilon \) is the dielectric constant,

\( I \) is the electric moment per unit volume, i.e. \( I = n.m. \)

where \( n \) is the number of molecules per cc.

Now consider a molecule in a small spherical cavity which is relatively large compared with the molecule but which is small in comparison with the distance between the plates. The total electrical intensity experienced by the molecule is made up of several parts:

1) \( E_0 \) due to the charges on the plates.
2) \(-4\pi I\) due to the charges induced on the surface of the dielectric in contact with the plates.
3) \(+\frac{3}{2}\pi I\) due to the charge on the surface of the cavity.
4) a field due to the molecules within the cavity; no general expression can be given but it is zero for non-associated liquids, or gases with random orientation of the molecules.
\[ F = E \cos \theta - 4\pi I + \frac{4\pi}{3} \theta I \]  

\((\text{III})\)

but \( I = m \eta \), \( E = E \eta \)

and introducing (II)

\[ F = \left( \frac{4\pi E}{e-1} - 4\pi + \frac{4\pi}{3} \right) m \eta \]

\[ = \frac{4\pi (E+2) m \eta}{3 (E-1)} \]

also \( \eta = \frac{dN}{M} \) where \( M \) is the molecular wt. and \( d \) the density of the substance concerned, and \( N \) is the Avogadro number.

\[ \therefore \quad \frac{m}{F} = \frac{(E-1)}{(E+2)} \frac{3}{4\pi N d} \]

Hence with (I) we obtain

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

\((\text{IV})\)

The quantity on the left hand side of this equation is known as the "total molecular polarization" \( \mu^P \) and the three terms

\[ \frac{4\pi N}{3} \alpha_E \quad ; \quad \frac{4\pi N}{3} \alpha_A \quad \text{and} \quad \frac{4\pi N}{3} \frac{\mu^2}{kT} \]

the electronic \( \mu^E \), atomic \( \mu^A \) and orientation polarizations \( \mu^P \) respectively. The sum of \( \mu^E + \mu^A \) is often referred to as the distortion polarization \( \mu^P \).

The derivation of this expression assumes that there is no interaction between the molecules, a condition that is only valid for gases at low pressures.

Evaluations of the three polarizations can be made by means of the Bouef-Cleraus equation using values of \( E \) determined.
under specified conditions.

It is almost invariably measured as the ratio of the
capacities of a condenser with and without the dielectric, employing
an alternating field supplied by an oscillator. At low frequencies
(< 10⁵ cps) the dielectric constant is equal to the value obtained
with a steady field and remains constant with rise in frequency
until the duration of the field becomes comparable with the
relaxation time of the molecules of the dielectric. The polar
molecules are then unable to take up their positions of dynamic
equilibrium before the applied field has reversed its direction
with the result that a diminution in \( \bar{m}_0 \) occurs, until, when the
frequency is high enough, \( \bar{m}_0 \) falls to zero. At this point the
orientation polarization is zero and the molecular polarization
equals the sum of the atomic and electronic polarizations. At
still higher frequencies the atomic nuclei are unable to follow
the field and thus a second drop in polarization occurs, with the
electronic polarization remaining.

There will, however, be discontinuities in the polarization/
frequency relationship corresponding to absorption bands due to
resonance of the atomic nuclei and electron. For a polar material
the dependence of the total polarization on frequency may be
represented by a curve as shown on Page 12, where only two
absorption bands due to the nuclei and electrons respectively
are shown.
This variation of the total polarization with frequency provides a method of measuring the three polarizations.

It is, however, not possible to measure $\varepsilon$ at the very high frequencies required to completely exclude $\mu P$ and use its mode of a relation due to Bowell (1821). He showed that for substances with symmetrical molecules and at the same frequency $\varepsilon = n^2$ where $n$ is the refractive index of the substance and hence $\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right) \frac{M}{d}$ can be replaced by $\left(\frac{n^2 - 1}{n^2 + 2}\right) \frac{M}{d} = \mu R$ the molecular refraction.

Thus provided the refractive indices are measured at frequencies well removed from absorption bands the molecular refraction for the long infra-red frequencies will give $\varepsilon P + \mu P$ and the ultra violet will give $\varepsilon P$ only. Finally $\varepsilon$ measured at low frequencies will give $\varepsilon P + \mu P + \mu P = \tau P$.

This procedure is, however, experimentally difficult and attention has usually been directed towards the values of $\mu$ and therefore of $\mu P$, methods therefore have been adapted which aim at eliminating $\mu P$. Those generally employed and the underlying theory are outlined below.

(a) The ability of a polar molecule to follow an applied field will depend on the restoring forces due to the surrounding molecules — in the case of a gas at low pressure these
are negligible. Compared with the vapour (or gas) the total polarization of the liquid is smaller and for the solid dielectric lower still and usually almost independent of the temperature well below the freezing point. The interpretation given to these phenomena is that the orientation polarization is absent in the solid state due to the molecules being held rigidly in the crystal lattice leaving only the electronic and atomic polarizations operative. The last two are then assumed to have the same values as in the gas phase, thereby permitting \( \mu P \) to be calculated as the difference between \( P \) for the gas and for the solid.

This method is open to several objections. The accurate measurement of \( e \) for solids is very difficult, particularly if they must be held at low temperatures, also it does not follow that the value of \( \mu P \) and \( P \) for the solid will be the same as that for the gas. In general, unless the molecules are electrically isotropic, the preferred orientation obtained in the crystalline state will result in an anisotropic solid with values of \( \mu P \) and \( P \) dependent on the direction of the crystal axes relative to the applied field. The assumption that \( \mu P \) is zero in the solid state is not always justified, in fact, some corporals exhibit almost complete free rotation at temperatures well below the melting point, the change in \( P \) on freezing being almost entirely due to the change in density.

\[
\mu P = 10^7 [P]_0
\]
(b) The value $\bar{p}^P$ can be calculated from the density and refractive index for infra-red frequencies (well removed from absorption bands). This procedure is, however, experimentally difficult and values have made certain simplifying assumptions.

(iii) The molecular refraction for the Na D line may be taken as equal to $\bar{p}^P$ then the difference between this and $\bar{p}^P$ is regarded as $\mu^P$.

(iv) The molecular refraction may be obtained for several frequencies in the visible spectrum the value for light of infinite wavelength calculated by one of the extrapolation formulas, e.g.,

$$R^\infty = \frac{\lambda_{a}^2 - \lambda_{b}^2}{\lambda_{a}^2 - \lambda_{b}^2}$$

where $R_a$ and $R_b$ are the molecular refractions for the wavelengths $\lambda_a$ and $\lambda_b$ respectively both of which must be well removed from absorption bands. $R^\infty$ is then regarded as identical with the electron polarizability alone.

(iii) Alternatively, the molecular refraction for one frequency, usually the Na D line, may be corrected to give $\bar{p}^P$; Cavos and Eggen (3) have suggested that $\bar{p}^P$ is small and that it is sufficiently accurate to take

$$\bar{p}^P = 1.05 [R]_D.$$
The normal refractivity methods for eliminating $\rho^0$ are satisfactory when $\mu^0$ is large but when this is not the case $\rho^0$ is the small difference between two large numbers and since it may contain their accumulated errors it becomes a very unreliable quantity.

(c) Since $\rho^0$ and $\rho^0_{A}$ are both independent of temperature the Boocott-Clarius equation (IV) may be written in the form

$$\rho^0 = \left( \frac{\varepsilon_{A} - 1}{\varepsilon_{A} + 2} \right) \frac{M}{d} = A + \frac{B}{T}$$

where

$$A = \varepsilon_{A} \rho^0 + \rho^0_{A}$$

and

$$B = \frac{4\pi N n^2}{q_k} = \mu^0 \times T.$$

Thus $\rho^0$ should be linear with respect to $\frac{1}{T}$ and $\mu^0$ can be obtained from the slope of the line. The distortion polarization is the intercept at $\frac{1}{T} = 0$ which together with $\rho^0$ calculated from refractivity data permits $\rho^0_{A}$ to be evaluated by difference. This method is in error, however, if the dipole moment of the compound varies with temperature as is possible with molecules of a "flexible" type (\textit{a}).

Calculations are often based on the Boocott-Clarius equation but this can be applied only when dipolar interaction is absent - a condition fulfilled by gases at low pressure. However, accurate measurements on gases are very difficult and being restricted to compounds having a relatively high vapour pressure the field of investigation is small.
2. SOLUTIONS IN CONCERN

In 1931, Debye pointed out that on the analogy of the kinetic behaviour of a solute in a dilute solution, the equation derived for the molecular polarization of a substance in the ideal gas state should be applicable to a solute in dilute solution in a non-polar solvent provided mutual interaction were absent. The degree of dilution should obviously be as great as possible to avoid interaction between solute molecules but limits are set by the accuracy of measurements and the calculated polarizations. The use of solution however does permit of the investigation of many more compounds but the results must be accepted with caution as discussed later. The polarization of the solvent is usually assumed constant and equal to that for the pure material, while the polarization of the solution is taken as the sum of the polarization of its components.

In the latter has been proved by careful experiment for molecular extinction (5) and a similar relationship is assumed to hold for the polarization. Consider 1 cc of solution:

If the total polarization is given by \( \frac{e_{12} - 1}{e_{12} + 2} \) and that of each component by \( \frac{4}{3} \pi V_1 \alpha_1 \) and \( \frac{4}{3} \pi V_2 \alpha_2 \)

\[
\begin{align*}
\frac{e_{12} - 1}{e_{12} + 2} &= \frac{4}{3} \pi \left( V_1 \alpha_1 + V_2 \alpha_2 \right) \\
\alpha_1 &= \frac{V_1}{V_1 + V_2} \quad \alpha_2 = \frac{V_2}{V_1 + V_2} \quad d_{12} = \frac{V_1 \alpha_1 + V_2 \alpha_2}{N} \\
\frac{e_{12} - 1}{e_{12} + 2} \left( \frac{1}{d_{12}} \right) &= \frac{4}{3} \pi \left[ \frac{(V_1 + V_2) \alpha_1 \int_1 + (V_1 + V_2) \alpha_2 \int_2}{(V_1 + V_2) \int_1 \frac{M_1 \int_1 + (V_1 + V_2) \int_2 \frac{M_2 \int_2}{d_{12}}}{}} \right]
\end{align*}
\]

\[\varepsilon = \frac{e_{12} - 1}{e_{12} + 2} \left( \frac{M_1 \int_1 + M_2 \int_2}{d_{12}} \right) = \frac{4}{3} \pi N \alpha_1 \int_1 + \frac{4}{3} \pi N \alpha_2 \int_2. \text{ Page 10.} \]
\[ t_{P_2} = \int \int t_{P_2} \, f_2 \] ............. (v)

Similarly
\[ R_{\mu} = \int \int R_{\mu} \, f_2 \] = \left( \frac{n_2^2 - 1}{n_1^2 - 1} \right) \left( \frac{M_1 \, f_1 + M_2 \, f_2}{12} \right) \] ............. (vi)

where \( \alpha \) is the total polarizability;
\( v \) the number of molecules per cc;
\( f \) the mole fraction;
\( P \) the total molecular polarization
\( R \) the molecular refraction;

the subscripts 1, 2, and 3 denoting solution, solvent and solute respectively.

Thus \( P_2 \) or \( \frac{P_2}{R_2} \) can be calculated and it is found that \( P_2 \) decreases with increasing concentration. This effect is often attributed to an increase in association of the solute with increasing concentration but it has been pointed out by Bury and Jenkins (6) that it is possible for association to lead to an increase in \( \frac{P_2}{R_2} \). To date, however, no case is known where increases with increasing concentration and it is unlikely that association is the only factor operating. In order to eliminate the dependence on concentration the data are usually extrapolated to \( f = 0 \) to give the "polarization at infinite dilution, \( \frac{P_2}{R_2} \), when the solute molecules are considered to be outside the range of mutual interaction and each is surrounded by non-polar molecules of the solvent.

It is also found that solutions exhibit the same temperature dependence as gases, the solute polarization at infinite dilution...
varying linearly with the reciprocal of the absolute temperature. Thus the variables polarizations can be evaluated either by the temperature method (requiring observations at a number of temperatures) in conjunction with \( \varepsilon \) from refractive index data or by the refractivity method in which \( \varepsilon_2^2 \) is found at one temperature and \( \varepsilon + \delta \) eliminated by measurements of the molecular refractivity. The latter can be determined either on the pure polar solute, if this is a liquid, or more satisfactorily, by measurements on the solutions and application of equation VI. In most cases it is found that the values of \( R_2 \) so deduced are sensibly independent of the concentration.

2. SCHEL IRISH

The experimental work required for the evaluation of polarizations by the solution method is not difficult or complicated but the results frequently do not agree with those from vapour phase measurements. It has already been mentioned that the value of \( \varepsilon_2^2 \) is a function of the concentration and in addition it is found that \( \varepsilon_2^2 \) is not independent of the solvent used, i.e. there is a "solvent effect".

H. Miller (7) was the first to show clearly the dependence of the total polarization on the solvent used and many workers since have examined the problem and attempted to explain the phenomenon quantitatively. Consequently there are considerable data available for polarizations measured in solution together...
with many attempts to explain the solvent effect quantitatively, but the molecular types investigated have not been as simple as could be desired for the investigation of what is undoubtedly a very complex phenomenon. The present investigation has therefore been directed towards obtaining data with solutes of the simplest molecular configuration possible consistent with the requirements outlined below.

4. STATE OF EXPERIMENTATION

The object of the work is the effect of the shape of the solute molecule on the measured values of \( P_c \) and the applicability of the various equations that have been proposed. In order that the minimum of complications should be introduced and to reduce the investigation to as fundamental a basis as possible it was decided that non-polar solvents would be used; 'non-polar' that is in the broadest sense of the term since such materials as carbon tetrachloride and carbon disulfide were to be included. It was also realised that the order of the effects produced by the change in molecular shape would be small, requiring accurate measurements of dielectric constant. This is only possible with solutions of low dielectric constant and is discussed fully in the experimental section.

Choice of the solute was governed by the following considerations:

1) The simple molecular shapes are frequently used for theoretical treatments - a sphere and an ellipsoidal (prolate
spheroid) and it was decided to examine the difference in solvent effect associated with these two models.

3) The materials should not be known to form compounds with the more common non-polar solvents.

3) Free rotation in the molecules of a type that could alter their shape or the direction of the dipole had to be absent.

4) To facilitate handling and ensure the greatest possible accuracy in mixing up the solutions the materials should be either high boiling liquids or preferably solids.

5) If possible, the dipole moments of the two substances should be the same or very similar.

It proved impossible to fulfill all these conditions and the materials chosen were liquids:

\[ \text{\textit{1-buty1 chloride B.P. 50.0\(^\circ\)C.}} = 2.15^a \]

as the spherical molecule

\[ \text{\textit{Ethyl cyanide B.P. 51.7\(^\circ\)C.}} = 3.99 \]

As the ellipsoidal molecule.

Evidence of the spherical nature of the \(1\)-butyl chloride molecule is given by Bosch and Stevenson from an electron diffraction study (8); Baker and Smyth - proof of free rotation of the pure material in the solid state (9); Connor and Smyth - proof of the formation of a continuous series of solid solutions

\[ \text{* D = Debye Unit = 10^{-12} cm} \]
of 4-butyl chloride in carbon tetrachloride (10); Goss and Hardy
by the evaluation of a solvent effect constant and the fact that $P$
for Cl atom = 5.7 cc and $P$ for a methyl group = 5.0 cc (11).

It was of considerable interest to employ mixed non-polar
solvents, particularly if the dielectric constant could be matched
to that of one other solvent in use. This required a material
either liquid or solid, that was non-polar but which had a
considerably higher polarization than a reference solvent.

$\beta$-Dichlorobenzene proved satisfactory and solutions in carbon
tetrachloride and 1,4-dioxan were made up of approximately the
same dielectric constant as benzene.

The solvents used covered as wide a range of dielectric
constants as possible and included $\alpha$-xylene, $\beta$-heptene, benzene,
totalin, 1,4-dioxan, carbon tetrachloride, carbon disulphide,
dioxan + $\beta$-dichlorobenzene and carbon tetrachloride +
$\beta$-dichlorobenzene. Their preparation and physical constants
are given in Section 6. (Experimental) together with all
measurements on the solutions prepared from them.
G.

EXPERIMENTAL
The experimental data required were the composition, refractive index, density and dielectric constant of solutions of the solutes in each of the solvents. In order that the data could be extrapolated to infinite dilution (graphically or mathematically) when sufficient material was available, a set of eight solutions of increasing concentration of each solute in each solvent was used. This number of solutions required relatively large quantities of pure solvents but a survey of literature results had shown that the use of a smaller number was inadequate to yield a satisfactory plot for extrapolation. Experimental results are given in Tables 1 to 22 which include work by other authors at the same temperature.

1. AUXILIARY AND RELEVANT ERROR CONSIDERATIONS

The accuracy obtainable for the experimental data is limited by the type of measurements required but if calculations are finally based on the Nernst-Clapeyron equation then the value of $\mathcal{P}_2$ calculated is related to $f_2$, $e_{12}$, $d_{12}$, $\eta_{12}$ and the error in $e_{12}$ and $d_{12}$ as shown below (12):

$$\left(\frac{e_{12}-1}{e_{12}+2}\right)\left[M_1(1-f_2)+M_2f_2\right] = \mathcal{P}(1-f_2) + \mathcal{P}_2f_2 = \mathcal{P}_1$$

Now the accuracy with which $\mathcal{P}_2$ can be measured clearly depends on the concentration of the solution, for as $f_2$ diminishes so does the quantity $\mathcal{P}_3f_2$ and errors in the value of $\mathcal{P}_2$ derived at low concentration may be considerable. The influence of the other variables may be derived as follows:-
partial differentiation with respect to \( \varepsilon_{12} \) gives
\[
\frac{dP_2}{P_2} = \left[ \frac{3 \varepsilon_{12}}{\varepsilon_{12}^2 + \varepsilon_{12} - 2} \left( \frac{P_2}{P_2'} \right) \frac{1}{f_2} \right] \frac{d\varepsilon_{12}}{\varepsilon_{12}}
\]
where it is seen that the inaccuracy \( \frac{d\varepsilon_{12}}{\varepsilon_{12}} \) in the determination of the dielectric constant will cause a corresponding error \( \frac{dP_2}{P_2} \times K \)
in the molecular polarization of the solute. Similarly the error due to the inaccuracy \( \frac{d\delta_{12}}{\delta_{12}} \) can be expressed as
\[
- \frac{P_2}{P_2'} \cdot \frac{1}{f_2} \frac{d\delta_{12}}{\delta_{12}}
\]
italics differ from the equation involving dielectric constant by
leaking the factor \( \frac{3 \varepsilon_{12}}{\varepsilon_{12}^2 + \varepsilon_{12} - 2} \). This, for non-polar solvents, is approximately unity and hence dielectric constants must be measured with at least the same accuracy as densities. In addition for each case the error in \( P_2 \) is inversely proportional to \( f_2 \) and therefore becomes the more serious the lower the concentration.

Calculation of \( \beta \) based on refractive index requires the accuracy of \( n^2 \) to be the same as that of \( \varepsilon \) but the accuracy obtainable for \( n \) was limited to ca. \( \pm 0.01 \) for \( n = 1.5 \) by the apparatus available. Measurement of density with this or higher order of accuracy was not difficult even for the most volatile liquids used although a special pycnometer was required (see later).

The controlling factor in the accuracy of the results was the determination of dielectric constants and to obtain the above degree of accuracy it was necessary that values of \( \varepsilon \) ca. 2.9 should be obtained to within \( \pm 0.0003 \) units of the stated value. The design and construction of an apparatus inherently capable of giving this accuracy is discussed later.
The general arrangement of the apparatus is shown in Figure 1.

(a) Thermostat

The initial consideration of almost all research in physical chemistry is the provision of a thermostat, the temperature control of which is such that the variations occurring in terms of the constants being measured are less than the accuracy obtainable in the measurements. Taking benzene as a typical solvent its temperature coefficients are:

<table>
<thead>
<tr>
<th>Property</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant</td>
<td>-0.0008 units/°C</td>
</tr>
<tr>
<td>Refractive index</td>
<td>-0.0001 &quot;</td>
</tr>
<tr>
<td>Cubical expansion</td>
<td>+0.0010 &quot;</td>
</tr>
</tbody>
</table>

Thus to obtain an accuracy of better than 0.01% the temperature control required for

- Dielectric constant is $\Delta T < 0.1°C$
- Refractive index $\Delta T < 0.1°C$

The influence of temperature on the density measurements can best be found as follows:

If the parameter is glass (cubical expansion $2.50 \times 10^{-6}$) and has a volume of 10 ml at 30°C, its volume at 25.1°C will be

$$10 \left(1 + 2.50 \times 10^{-6}\right) \text{ml}.$$

If the density of benzene at 20°C is 0.70350 g/ml then its density at 25.1°C will be

$$0.70350 \times 1.002104.$$
. . actual mass of benzene in pyrimeter at 25.1°C (its volume being assumed 10 ml) is \( \frac{0.8723}{1.000284} \times 10 (1 + 0.03 \times 10^{-3}) \) and its "density" (measured) = \( \frac{0.8723}{1.000284} \times 10 (1 + 0.03 \times 10^{-3}) \)
\[ \text{\( = 0.8722 \text{ g/ml} \)} \]
\[ \text{\( \)} \]
\[ \text{i.e. a decrease of 1 unit in the 4th place.} \]
\[ \text{Therefore an accuracy of \( \pm 0.03\% \) requires a temperature control of} \]
\[ \text{\( \pm 0.05^\circ C \).} \]

A volume-accuracy regulator and efficient stirring will give better control than to \( \pm 0.03^\circ C \) but at the commencement of this work it was impossible to obtain a glass regulator or a tank of the required dimensions and one of each was constructed. The regulator was made with insufficient volume to provide the required degree of control and fortunately there became available a commercial model which proved satisfactory. The stirrer used was a fixed propeller direct coupled to a 0.01 H.P. motor, all the electrical connections being taken to a small control panel for operation from 110 v. A.C. The temperature control finally obtained was \( \pm 0.0005^\circ C \) and there was no gradient either horizontally or vertically in the centre of the bath.

(b) Balance, Weights and Weighings

All weighings up to 200 g were made on a balance sensitive to 0.05 mg. The temperature of the balance case was kept between 22-23°C but no attempt was made to adjust the humidity, a justifiable procedure since all weighings were by difference and each set made on the same day.

A set of aluminium plated brass weights were calibrated.
by the method of Richards (13). Throughout the calibration each
next point of the balance (by the method of swigs) was taken as
many times as required to obtain successive readings differing by
less than 0.05 mg. This ensured that the accuracy of the calibration
was better than that required for subsequent work and since all
calculations were based on the ratio of weights there was no need
to correct to absolute values or determine the ratio of the sums of
the balance. The 5 g. piece was taken as standard. Weighings over
300 g. were made on an oscillating balance sensitive to 5 mg. which was
sufficiently accurate for making up the mixed solvents since the
weights of materials involved were greater than 100 g.

All solutions were made up in 100 ml. stoppered flasks
curling to their necks it was necessary to leave each one in the
balance to equilibrate before weighing. Four flasks were kept in
the case at any one time, one of which was on the balance pan, so
that each flask had a residence time of about 15 minutes but the
total weighing time was kept to a minimum. The pyrometer was
left on the balance 10 minutes before weighing and a balance zero
was taken at the beginning, middle and end of each set of weighings.
A buoyancy correction was applied to all weights and was calculated
as follows:
Let $M$ be the apparent mass of the object in air where

the force (absolute) value of the 'weights' used.

\[ \rho = \text{absolute density of the 'weight' material.} \]

\[ \delta = \text{absolute density of the object weighed.} \]

\[ \sigma = \text{ambient air density.} \]

\[ X = \text{correct mass of object in vacuo.} \]

\[ \lambda = \text{ratio of lengths of arms of balance.} \]

\[ \lambda \frac{M}{\rho} (\rho - \sigma) g = \frac{X}{\delta} (\delta - \sigma) g \quad \text{or} \quad X = M \frac{\delta}{\rho} \left( \frac{\rho - \sigma}{\delta - \sigma} \right) \lambda \]

\[ \therefore \text{The correction to be added to } M \text{ is:} \]

\[ M \frac{\delta}{\rho} \left( \frac{\rho - \sigma}{\delta - \sigma} \right) \lambda - M \lambda = M \frac{\delta}{\rho} \left( \frac{\rho - \delta}{\delta - \sigma} \right) \lambda \]

or neglecting $\sigma$ of $\delta$ and since $\lambda$ differs only slightly from unity

\[ \approx M \sigma \left( \frac{1}{\rho} - \frac{1}{\delta} \right) \]

A curve was drawn giving the correction to $M$ in mps/g for various densities measured assuming the air to be 53% saturated with water.

(c) Refractometer Tests

This was measured for sodium light by means of a Folsenich refractometer, temperature control being affected by circulating water from the thermostat. It was found necessary to pull the water through the instrument and not connect it to the delivery of the centrifugal pump since the latter caused a temperature rise of 2-3°C due to the small flow obtainable.

The losses from the open cell were a source of error and to reduce this to a minimum it was filled to 2/3rd of its depth.
with solution that had been thermostated for 15 minutes. This ensured that readings could immediately be taken without waiting for temperature equilibrium to be established. It was unfortunate that only one prism was available fitted with a cell, with the result that the refractive index of the solution in carbon disulfide could not be measured.

(d) Pyknometer and Density Determinations

Owing to the volatility of the solutions used and the accuracy required the choice of pyknometer was somewhat limited. A modified form of the Perkin-Elmer direct pyknometer (14) was finally adopted and is shown in Figure 2. Since solutions were contained in stoppered 100 ml. graduated flasks and to avoid handling errors the side arms were made of sufficient length to reach to the bottom of the flasks for direct filling. It was constructed of standard soda glass tubing the positions of attachment of the side arms and their slope relative to the main bulb being chosen to avoid trapping air bubbles on filling. Its volume was 7.74 ml.

Duplicate determinations by different observers with different pyknometers (of this design) have consistently given values of the density of benzene differing by only ±0.001 and it was shown experimentally that with solutions in volatile solvents it was inessential whether filling was effected by gentle suction or pressure. The former was adopted since it enabled the following simple technique to be used. The pyknometer was dried by a stream of dry nitrogen and weighed empty before each set of determinations. It was rinsed out twice with each fresh...
solution (taken in order of increasing solute concentration) and filled by inverting the shorter arm into the flask and applying very gentle suction to the other. Then fill it was removed, immediately inverted and placed in a container in the thermostat for 15 minutes with the water level $\frac{3}{4}$ below the top of the arm. The volume of solution was adjusted by applying a folded filter paper to the top of the shorter capillary to bring the level in the other arm to the mark. The arms were then fitted and the pyrometer removed, dried and polished with a silk cloth before weighing. The solution level could be set to closer than 1 mm of the mark and even allowing an error of this magnitude the discrepancy introduced into the density would not have been greater than 0.001%. The pyrometer was calibrated with air-free distilled water at various times throughout the week.

(c) Determination of Dielectric Constants

All methods are ultimately based on the capacity of a condenser and therefore the experimental work is that of measurement of capacity. The type of apparatus required depends on the minimum charge of capacity to be measured. Based on previous experience the capacity of the condenser-cells for liquids but with air as dielectric was at most $1000 \mu F$ then to a first approximation $1000 \mu F$ was the capacity for containing a liquid of dielectric constant $\epsilon$. It was necessary for the dielectric constant to be

\[ * \mu F = \frac{\mu}{\epsilon} = 10^{-13} \text{Fermi is used throughout.} \]
measured to \( \pm 0.003 \) of a unit (0.017 of 2.0) and therefore the
capacity was required with an accuracy of \( \pm 0.03 \) pF. This set
the limit for the minimum sensitivity of the apparatus and also the
range of dielectric constants that could be measured since at all
times one had to be able to match the standard condenser to the
test-cell and simultaneously read the standard condenser to \( \pm 0.03 \) pF.

Capacitance are almost invariably determined by a method
employing alternating current, and it was important that the
frequency should not be too high to avoid introducing the
complication of anomalous dispersion (the decrease of \( \varepsilon' \) and the
polarization with increasing frequency). About 1 megacycle/sec
was considered most suitable. Since maximum sensitivity was
required the circuits employed for gases were investigated as
robustness could be obtained by some sacrifice in sensitivity
without the accuracy falling below that required. A modified
form of a circuit employed by Le Fevre and Russell (12) was built,
and is given in Figure 5 together with component values.

Essentially it consisted of a crystal microphone, driven
coupled to a regenerative oscillator, the tuned circuit of the
latter having a fixed inductance and variable capacity made up of
the condensers shown in Figure 6. Details of the precision
condensers are given in the section dealing with the calibration
of this instrument. Resistors were chosen for the valves in the
oscillator because of the ease of control of the radio-frequency
power developed by variation of the screen voltage and in the
wave-meter to take full advantage of the high gain available.
permitting the minimum of coupling between the two circuits while maintaining full-scale deflection on the microammeter at resonance.

(4) The oscillator was of the regenerative type with the tuned circuit parallel fed so that all the condensers were at zero D.C. potential. The components were chosen so that the fundamental frequency was ca. 1000 hertz and the oscillator could be set at this frequency with materials of dielectric constants 1.5-5.5 in the condenser cell (capacity ca. 100 pF when containing air). Initially all condensers were permanently in the tuned circuit, it being proposed to bring the frequency to a fixed value at the start of a run and then condense for subsequent changes of $C_x$ by variation of $C_1$. It was found, however, that the frequency stability was unsatisfactory, exhibiting a drift of about 1500 c.p.s. over 6 hours - equivalent to a 1.6 pF change of capacity. This drift could have been eliminated by the separation and thermostating of components, but its presence was rendered unimportant by using a substitution method in which the capacity of the standard condenser was always matched to that of the liquid cell. To make the change of circuit required to substitute the cell for the standard condenser as rapid as possible a magnetic relay was used the two capacities being compared over such a short period of time that the change of frequency due to the drift was negligible. It was considered advisable to screen the relay coil magnetically and all the connecting leads were kept as short and rigid as possible.
An initially unexpected source of error was the small capacity (say \( n \), Figure 4) from the centre 'leaf' of the relay to earth via the other 'leaf' not in use, the latter being returned to earth through the cell or standard condenser. \( n \) varied with the capacity of its series condenser and to make it a constant it was arranged that the contacts not in use were automatically earthed.

The oscillator and wave-meter (see later) were built in a steel case providing effective electrostatic and magnetic screening; the only connection between the oscillator and wave-meter being by a very loose link coupling passing through the internal screen. The front panel was fitted with the microammeter, the battery connection, the oscillator condenser controls and a coaxial connection. The change-over relay was mounted on the side of the thermostat and connected to the oscillator by a length of coaxial cable, rigid wiring only being necessary from the relay to the cell and standard condenser. The range required for the latter was governed by the accuracy with which it could be read and the fact that under all conditions it must be capable of matching the capacity of the cell. To maintain the same percentage accuracy throughout all measurements the smallest values of dielectric constant measured required the greatest sensitivity. Taking the limit as \( \varepsilon = 1.0 \) (air), to be determined to 0.01\% the capacity of the cell (air dielectric) as 100 \( \mu F \) and the accuracy of setting the standard condenser as \( \frac{1}{3} \) of the total capacity change - the total capacity change required was

\[
100 \times 0.001 \times \frac{1}{3} \times 50,000 = 300 \mu F
\]

The standard condenser was built to have this capacity.
range over the arc covered by the engravings while its total capacity
range was 20-300 pf. Thus the maximum dielectric constant that
could be measured using a cell of 100 pf capacity (with air) was
ca. 3.0.

The remaining condensers in the oscillator were of
good quality and chosen so that the frequency could be brought to
1000 kc/sec for all settings of the precision condenser and at the
same time provide a sufficiently fine control necessitated by the
sharpness of the setting point.

At 1000 kc/sec the oscillator developed ca. 35 volts
P.M.S. and visual examination of the waveform on a cathode ray
oscilloscope did not show any deviation from a sine wave.

(i) The frequency was essentially a valve voltmeter employing
self bias and anode blank detection with a 0-500 microammeter on
the anode load. A 1000.0 kc/sec quartz crystal was connected in
parallel with the grid tuning, the latter being preset to 1000 kc/
sec by means of a master oscillator.

On tuning the variable oscillator through 1000 kc/
sec the anode current of the master rose and fell with the
characteristic form of a resonance curve but as the frequency
passed that of the crystal the current fell sharply almost to the no
radio-frequency voltage reading and back again:-
The width of the resultting dip was equivalent to a change of capacity of ca. 0.4 $\text{pF}$ and working on the sides of this envelope the condenser could be set to within $\frac{1}{100}$ of this value, i.e. 0.004 $\text{pF}$.

If a galvanometer had been used in place of the microammeter the sensitivity could have been increased considerably but this was not required for the present work as other factors gave rise to errors of greater magnitude.

(iii) Theory of Resonance: The behaviour of a quartz plate in the above manner can be explained as follows— (13).

A quartz resonator can be shown to be equivalent to the following circuit

\[ \begin{align*}
 &L \quad R \quad \frac{1}{C} \\
 &\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad K \quad K_1
\end{align*} \]

$L$, $R$ and $C$ are due to the quartz itself, $K$ to the charges on the face of the quartz and $K_1$ the capacity from the electrodes to the quartz faces.

$L$, $C$ and $R$ are related to the chemical properties of the quartz plate.
At any frequency the network LC is in parallel with E and behaves as a certain resistance $R_o$ in series with a certain capacity $C_0$. This equivalent circuit is itself in series with $R_2$ so that at some frequency the whole system will be in resonance and the effective impedance will equal $R_0$; that is provided $R_2$ is not so small as to require an apparent inductance larger than the quarts network can provide.

If the whole system is placed in parallel with a tuned circuit then at some frequency this circuit will in effect be shunted by a non-inductive resistance. In this condition we shall reach the bottom of the curve as described previously or at any rate be very near it. It is evident that the frequency corresponding to the bottom of the curve will depend slightly both on the value of the air gap $R_2$ and the proximity to resonance of the tuned circuit. The effective decrement of the quarts is, however, so small that the effect of the air gap on the circuit is negligible within wide limits. The main effect of detuning is to 'blunt' the bottom of the curve as but the displacement is negligible. The stability of the frequency at which the dip occurs will be almost that of the crystal itself which is 2 parts in $10^6$ per °C.

Examination of the actual resonance curve obtained, Figure 5, will show that there are present six small dips, all except one on the same side of the largest. In this connection Hefflin says "Quartz plate resonators used in this manner have the great practical difficulty that usually there are several natural
frequencies all very close together and there may well be as many as
four cross-over within a frequency range of 12. The cause of these
alternative frequencies is unknown; it may be due to irregularities
in the quartz, the shape of the boundary or possibly it is a necessary
consequence of the mechanics of the system - the trouble seems to be
absent in bar oscillators but with plates it renders it difficult to
be sure which cross-over belongs to which frequency."

Considerable difficulty was experienced due to these
'spurious' frequencies and initially each was capable of giving a
full dip of the anode current. The trouble was only removed when
the crystal was connected in the circuit through a 25 pF condenser
to the grid of the valve and the stray-capacity of the holder to
earth. As can be seen this did not completely eliminate the trouble
and one cannot state rigidly that the remaining cross-overs was at the
radiofrequency of the crystal (1000.6 kec/sec). It does, however,
soon reasonable to assume that the frequency for which the crystal
was cut could be that of its most easily excited mode and therefore
the frequency of the largest dip was taken as that quoted by the
maker. Fortunately the purpose for which it was required the
precise value of the frequency was immaterial, provided it remained
constant.

(iv) Effect of Conductivity of Solution. Fundamentally all
measurements were based on the oscillator being tuned to a fixed
frequency and therefore the 'Q' of the circuits involved was
unimportant as also were any variations in radio-frequency power

Page 37.
that occurred with change of frequency. It was necessary, however, that the oscillator frequency should not be affected by the conductance of the liquid cell and that this was so may be shown as follows:

\[ I = \frac{E_0 \sin \omega t}{\sqrt{R^2 + L^2 \omega^2}} \]

where \( L \) is inductance of coil in henries,
\( R \) resistance of coil and leads in ohms,
\( C \) capacity of condenser in farads,
\( R \) all resistive losses in the condenser, connectors, valves, etc. in ohms.

Let the frequency of the alternating e.m.f. between the points shown be \( \frac{\omega}{2\pi} \) and at any instant its value \( E_0 \sin \omega t \). Where \( E_0 \) is the peak value.

The instantaneous current through \( L \) and \( R \) will be

\[ I_L = \frac{E_0 \sin (\omega t - \theta)}{\sqrt{R^2 + L^2 \omega^2}} \quad \text{and lags the applied voltage by} \quad \theta = \tan^{-1} \frac{\omega}{R} \]

The instantaneous current through \( R \) will be

\[ I_R = \frac{E_0 \sin \omega t}{R} \quad \text{and is in phase with the applied voltage} \]

The instantaneous current through \( C \) will be

\[ I_C = \omega CE_0 \sin (\omega t + \frac{\pi}{2}) \quad \text{and leads the applied voltage by} \quad \frac{\pi}{2} \]

For parallel resonance (i.e. oscillating condition of circuit) the
resultant current must be in phase with the applied voltage. The resultant current is:

$$I = I_L + I_R + I_C$$

and with due regard for phase differences

$$I = E_0 \sin \omega t \sqrt{\left(\omega C - \frac{L_\omega}{r^2 + L_\omega^2}\right)^2 + \left(\frac{1}{R} + \frac{r}{r^2 + L_\omega^2}\right)^2}$$

leading the applied voltage by

$$\phi = \tan^{-1} \left(\frac{\omega C - \frac{L_\omega}{r^2 + L_\omega^2}}{\frac{1}{R} + \frac{r}{r^2 + L_\omega^2}}\right)$$

This is in phase with $E_0 \sin \omega t$, when $\phi = 0$

$$i.e. \omega C = \frac{L_\omega}{r^2 + L_\omega^2}$$
or

$$\omega = \frac{1}{\sqrt{LC}} \sqrt{1 + \frac{L_\omega^2}{r^2}}$$

which is independent of $R$.

The effect of $R$ is to decrease the radio frequency power developed by the oscillator resulting in a lower peak rotor reading but the capacity required to tune to the bottom of the curve is unaffected.

(v) The Standard Precision Capacitor was manufactured by

Necora. Daro Instruments Ltd. of Brentford, Middlesex, and had a nominal capacity range of 50-350 pF. The rotor was worm driven and the micros claimed a discrimination of about 1 part in 25,000 of the full scale setting and a temperature coefficient of 40,000/°C.

Before calibration a new vernier was fitted, dividing the scale into 200,000 divisions, but the use of this was limited by the variation in thickness of the micros cogwheels. To eliminate errors due to backlash all readings were taken on the leading edge of the cogwheels approaching the setting in the direction of increasing capacity.
(vi) Calibration of the standard condenser was affected by a small variable capacity and high grade fused condenser in parallel with the precision condenser and it was found that the capacity of the standard condenser showed a marked dependence on the rotations of the control knob. This was due to an error in either the calibration of the dial or, more likely, the generation of the varnish and to facilitate interpolation between the points obtained an attempt was made to fit a recurrent waveform along the calibration curve. This was not possible and after critical examination showed that the step value (ca. 2.0 pF) had not been constant during calibration. This was a result of the small 'step' condenser not being thermostatted and the fact that setting the standard condenser was lengthy as a result of a heavy spring in the motion thereby requiring two days to calibrate the complete range. Subsequently a condenser made by H. S. Sullivan Ltd. became available which was readily calibrated by the step method in a short period of time (less than one day) and the Darr's condenser was calibrated directly against it. This procedure was adopted because the two condensers could readily be compared using the relay system employed for dielectric constant measurements and did not involve so many resettings of the Darr condenser. The calibration of the Sullivan condenser was not questioned as the change in reading for each step was constant over almost the whole of the dial, a check that was not possible with the Darr's instrument due to the complex form of the calibration curve.
(vii) The conductivity-cell for liquids was a modified form of that introduced by Sayles and Balinec (17) and is shown in Figure 6. It consisted of two concentric glass tubes fused into a unit at one end, inlet and outlet tubes being provided for the smaller space. The outer surface of the inner tube and the inner surface of the outer tube were heavily silvered for about \( \frac{1}{3} \) of the length. Connection to the silver plates was made by platinum wires sealed through the respective glass surfaces, passing into the interior of the inner tube and into a side arm sealed to the outer tube respectively. In both cases contact with the main leads was effected via a pool of mercury, the centre lead being taken to a glass cup, integral with the top of the cell. Connection to the oscillator was by means of rigid copper leads from A and B to steel cups containing mercury and mounted on a 'Picotone' block at the side of the thermostat. To make the cell more rigid and less fragile tie-bars of glass rod were fitted between all the vertical side arms and the central tube, the latter being kept as wide as possible to reduce the capacity between the central wire and the water of the thermostat (See section 6. 2. (c) (viii) page 44). To ensure that the cell was always in the same position in the thermostat it was held in a submersed brass frame and to avoid variations in strain exposure the water level was kept constant and stirring stopped while taking readings. Silvering of the cell was carried out, applying the solution and technique used by Sayles (17) - the quality of the films obtained fully supporting his claims. No Ostwald corrections to be applied to the measured
diemctric constants (see later) the same cell was used throughout and always silicoided up to the same level; its capacity when containing nitrogen was about 130 pF. The cell was filled directly from the flask holding the liquids by pressure of dry nitrogen from a cylinder, the glass delivery tube being ground to make a ball joint with the cell side arm 6 (Figure 7). The solutions were used in order of increasing solute concentration and the cell washed out twice with 5 or 6 ccs of each new solution before filling. To ensure that air bubbles were not trapped the solution was pumped up and down the annular space by squeezing a rubber tube on the side arm 5 before putting on the cap. The dielectric constants were evaluated as follows:

The cell was washed with pure benzene and dried by passing nitrogen from a cylinder for at least half an hour. (The nitrogen was found to be so dry that it had no effect on phosphorus pentoxide after several hours of use). It was then placed in the thermostat and after fifteen minutes matched by the standard condenser. With the cell in the circuit the oscillator was tuned on the side of the crystal dip, the standard condenser substituted and adjusted to bring the oscillator to the same frequency as before. Several change-overs from cell to condenser were made to check the match. Should the standard condenser have been set too high it was reduced below the required value and reset in the direction of increasing capacity. The standard condenser was then returned to the cell containing dry nitrogen, benzene and all the solutions in order of increasing solute concentration. Readings
for benzene, nitrogen and the solvent were taken before and after each set of solutions.

Let \( C_0 \) be the capacity of the evacuated cell

\[ C_2 \] the S.I.C. of the solution at 25°C

Let \( C_2, C_3 \) and \( C_4 \) be the capacity in the standard container required to match the cell containing nitrogen, benzene and solution respectively.

Let \( a \) be the stray capacities associated with the cell

\[ b \] standard container.

The S.I.C. of nitrogen and benzene at 25°C were taken as 1.0005 and 2.3725 \((10)\) respectively.

Then

\[ 1.0005C_0 + a = C_1 + b \]

\[ 2.3725C_0 + a = C_2 + b \]

\[ \epsilon_2C_0 + a = C_3 + b \]

where \( C_0 \) \((2.3725 - 1.0005) = C_2 - C_1 \)

\( C_0 \) \((\epsilon_2 - 1.0005) = C_3 - C_1 \)

\[ \therefore \epsilon_2 = C_3 - C_2 \quad (1.2725) + 1.0005 \]

\[ \epsilon_2 = C_1 \]

Since this equation involves only the ratio of changes in capacity of the standard container the units of the calibration were immaterial and the absolute capacity was not required.

(viii.) Formation of Determined Dielectric Constant. Theoretically the liquid container should afford direct proportionality between dielectric constant and capacity, in practice an ideal that can never be reached because the dielectric medium cannot fill the whole space between the coacting plates. In the type of container adopted, however, the deviation from proportionality is very small.
and is due to the region at the edge of the silvering and the capacity from the central wire to the thermostat water. The errors arising from these sources could have been reduced to negligible proportions by the use of oil instead of water in the thermostat but difficulties would have been experienced in using the pyrometer and thermostating the refractometer. It was decided therefore to use water and apply corrections to the dielectric constants measured. Consider the conventionalised form of the cell:

Let dielectric constant of

\[ \text{air} = 1 \]

" dielectric constant of

\[ \text{glass} = \varepsilon_1 \]

" dielectric constant of

\[ \text{solution} = \varepsilon_2 \]

Assuming that everywhere the tubes of induction are perpendicular to the central wire we may write

dom expressions for the stray capacitance. The capacity between the central wire and the water over the length \( l_1 \) is constant and independent of the solution. The capacity for the length \( l_2 \) however, is variable and given by
\[ C_{l_2} = \frac{\log_{10} \frac{a}{r}}{\epsilon_1} + \frac{\log_{10} \frac{a+t}{a}}{\epsilon_2} + \frac{\log_{10} \frac{a+d+1}{a+1}}{\epsilon_2} + \frac{\log_{10} \frac{a+d+2t}{a+d+t}}{\epsilon_1} \] \]

This contains a term including the dielectric constant of the solution so that \( C_{l_2} \) is neither constant nor proportional to \( \epsilon_2 \).

For the cell used the values were:

\[
\begin{align*}
r &= 0.05 \text{ cm}, & a &= 1 \text{ cm}, & d &= 0.12 \text{ cm}, \\
t &= 0.11 \text{ cm}, & l_2 &= 6 \text{ cm}
\end{align*}
\]

Hence \( C_{l_2} \) with air in the cell is 1.035 pF,

\[ C_{l_2} \] with a liquid of \( \epsilon = 3.5 \) is 1.000 pF

This variation of 0.035 pF will be the maximum encountered and is well below the permissible variation required to obtain dielectric constants of about 3.5 with an accuracy of \( \pm 0.03 \% \) (\( \pm 0.02 \% \) of \( 100 \times 3.5 = \pm 0.005 \) pF). It has therefore been neglected.

The greatest source of error is the 'edge-effect' due to the capacity from the inner silver electrode to the thermostat wall. Geplin (19) has considered this in detail and he records an attempt to eliminate it by the use of a glass ring but the clearance required was too small to deposit one of silver.

Since the edge-effect correction is complex and not capable of calculation it was determined experimentally. Initially the water thermostat was used and the changes of capacity measured as the water level was lowered below the edge of the silvering but this did not prove satisfactory as the outside of the cell was not left dry. A second attempt reversing the procedure and raising the water in steps until the dry cell still gave inconsistent results and the method was abandoned.
The thermostat was then successfully converted to
air operation by fitting a cardboard lid and a small motor-driven
fan. The cell was fitted with an earthen sleeve that could be
moved up and down to add or remove the edge capacity from the
total. The sleeve was of annealed copper foil and soldered to a
semi-ring of wire and was held to the walls of the cell by rubber
bands. The wire ring was added to avoid distortion by the torque
applied when moving cell to provide an earthing connection. It
was not possible to remove the cell from the carrier when fitted
with the sleeve so that it had to be filled and emptied in situ and
to ensure as rapid thermostating as possible solutions were kept in
a water thermostat at 25°C. To provide a series of liquids of
increasing dielectric constant a mixture of carbon tetrachloride
and chloroform was used and was forced into the cell by nitrogen
pressure. At the end of each set of measurements the solution was
withdrawn into the original flask to which more chloroform had been
added, well mixed and returned to the cell. Three positions of
the shield were used with all solution:

\[ \text{Positions of Top Sleeve} \]

\[ \text{Length of Sleeve} \]

\[ \text{Central Wire} \]

\[ \text{Silver Electrode Layers} \]

The difference between positions 1 and 2 provided data for the
capacity between the shield and the central wire to correct the
edge-effect difference $E$ minus $E$. Results were obtained for 15 different solutions in the cell and the 'edge-capacity' plotted against dielectric constant. The results all lie fairly well on a curve, Figure 3, but exhibit considerable spread at the highest dielectric constants; they are however quite satisfactory for the present work and yield results within the order of accuracy required. To facilitate calculations the dielectric constant corrections (in units of the 6th decimal place) were calculated and plotted against the dielectric constant as measured (i.e. uncorrected). These curves were only applicable to the specific condenser-cell used at 25°C.

2. PREPARATION OF SOLUTIONS

The following solutions were investigated:

- $\text{D}_{4}$-dichloroethane and tetrahydrofuran in benzene, carbon tetrachloride,
- 1:4-dioxane, $\text{p}$-laxene, carbon disulphide, toluene, $\text{p}$-dichlorobenzene + carbon tetrachloride, $\text{p}$-dichlorobenzene + 1:4-dioxane.
- $\text{D}_{4}$-dichloroethane in $\text{p}$-heptane.

100 ml stoppered graduated flasks were used throughout, dried at 110°C, blown out with dry nitrogen and cooled in a desiccator over calcium chloride. In all cases they were weighed empty at the beginning of a run. Since volatile solvents and solutes were used special care was needed for the preparation of the sets of solutions. Three different techniques were used as follows:

(a) The solvent was first weighed out into the flasks, solute added from a burette and the solution weighed. This method was used for $\text{D}_{4}$-dichloroethane in benzene, carbon
tetramethyloxane, dioxan, 2-hexane, 2-hexyne, tetralin, carbon tetramethyl iodide, dioxan, carbon tetraiodomethane, dioxan + 2,2-dichlorobenzene.

(b) A ca. 10% wt. solution was made up by weighing solute
into solvent. This concentrated solution was weighed
out into the flasks from a burette, more solvent added and the
final solution weighed. This method was used for methyl cyanide
in: 2-hexane, carbon tetramethyl iodide, dioxan, carbon tetraiodomethane + 2,2-dichlorobenzene, dioxan + 2,2-dichlorobenzene.

(c) The neat concentrated solution required was prepared in
bulk (500 ml.) by weighing out the solvent and adding the
weighed solute in a sealed capsule which was then broken. This
solution was weighed out into the flasks, further solvent added and
reweighed. This method was used for methyl cyanide in:
2-hexane, carbon disulphide, tetralin; 2-butyl chloride in carbon
disulphide.

In all cases the solvent was transferred by pressure of dry nitrogen.
Methyl cyanide presented some difficulties due to the low
concentrations required and its surprisingly low solubility in
2-hexane and carbon disulphide. The solutions of 2-butyl
chloride in carbon disulphide were prepared by method 3 since it
seemed probable that the minimum of errors would be introduced by
vapour losses (due to the low boiling points of both materials
(52°C and 40°C respectively). Any one set of solutions was made
up in one day, each solution being 50-60 ml. in volume. This
was the minimum quantity on which all the measurements could be
made, the object being to keep the total volume of solvents required
to a minimum.
The 'mixed solvents' used were prepared in a 500 ml. stoppered graduated flask, the p-dichlorobenzene being weighed in first and the carbon tetrachloride or dichlor ethane second, the quantities required having been determined previously to give a solution of dielectric constant of about 2.27. Before the final weighing and owing to the large fall in temperature on preparation of the solutions it was necessary to allow the flask and contents to stand for about one hour until the condensed film of moisture evaporated.

Examination of results in the literature showed that the use of only four or five solutions did not provide sufficient data for extrapolation when the experimental errors were taken into account. It was decided, therefore, to use not less than eight solutions for all the solvents investigated this being chosen as a compromise between too few results and protracted experimental work.

4. COND. OF MEASUREMENT

Of the three physical constants required for each solution, dielectric constant is the most susceptible to changes of concentration or absorption of water. This therefore was determined first and on the first day following the preparation of the solutions. Density and refractive index were measured simultaneously on the second day.

5. PREPARATION OF SOLVENT AND SOLUTION

(a) Distillation

The preparation of relatively inert pure liquid compounds with low freezing points is a matter of some difficulty and usually involves several distillations. To take full advantage of the latter
operation two glass fractionating columns were constructed with the
general arrangement as shown in Figure 9. They were packed with
3/16" diameter Pernex glass helices, the packed sections being 3' 5"
x 1" diameter and 2' 3' x ½" diameter and equivalent to 35 and 20
theoretical plates respectively. A reflux ratio of about 15/1 was
used but since gas heating was employed it was not possible to
control this closely or to ensure that operation was always optimum
(about 84% of the flood point). Before use the columns were
thoroughly purged with dry nitrogen. Except in the case of
tetralin all liquids were finally fractionated and collected and
stored in long necked containers (Figure 10), the smaller column
being used for 2-butoxy chloride and methyl cyanide only. Fractions
from the columns were only collected after effluents had started and
the column head temperature had risen to a constant value. Since
only almost pure single substances were fractionated and the column
heads were well lagged, the column head temperature, after
correction to 760 mm of mercury pressure, has been taken as the
nominal boiling point.

(b) Symbols

The symbols for physical constants have the following
significance unless otherwise stated:
\( d_{4}^{25} \) Density at 25°C g/ml.

\( n_{D}^{25} \) Refractive index for the sodium D lines at 25°C.

\( \varepsilon_{25} \) Dielectric constant at 25°C.

B.P. Boiling point 90° C under 760 mm mercury pressure.

(i) \( \beta \)-Butyl Chloride. Molecular Weight 92.87 British Drug

Rusca Laboratory Reagent \( \beta \)-butyl chloride, was distilled, about 7% being rejected at the beginning and end. It was dried over two lots of freshly heated potassium carbonate and fractionated from freshly heated anhydrous sodium sulphate. Samples were collected and sealed in glass capsules - each being sufficient for one set of solutions. Two preparations were made starting from fresh material each time and the physical constants obtained were:

I  
\( d_{4}^{25} \) 0.83714;  \( n_{D}^{25} \) 1.3236;  B.P. 50.8;

II  
" 0.83703;  " 1.3235;  " 50.8;

Previously reported figures are:

\( d_{4}^{25} \) 0.8347 (20);  0.83529 (21);  0.8373 interpolated (22) (23);

" 0.8377 extrapolated (24).

B.P. 50.6 (25);  50.7 (21);  50.6, 50.8/755 mm (23).

(ii) Isobutyl Chloride. Molecular Weight 94.83 Material supplied by Light and Co. of Gravesbury was purified by the method proposed by Codley and Hartington (27). It was kept over solid
potassium hydroxide for one week to remove traces of acetic acid,
formed by hydrolysis, then allowed to stand for one week over anhydrous
calcium chloride to remove any ammonia present. It was finally refluxed
over phosphorus pentoxide and distilled onto fresh phosphorus pentoxide
ten times, a procedure carried out by Walden and Birk (23), who claimed
to have finally obtained methyl cyanide that did not form an orange
colour with this reagent after six treatments. This claim was not
substantiated during the present writer's work, the methyl cyanide
still forming orange material on the tenth treatment. However,
since the physical properties after the third and tenth treatments
were identical the material was fractionated and samples, each
sufficient for one run, collected and sealed in glass capsules.

The preparations were made:

\[
\begin{align*}
I & : d^{25} = 0.77074; \quad \nu_D^2 = 1.5210; \quad \text{B.P. 61.7.} \\
II & : \quad 0.77070; \quad \nu_D = 1.5415; \quad \text{61.7.}
\end{align*}
\]

Previously reported figures are:

\[
\begin{align*}
d^2 & : 0.77033 (23); \quad 0.7705 (23); \quad 0.7772 (52); \quad 0.7770 (I.C.T.). \\
\nu_D^2 & : 1.5415 (23); \quad 1.512 (52). \\
\text{B.P.} & : 61.8 (27); \quad 61.2/703 \text{ mm} (23); \quad 61.6 (52); \quad 61.6/703 \text{ mm} (52); \\
& \quad 61.4/703 \text{ mm} (23).
\end{align*}
\]

(iii) \textit{Aniline. Molecular Weight 93.12} \quad \text{British Drug Houses Ltd.}

"Redistilled" aniline was vacuum distilled from zinc dust and
dried for six days over freshly prepared barium oxide. It was
vacuum distilled off fresh barium oxide immediately before use.
was a colourless liquid.

\[ d_{4}^{25} = 1.174; \quad \text{B.P.} = 70.5 - 70.6/10 \text{mm}. \]

Hartley and Collie (33) \[ d_{4}^{15} = 1.0178. \]

Fos and Smith (72) \[ \ldots 1.0174. \]

(17) **p**-Dinitrobenzene. Molecular Weight 168.11 A technical sample was recrystallised three times from industrial methylated spirit and dried over concentrated sulphuric acid for six weeks. Very pale yellow needles. B.P. 30.6° - 30.9°.

(c) **Solvents**

(1) **p**-Dichlorobenzene. Molecular Weight 147.11. British Drug Houses Ltd. "Laboratory Reagent" **p**-Dichlorobenzene was recrystallised three times from 93% ethanol and dried over powdered calcium chloride.

Three samples were prepared and dried for from 2 to 7 weeks but they all melted at 61.6°.

(11) **Hexadur intervention**. Molecular Weight 61.17. A sample was kindly supplied by the Anglo-Iranian Oil Co. Ltd. It was dried over phosphorus pentoxide and distilled from fresh phosphorus pentoxide.

\[ d_{4}^{25} = 0.6302; \quad n_{D}^{25} = 1.5787; \quad \varepsilon^{25} = 1.3700; \quad \text{B.P.} = 60.7°. \]

The quantity available was about 400 ml and after it had been used as solvent for **p**-bromobenzyl chloride it proved very difficult to recover.
Prolonged washing with silver nitrate solution
decomposed the 2-buty1 chloride but the volume of hexane recovered
was only sufficient for five solutions and therefore it was decided
to prepare a sample from laboratory hexane. British Drug Houses
Laboratory Reagent µ-hexane boiling range 67-69°C was shaken five
times with 20% chloro to remove aromatics. Since the acid after the
fifth treatment was still very faint brown it was suspected that there
might have been some reaction taking place (51) and three further
treatments were made using a mixture of 4 volumes concentrated
sulphuric acid to 1 volume chloro. The final acid showed some
discolouration but the hexane was then washed successively with water,
sodium hydroxide solution and water again, dried over phosphorus
pentoxide and fractionated from fresh phosphorus pentoxide. The
initial column head temperature was 60°C and after off-take had started
it rose and settled at 68.3°C when collection of the sample was
started. The temperature then slowly rose to 68.5°C when
sufficient material had been obtained and the distilling flask
contained very little sample.

\[
\begin{align*}
   d^4_4 & = 0.6377; &   n^3_5 & = 1.3762; &   1.8931; &   \text{B.P. 62.2-63.9.}
\end{align*}
\]

It is obvious that the sample obtained was very impure but in view
of the difficulty of preparing pure hydrocarbons it was not considered
feasible to attempt further purification with the apparatus available.

Previously reported figures for µ-hexane are probably
the most accurate available now:

\[
\begin{align*}
   d^4_4 & = 0.6343 (23); &   n^3_5 & = 1.37283 (23); &   \text{B.P. 63.78°C (23).}
\end{align*}
\]
(411) **Benzene. Molecular Weight 78.11**. This was a sample supplied by the Anglo-Iranian Oil Co. Ltd. and it was dried over phosphorus pentoxide and distilled from fresh phosphorus pentoxide.

\[ \rho_2^F = 0.6752; \quad \eta_2^F = 1.3303; \quad \varepsilon_2^F = 1.0000; \quad \text{B.P.} \ 80.8. \]

Previously reported figures and probably the most accurate available are:

\[ \rho_2^F = 0.6752 \pm 0.0001 (35); \quad \eta_2^F = 1.3303 \pm 0.0002 (35); \quad \text{B.P.} \ 80.4 \pm 0.1 (35). \]

(47) **Benzene. Molecular Weight 78.11**. A mixture of Kay and Berlin "Thiophene-free crystallizable" and British Drug Houses "Analar" benzene was shaken with several portions of concentrated sulphuric acid, washed with water, 10% sodium hydroxide solution, water and dried over calcium chloride. It was then fractionally frozen until a glassy mass was obtained as distinct from fatty crystals. It was finally dried over two lots of phosphorus pentoxide and fractionated from fresh phosphorus pentoxide.

Since benzene was used as a standard of dielectric constant, samples were collected during fractionation and sealed in 50 cc. glass ampules, one of which was used for each run. Benzenes to be used as a solvent was collected and stored in long necked flasks shown in Figure 13.

\[ \rho_2^F = 0.6752; \quad \eta_2^F = 1.4000; \quad \text{B.P.} \ 80.1. \]

Several samples of benzene were prepared but the physical constants showed very little variation; the boiling points were constant and the density and refractive index varied by

\[ \pm 0.0001 \] and \[ \pm 0.0002 \] units respectively. There are many reported figures for the physical constants of benzene but those quoted below (35) are believed to be the best available.
(v) Tetralin. Palmarin Oil. 124.70.

Tetralin supplied by L. Light and Co. Ltd., was initially dried by distilling off the first 5-10% as the usual drying agents (calcium chloride and sodium sulphite) appeared to be without action. The hydrieration was then carried with sodium (33) for 10 hours and distilled at atmospheric pressure from the tarry material formed. It was refluxed for a further 10 hours with fresh sodium and because of its high boiling point was 'fractionated' through a 13″ fraction column. It was realised that such a treatment would not give a pure sample but the material is extremely difficult to purify and a more elaborate scheme was not undertaken. Two colourless samples were prepared with the physical constants given under:

\[
\begin{align*}
\text{I} & : d_{15}^\circ = 0.9673; \quad \eta_0^{25} = 1.5434; \quad \epsilon^{15} = 2.7512 \\
\text{II} & : d_{15}^\circ = 0.9873; \quad \eta_0^{25} = 1.5435; \quad \epsilon^{25} = 2.7512
\end{align*}
\]

It will be noticed that the dielectric constant shows a big difference between the materials in spite of the agreement for density and refractive index but compared with the figures given below the two samples were very impure.

Previously reported figures and probably the most accurate available are:

\[
\begin{align*}
d_{15}^\circ & = 0.9663 \text{ (33)}; \quad \eta_0^{25} = 1.5333 \text{ (33)}.
\end{align*}
\]
(vi) 1st Plyose, Indium Iodide. M.F. 283.30. The method of purification was that used by Eigerhaver (49). Purissimum grade indium on I. Light and Co. Ltd., was refluxed for 8 hours in a stream of nitrogen with 12% vol. dilute hydrochloric acid to hydrolyse any glycol crystal present. It was then allowed to stand over solid potassium hydroxide to remove hydrochloric acid and water. The separated supernatant solution was refluxed with sodium metal for 24 hours when the latter remained as bright balls without further action. The solution was then distilled off, fractionally frozen twice, again refluxed with sodium until the latter remained bright (ca. 6 hours) and fractionated.

The material thus prepared was very hygroscopic as was shown by the dielectric constant, and the sample used in Table 4 was prepared before this property was fully realized and the high dielectric constant observed is attributed to the presence of a trace of water. The physical data obtained and given below are the best values of nine determinations made in order to establish these constants in view of the unsatisfactory position in the literature.

\[ \begin{align*} 
  \text{D}^{25} & = 1.0282; \quad \text{H}^{25} = 1.4002; \quad \text{C}^{25} = 2.3540; \quad \text{B.P.} = 102.6; \\
  \text{Melting Point} & = 117.3^\circ C.
\end{align*} \]

Literature data which are tabulated in Table 25, show a remarkable spread for dielectric constants and density; in general the low densities (relative to the writer's) are associated with higher dielectric constants and probably indicate contamination with water.

(vii) Carbon Tetrafluoride. M.F. 151.91. The method of purification was that used by Smith (41) and Milligan and...
Purification:

The commercial carbon disulfide used was purified by the method described by Harris and Niswold (46). After shaking with solid potassium permanganate for 15 hours, and then with pure mercury for 6 hours, it was distilled off leaving a little black powder and again shaken 6 hours with mercury. No further blackening occurred and it was shaken for 5 hours with mercuric sulphate. It was dried with phosphorus pentoxide and fractionated from fresh phosphorus pentoxide. The product had a pleasant ethereal smell with only a trace of the odour usually associated with carbon disulfide. This
Samples were prepared:

I  $d_{14}^5$ 1.2583;  $\varepsilon_{25}^5$ 2.6335;  B.P. 43.2.

II  "  1.2583;  "  2.6335;  "  43.2.

Previously reported figures are:

$\sigma_{44}^5$ 1.2533 (44);  1.253 (47);  1.2533 (46)

$\varepsilon_{25}^5$ 2.6333 (44);  2.633 (47).

B.P. 45.8/758 m (44);  46.3 (43);  45.25 (42).
6. EVALUATION AND INTERPRETATION OF PHYSICAL RESULTS

(a) General

The purity of the solvents is difficult to judge due to the scarcity of literature data and the discrepancies existing in the values reported. Boiling points are unsatisfactory for comparison purposes and the density and refractive index only have been considered. Two completely separate preparations of both 2-bulyl chloride and methyl cyanide have yielded material the constants of which differ, at the most, by the experimental error (see later) and which are within the possible spread of the reported values. In view of the purification and fractionation technique used, and the consistent data obtained, the writer's figures are believed to be better than those in the literature and the purity was considered satisfactory for the present investigation. It should be noted that the densities at 25°C for 2-bulyl chloride reported by Cramble et al (20) and Timmemaes and Delcourt (21) are well outside any experimental deviations and are either seriously in error or their samples were very impure.

The physical constants of the solvents (except tetralin) are in satisfactory agreement with the literature but slight impurities have little effect on the general trend of results, provided (as was assumed) there is no interaction between the impurity and the solute. In the case of tetralin a very lengthy purification procedure would have been required to give a sample approaching the purity of the other solvents and as it was believed that this was not justifiable the material was only treated with sodium. To minimize the electrical apparatus determinations were made of the polarisations of toluene and m-dinitrobenzene in benzene and the data obtained are given in Tables...
19 and 21. Results published by other authors are given in Tables 20 and 22, and by comparison with these it was decided that the apparatus was satisfactory for the present investigation and capable of giving results of the required accuracy.

The data obtained for the series of solutions using 1,4-dioxane and methyl cyanide given in Tables 1 to 16 has been used to calculate the solute polarisation at each concentration by the classical Nicoletti Clusius relationship using the concept of 'specific polarisations' introduced by Sugden (50) which considerably reduces the calculations required.

From Page 16 we have:

$$\frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} = \frac{2}{3} \pi \left( V_1 \alpha_1 + V_2 \alpha_2 \right)$$

But

$$\frac{V_1 M_1}{N} V_1 = \omega_1 \quad \text{and} \quad \frac{V_2 M_2}{N} V_2 = \omega_2$$

where \( \omega \) is the weight fraction and \( \varepsilon \) the specific value and if \( \frac{\varepsilon - 1}{\varepsilon + 2} \), \( \varepsilon = \rho \) the specific polarisation.

$$P_{12} = \frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} V_{12} = \frac{2}{3} \pi N \left( \frac{\alpha_1}{M_1} + \frac{\alpha_2}{M_2} \right)$$

But

$$P_1 = \frac{2}{3} \pi N \frac{\alpha_1}{M_1} \quad \text{and} \quad P_2 = \frac{2}{3} \pi N \frac{\alpha_2}{M_2}$$

\[
\therefore \quad \tau P_{12} = \tau P_1 \omega_1 + \tau P_2 \omega_2.
\]

or

\[
\tau P_{12} = \tau P_1 + \left( \frac{\tau P_{12} - \tau P_1}{\omega_2} \right)
\]

Similarly

$$v_{12} = v_1 \omega_1 + v_2 \omega_2$$

where \( v \) = specific refraction = \( \left( \frac{n^2 - 1}{n^2 + 2} \right) \frac{1}{d} \)

(b) Possible Error in the Calculated Polarisations

It was shown in section 5.1, that approximately the same fractional error in the calculated polarisation would arise for equal
fractional errors in the determined density and dielectric constant but account was not taken of the maximum possible absolute error in \( \frac{P_2}{P_1} \) due to all the experimental errors involved. This has been calculated as follows. Examination of the results shows that the possible experimental errors are in general:

<table>
<thead>
<tr>
<th>Property</th>
<th>Error Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive index</td>
<td>± 0.0001 unit</td>
</tr>
<tr>
<td>Density</td>
<td>± 0.0003 g/ml</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>± 0.0003 unit</td>
</tr>
<tr>
<td>Weight fraction</td>
<td>± 0.023</td>
</tr>
</tbody>
</table>

Drop the prefix \( T \) and using \( P \) to represent the total specific polarization we have

\[
P = \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right) V; \quad P_2 = P_1 + \left( \frac{p_2 - p_1}{\omega_2} \right)
\]

where \( V = \frac{1}{d} \)

Now

\[
\Delta P = \frac{3V\Delta\varepsilon}{(\varepsilon+2)^2} - \left( \frac{\varepsilon - 1}{\varepsilon+2} \right)V^2\Delta d
\]

(\text{where} \( \Delta \) \text{ denotes the absolute error in any quantity})

and the maximum numerical value of \( \Delta P \) arises when \( \Delta d \) and \( \Delta \varepsilon \) are negative and positive respectively. Similarly

\[
\Delta P_2 = \frac{1}{\omega_2} \left[ \Delta P_{2a} - \omega_1 \Delta P_1 - \left( \frac{p_2 - p_1}{\omega_2} \right)\Delta \omega_2 \right]
\]

and the maximum numerical value of \( \Delta P_2 \) arises when

\( \Delta P_{2a} \) is maximum positive value,
\( \Delta P_1 \) is maximum negative value,
\( \Delta \omega_2 \) is maximum negative value.

Applying this to the lowest concentration of \( \text{4-buty1 chloride in carbon tetracloride} \) (Table 5):
\[
\begin{align*}
\alpha_1 &= 0.10211, & \nu_1 &= 0.65114 \\
\alpha_2 &= 0.10373, & \nu_2 &= 0.65633 \\
\epsilon_1 &= 2.3391, & \omega_1 &= 0.99984 \\
\epsilon_2 &= 2.3155, & \omega_2 &= 0.999370
\end{align*}
\]

\[
\begin{align*}
\Delta \alpha_1 \text{ (max)} &= \frac{3 \times 0.65114 \times 0.0003}{(4.2261)^2} + \frac{1.2281 \times (0.65114)^2 \times 0.0003}{4.2261} \\
&= 0.00000788 \\
\Delta \alpha_2 \text{ (max)} &= \frac{3 \times 0.65333 \times 0.0003}{(4.2263)^2} + \frac{1.3125 \times (0.65333)^2 \times 0.0003}{4.2263} \\
&= 0.00000044 \\
\Delta \alpha_2 \text{ (max)} &= \frac{1}{0.000070} \left[ 0.00000070 + 0.0000003 \times 0.0003 \right] \\
&= 0.00014
\end{align*}
\]

The maximum possible error in \( \bar{\alpha}_2 \) is \( \pm 1 \Delta \bar{\alpha}_2 = \pm 0.075 \text{ cc.} \)

Corresponding to the experimental errors given above. It is realized, however, that in some cases the error in determinations may exceed these values in which cases there will be correspondingly larger errors in \( \bar{\alpha}_2 \).

Similar calculation for other solutions show that the errors in are as follows:

<table>
<thead>
<tr>
<th>for 1-Butyl chloride in:</th>
<th>Carbon tetrachloride</th>
<th>p-bromo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lowest concentration</td>
<td>( \pm 0.2 \text{ cc.} )</td>
<td>( \pm 1.4 \text{ cc.} )</td>
</tr>
<tr>
<td>Highest concentration</td>
<td>( \pm 0.1 \text{ cc.} )</td>
<td>( \pm 0.2 \text{ cc.} )</td>
</tr>
</tbody>
</table>
Substituting in \( P = \frac{P_t}{P_s} \), we get:

\[
\frac{P_t}{P_s} = A(M_0 - \beta A/d_0) + C x E_1,
\]

where

\[
A = \frac{A}{(T + E)^2}, \quad B = \frac{1}{M_0}, \quad C = \frac{C}{(T + E)^2},
\]

Substituting in \( P = \frac{P_t}{P_s} \), we get:

\[
e_0 = \frac{d_1 + \theta f_2}{d_1},
\]

Substituting in \( P = \frac{P_t}{P_s} \), we get:

\[
f_0 \to 0
\]

The value of \( P \), calculated by the least squares method, is the best estimate of the experimental error at low concentrations (where the experimental error is not reached). Indicating that to a large extent the experimental errors may be not reached, indicating that to a large extent the experimental errors may be not reached.
The use of specific polarizations considerably simplifies the calculations and the method has been modified by Halverstadt and Kliner (52). These authors assume that the dielectric constant and specific volume are linear functions of the weight fraction:

\[ \varepsilon_{12} = \varepsilon_1 + \alpha \omega_2 \quad \text{and} \quad V_{12} = V_1 + \beta \omega_2. \]

There is no theoretical justification for either authors dielectric constant equation or Hededstrum's relation between density and mol. fraction but the second relationship of Halverstadt and Kliner is based on the additivity of specific volumes. If the solution behaves as a regular mixture:

\[ V_{12} = \omega_1 V_1 + \omega_2 V_2 \]

i.e.

\[ V_{12} = V_1 + \omega_2 (V_2 - V_1) \]

so that \( \beta = (V_2 - V_1) \) the difference in specific volume of solute and solvent and may be positive or negative.

Considering the expression:

\[ P_2 = P_1 + \frac{(\rho_2 - P)}{\omega_2} \]

The value of \( P_2 \) as \( \omega_2 \to 0 \) is

\[ P_1 + \left( \frac{\delta P_2}{\delta \omega_2} \right) \omega_2 \to 0 \]

now

\[ P_{12} = \left( \frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 1} \right) V_{12} \]

\[ \frac{\delta P_{12}}{\delta \omega_2} = V_{12} \left( \frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 1} \right) \frac{\delta V_{12}}{\delta \omega_2} + \left( \frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 1} \right) \frac{\delta V_{12}}{\delta \omega_2} \]

\[ = \frac{3 V_{12}}{(\varepsilon_{12} + 2)} \frac{\delta \varepsilon_{12}}{\delta \omega_2} + \left( \frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} \right) \frac{\delta V_{12}}{\delta \omega_2} \]
\[ \text{Let } P_2 \bigg|_{\omega_2=0} = \left(\frac{\epsilon_{1-1}}{\epsilon_{1+2}}\right) V_1 + \frac{3 V_1 \alpha}{(\epsilon_{1+2})^2} + \left(\frac{\epsilon_{1-1}}{\epsilon_{1+2}}\right) \beta \]

or \[ \tau_P^\infty = \left(\frac{\epsilon_{1-1}}{\epsilon_{1+2}}\right) V_1 + \frac{2 \alpha V_1}{(\epsilon_{1+2})^2} \]

It has been assumed that both the \( \epsilon_{12} \) and \( V_{12} \) are linear functions of \( \omega_2 \) but, as has been pointed out by Haldestrand (SI) and Otto (53), the above equation for \( \tau_P^\infty \) holds independently of the relationship between \( \omega_2 \) and \( \epsilon_{12} \) or \( V_{12} \).

In general, we may write
\[ \epsilon_{12} = \epsilon_{1} + \alpha \omega_2 + \alpha' \omega_2^2 + \alpha'' \omega_2^3 + \ldots \]
\[ V_{12} = V_1 + \beta \omega_2 + \beta' \omega_2^2 + \beta'' \omega_2^3 + \ldots \]

from which it will be seen that \( \alpha \) or \( \beta \) are the slopes of the two curves at \( \omega_2 = 0 \). These values can readily be obtained if the equations are used in the form:
\[ \frac{\epsilon_{12} - \epsilon_{1}}{\omega_2} = \frac{\Delta \epsilon}{\omega_2} = \alpha + \alpha' \omega_2 + \alpha'' \omega_2^2 + \ldots \]
\[ \frac{V_{12} - V_1}{\omega_2} = \frac{\Delta V}{\omega_2} = \beta + \beta' \omega_2 + \beta'' \omega_2^2 + \ldots \]

then a plot of \( \frac{\Delta \epsilon}{\omega_2} \) or \( \frac{\Delta V}{\omega_2} \) against \( \omega_2 \) for a set of solutions will give a curve the intercept of which at \( \omega_2 = 0 \) being \( \alpha \) or \( \beta \) respectively (Figure 11). It has been found that this plot is either a very shallow curve or a straight line so that the value of \( \alpha \) or \( \beta \) may be obtained with a high degree of accuracy.
In addition to giving a parameter derived from data for all $i$ of the solutions of a set this method immediately indicates experimental results that are unsatisfactory since the plots of $\frac{\Delta \varepsilon}{\omega_2}$ and $\frac{\Delta \gamma}{\omega_2}$ against $\omega_2$ are found to be very critical. It should be noted, however, that the density or dielectric constant of the solvent occurs in the equations for each solution and the values of $\beta$ or $\alpha$ evaluated are dependent on their accuracy, i.e. the method does not subject the data for the solvent to the same critical test as it does for the solutions. However, if $\varepsilon_1$ is in serious error relative to the values for the solutions the plot of $\frac{\Delta \varepsilon}{\omega_2}$ against $\omega_2$ leads to a curve which tends to become asymptotic to the $\frac{\Delta \varepsilon}{\omega_2}$ axis as $\omega_2 \rightarrow 0$.

Overweighting of the constants of the solvent is more serious when the value of $\frac{P_2}{P_1}$ is calculated from the expression:

$$\frac{P_2}{P_1} = \frac{P_1}{P_1} + \left( \frac{P_2 - P_1}{f_2} \right)$$

there being no check on the polarization of the solvent and the rapid rise in $\frac{P_2}{P_1}$ at low values of $f_2$ as reported by some authors is probably due to very small errors in the polarization assumed for $\frac{P_1}{P_1}$.

Heckler has pointed this out (110) and proposed overcoming the trouble by the use of the plot of $\frac{P_2}{f_2}$ against $f_2$ from which the solute polarization at any concentration is given by the slope of the curve at that concentration.

Hamburger and Heckler suspected that the dielectric constant of the solvent in the solution would differ from that of the pure material and suggested ignoring the determined value for the pure
 solvent particularly as each $\Delta \varepsilon$ depended on this one determination. They proposed, therefore, using the extrapolated value of $\varepsilon_1$ at $\omega = 0$ but there is no cause to expect that the $\varepsilon_1 / \omega_2$ plot should not pass through the determined $\varepsilon_1$ at $\omega = 0$. All the work carried out in these laboratories has confirmed this and a large scale plot of $\varepsilon_1$ against $\omega_2$ has been used as a check of $\varepsilon_1$; in a similar manner the specific volume of the solvent, $V_1$, has been checked. At the concentrations used for the present work it was found that the values of $\frac{\Delta V}{\omega_2}$ for any one set of solutions were constant, within the limits of experimental error, and equal to $\beta$; but since $\frac{\Delta V}{\omega_2}$ at the lowest concentrations can show large variations (the experimental error being a large fraction of $V_{12} - V_1$) the value of $\beta$ used has been calculated as $\frac{\sum \Delta V}{\sum \omega_2}$, where $\sum \Delta V = \sum (V_{12} - V_1)$.

It is not always possible to draw a satisfactory curve through experimental points (even with eight solutions) without some doubt about the intercept and slope at $\omega = 0$. If the plot is linear (as is often the case for $V_{12} / \omega_2$ plots), then the matter is relatively simple but, in general, this is not so, particularly for the dielectric constants. As an attempt to overcome this difficulty we have been much of a mathematical treatment based on the equation:

$$\varepsilon_{12} = \varepsilon_1 + \alpha \omega_2 + \alpha' \omega_2^2 + \alpha'' \omega_2^3 + \ldots$$

From observation of collected data Mr. J. T. Smith pointed out that in almost all cases the coefficients of $\omega_2^3$ and higher powers are negligible compared with the experimental errors obtaining, thus any set of data (provided they include at least 4 solutions and the solvent) can be split into three groups of three results to give
three simultaneous equations of the form

\[ \sum_{n=1}^{\infty} \prod_{j=1}^{n} (1 + \omega_j^2) \]

Solution of these will give a value of \( \epsilon_1 \) derived from all the measurements made, and similarly \( \alpha \), but it should be pointed out that the method is only of limited use since 3 solutions is too small a number and particularly if the experimental results are at all doubtful. However, with a good set of data it does provide a check on the value of \( \epsilon_1 \) actually measured and in almost all cases the two values are identical substantiating the experimental fact that \( \epsilon_1 \) should lie on the \( \epsilon_{12}/\epsilon_{22} \) curve.

The above discussion has been based on the use of the Clausius-Brandt relationship with the general equations connecting weight fraction and density and dielectric constants but it is obvious that a precisely similar treatment can be applied to any other equations that have been proposed for the calculation of polarisations. It is therefore not necessary to recalculate the data reported but merely to insert the limiting values of \( \frac{\Delta \epsilon}{\omega_1} \) and \( \frac{\Delta \nu}{\omega_2} \) in the appropriate equation for \( \frac{P}{\epsilon_{12}} \) derived by the same method as that on page 65.

The present work has been evaluated by the equations proposed by Kallmott and Kastler which were chosen because there is a theoretical backing for the connection between \( \sqrt{\omega_1} \) and \( \omega_2 \) but many other observers have used similar relationships. Mention has already been made of Koelddahl's relationships involving molecular fractions.

Le Ferve (51) proposed

\[ \epsilon_{12} = \epsilon_1 (1 + \alpha \omega_2) \]

\[ d_{12} = d_1 (1 + \beta \omega_2) \]

while Pasanik and Borov (52) proposed using

\[ \epsilon_{12} = \epsilon_1 (1 + \beta \nu_2) \]
and \( \chi_{12} = \chi(1 + \beta \chi) \) where \( \chi' \) is the volume fraction of the solute.

Distinct from the above equations which relate only constants for the solutions and pure solvent, use has been made by Parmarpo and Dower (53) of the equation due to Huglin (53)

\[
\frac{\tau_2}{\Pi_2} = A + B \left( \frac{E_{12} - 1}{E_{12} + x} \right) \quad \sigma = A + B \Pi_{12}
\]

By calculation from the Huglin-Clausius equation a value for the solute polarization at each concentration can be obtained and plotted against \( \Pi_{12} \) for the respective solutions. This has been done for the solutions of \( \text{a-butyl chloride and methyl cyanide and in all cases a linear plot is obtained one of which are shown in Figure 12.} \)

The methods of extrapolating the experimental data discussed above relate the effect of concentration on the solute polarization to the mol. fraction, weight fraction or volume polarization and as will be seen from Table 24 each gives very nearly the same value for \( \frac{\tau_2}{\Pi_2} \).

It is obvious that any other parameter could be used such as volume fraction, dielectric constant or density of the solution but it is preferable if the curve to be extrapolated is a straight line and therefore the parameter chosen should have this end in view.

Use of all these methods and critical examination of data has shown that the method of extrapolation to zero concentration is unsatisfactory provided the experimental accuracy is high but when this is not so then choice of method should be governed by obtaining 'best values' directly from the experimental results. It is under these conditions that a method such as that derived from the Harleman and Kihler treatment is to be strongly recommended but the constants of the solvent must be carefully checked. Literature data all too
frequently show that no attempt has been made to check results in this way and therefore large errors can arise particularly as the possible error in \( \tau \) calculated at low concentrations can be so very large.

The use of the method of Halverstadt and Malher is well illustrated by the excellent agreement it gives between the results obtained for \( \beta \)-bromo acetate in \( \beta \)-heptone by the author and these recalculated from the data of Smyth and Domke, Tables 2, 3 and 4.

(i) The Distortion Polarization is often calculated from the refractive indices. These can be examined in precisely the same way as the dielectric constants using \( \eta^2 \) in place of \( \varepsilon \):

\[
\eta^2 = \eta^2_1 + \gamma \omega_1 + \gamma' \omega_2 + \gamma'' \omega_3 + \cdots
\]

but this is only justifiable if the values of \( \eta \) are accurate to the 8th decimal place. Therefore, evaluation of the molecular refraction of the solute has been made at each concentration by the concept of specific polarizations, assuming that of the solvent to remain constant. Owing to the small differences between the refractive indices of the solutions and solvent, the accuracy of refractive index determinations (± 0.0001) and errors due to evaporation with such volatile materials the calculated molecular refraction of the solute in solution can show large variations and is even more dependent on the solvent constant than the specific polarization.

However it has been necessary to evaluate \( \gamma \) for use in certain equations and this has been done by means of the ratio

\[
\frac{\varepsilon(n^2 - 1)}{\varepsilon} = \omega_2
\]

since there appears to be little evidence which is outside experimental error to show that \( \gamma \) is a function of \( \omega_2 \).
The values of \( \varepsilon_{P_2} \) for some sets of solutions suggest that there may be a concentration effect (\( \varepsilon_{P_2} \) decreasing as \( \omega_2 \) increases) but it should be noted that this can be caused by a very small error in the refractive index of the solvent. In all cases the latter has been checked by plotting \( n_2^2 \) against \( \omega_2 \) in a manner similar to that for dielectric constants and with the materials used straight lines or very shallow curves were obtained which passed through \( n_2^2 \) for the pure solvent.

In view of the possible inaccuracy, where \( \varepsilon_{P_2} \) calculated differs from that of the pure solute the value has been accepted with considerable reserve and, in general, the results only serve to support the additivity of molecular refractions.
DISCUSSION
1. COMRA

On the basis of the theory of Frenck and Kirkram (57) as extended by Subramanyan (58) and Iau (59) it is to be expected that the molecular polarization $\mathbf{P}_m$ of a compound of which the molecule is anisotropic should vary with the dielectric constant of the medium ($\varepsilon_1$) in which it is studied, whilst for an isotropic molecule $\mathbf{P}_m$ should be independent of $\varepsilon_1$. A similar conclusion is reached from the theoretical considerations of Fauge (60), Frank (61) and Myar (62) (63). In addition these authors inferred that for the case where the axis of the dipole is coincident with the axis of maximum polarisability of the molecule, $\mathbf{P}_m$ should decrease with increasing $\varepsilon_1$, while if these axes are at right angles $\mathbf{P}_m$ right increase with increasing $\varepsilon_1$. Frank further showed that the molecular polarization in solution should be greater or less than that in the vapour phase according as the angle between the axes was greater or less than 90°.

Various attempts have been made to test these conclusions but the results have not been wholly satisfactory due, it is believed, to two causes. Firstly, the experimental data has usually not been very satisfactory or interpreted with enough care and, secondly, the choice of compounds has often been bad; with such materials as nitrobenzene and benzonitrile for example, as have been used in the past (64) (65), the electronic systems are so mobile that secondary interfering effects may be present which tend to cloud the issue. Therefore for the present investigation p-butyl chloride and methyl cyanide were
chosen as compounds in which this difficulty is avoided whilst at the same time representing the simplest possible polar molecules of the isotropic and anisotropic types respectively. Evidence has already been cited for proof of the sphericity of the 2,4-butyl chloride molecule and to show that the polarisability of the methyl and chloride groups are equal. For methyl cyanide since the two C atoms and the N atom are colinear the major axis of the molecule is about double the minor axis and it can also be safely assumed that the dipole axis is identical with the axis of maximum polarisability and length.

The effect of dielectric constant of the medium on the molecular polarisation of the solute can be studied in two ways:

a) through the variation of \( \mathcal{P}_1 \) with concentration in any specific solvent,

b) through the variation of the extrapolated values of the molecular polarisation at infinite dilution \( \mathcal{P}_1^\infty \) with the dielectric constants of the solvents used.

It is difficult to investigate b) using non-polar solvents owing to the small range of dielectric constants available and as carbon disulphide is the only common non-polar solvent with \( \epsilon_r > 2.5 \), tetralin was included. It is known that this latter material is polar owing to the presence of the reduced ring but it was not anticipated that this would lead to very anomalous results since its dipole moment is small, ca. 0.6 D (66).

To obtain further information as to whether \( \mathcal{P}_1 \) measured in solution is a function of the dielectric constant of the medium only,
or whether other factors contribute to the variations observed, measurements were made using mixed non-polar solvents chosen to have approximately the same dielectric constant as benzene. With such mixtures one component must have a relatively high polarisability and it is possible that due to the strong field in the neighbourhood of the polar solute molecules (ca. 10⁷ volts/m) these might become surrounded by molecules of the component of higher polarisability. Such a "sorting effect" has been proposed by Oster (67) for solutions of glycine and pyridine betaines in water/dioxan and water/alcohol mixtures, this view being supported by good qualitative agreement between experimental results and a simplified theoretical treatment. If this does occur it might be anticipated that \( \mathbf{P} \), measured in the mixed solvent would be similar to that observed in the pure solvent of higher polarisability. Since benzene was the reference solvent it was necessary to use two materials whose dielectric constant were above and below that of benzene respectively. Relatively few non-polar liquids of high \( \varepsilon \) are available but perchlorocarbon is reasonably soluble in non-polar solvents and proved suitable for the purpose. \( \varepsilon \) for solid at 25°C = 2.03 (30). It was used in conjunction with carbon tetrachloride (having a perfectly symmetrical molecule this compound is usually considered not to give abnormal effects, Oost considers it an ideal solvent (39)) on the one hand and with 1:1 dioxan on the other which is known to give anomalous results (73) probably due to hydrogen bonding (71) (72).
The total molecular polarization of any substance is the sum of the distortion and orientation polarizations but the evaluation of these requires a relationship between $\mathbf{P}$, $\mu$ and the measurable quantities $e$, $d$ and $n$ and the molecular dimensions. That derived by Mott and Morton has already been given, but, in view of the incomplete quantitative explanation of electrical behaviour that it affords, other relationships have been proposed. The experimental data has been examined in the light of these but in the first instance attention is confined to the Mott and Morton equation. The dipole moments calculated from the author's results are given in Table 26 together with those published by other authors. In general the agreement is satisfactory but there is doubt about the values of $\mathbf{P}$ to be used and both $\mathbf{P} = \left[ \begin{array}{c} R_{2} \\ \alpha_{2} \end{array} \right]_{D}$ and $\mathbf{P} = \left[ \begin{array}{c} R_{2} \\ \alpha_{2} \end{array} \right]_{D}$ have been used to evaluate $\mu$.

Due to its derivation the Mott and Morton relationship should only hold for gases at low pressures and therefore polarizations measured under those conditions should be used as the standard for comparison with those measured in solution.

2. VAPOUR PHASE MEASUREMENTS ON BUTYL CHLORIDE

Vapour phase measurements on butyl chloride have been made by Wlad and Bryn (26) and calculating on their values for $\mu = 2.18$ D (mean of 6 results) and $\mathbf{P} = \left[ \begin{array}{c} R_{2} \\ \alpha_{2} \end{array} \right]_{D} = 26.8$ cc. $\mathbf{P} = \left[ \begin{array}{c} R_{2} \\ \alpha_{2} \end{array} \right]_{D}$ at $25^\circ C = 120.2$ cc.

Similarly vapour phase measurements on methyl cyanide have been made by Groves and Sykes (31) who obtained

$\mu = 3.84 \pm 0.03$ D (mean of 3 results),
using \( P_2^\infty = 2.05 \left[ \frac{R_2}{c} \right]_D = 1.05 \times 11.1 = 11.7 \) cc.

Hence \( P_2^\infty \) at 20°C = 33.1 cc.

As these are the only data in the literature there is no check with other workers but they suffice to give an 'absolute' value for the solvent effect which otherwise would only be relative. Summarised data for the present work are given in Table 31 with values of \( P_2^\infty \) obtained by three methods of extrapolation; data by other workers are also included but it should be borne in mind that in several cases these have been calculated from data obtained at 20°C or reported values of \( \mu \) and there is doubt concerning the value of \( P_2^\infty \) to be used. In general the values of \( P_2^\infty \) are in agreement with Miller's original findings in that there is a decrease with increasing dielectric constant of the solvent except in the case of the normal paraffins.

The behaviour of the latter solvents is surprising in view of the general belief that they exhibit no dissociation (as do the iso-paraffins under certain conditions) and support the findings of Lewis and Sayth (23) who withheld publication of their data for methyl cyanide in p-xylene on the grounds of experimental error as the value of \( P_2^\infty \) obtained was less than that measured in solution in benzene.

The present author has found that this is also the case in p-xylene.

The polarisation anomaly with p-xylene may be due to the solute since Cowley and Hartington (9) have found (at 20°C) that \( P_2^\infty \) for propyl cyanide is greater in p-xylene than in toluene. Van Anderen and Wish (73) considered methyl cyanide as a compound which shows association in solution and they classified solvents in order of their dissociating power:

benzene > carbon tetrachloride > xylene. If the association of methyl cyanide is correct, and it leads to a lower moment, then one
would expect the polarisation in benzene to be $>\theta$ that in carbon
tetrachloride $>\theta$ benzene as is found. These authors believe benzene
the 'most normal' of the three solvents and considered that
p. dichlorobenzene would show the dissociating power of benzene to a
higher degree. They found this not to be so (although they do not
give their technique) and attributed it to the increase of volume due
to the chlorine atoms and their screening effect on the dipole counter-
balancing the effect of the stronger dipole moments of the limits. The
present author has found that the addition of p. dichlorobenzene results
in a fall in the measured polarisation of the solute compared with that
in the pure solvent, the converse of that which was expected by
van Arkel and Bruin.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau_2^\infty$ of</th>
<th>$\tau_2^\infty$ of</th>
<th>Range of solar fission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon tetrachloride</td>
<td>294</td>
<td>293</td>
<td></td>
</tr>
<tr>
<td>Carbon tetrachloride + p. dichlorobenzene</td>
<td>293 A</td>
<td>293 B</td>
<td>(0 11.33 to 1.42)</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>293</td>
<td>(0 22.40 to 3.61)</td>
</tr>
<tr>
<td>Dioxan</td>
<td>293</td>
<td>293</td>
<td></td>
</tr>
<tr>
<td>Dioxan + p. dichlorobenzene</td>
<td>293 C</td>
<td>293 D</td>
<td>(0 15.33 to 2.91)</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>293</td>
<td>(0 33.66 to 4.99)</td>
</tr>
<tr>
<td>Benzene</td>
<td>293</td>
<td>293</td>
<td></td>
</tr>
<tr>
<td>Vapour phase</td>
<td>118</td>
<td>293</td>
<td></td>
</tr>
</tbody>
</table>

This reduction in the polarisation would be expected if a screening
effect were operative and the solute polarisation lower in solvents
of high dielectric constant.
In another case however does the solute polarization tend to that in benzene solution although the mixed solvents had dielectric constants much closer to this material than either of the pure solvents, thus proving that the dielectric constant of the solvent is not the only parameter to be considered in the solvent effect a conclusion reached by work from theoretical consideration (31). It is realized, however, that the mixed solvents used for the present work do not approach the problem as simply as it appears at first. Although the dielectric constant of the 'solvent' for all solutions of a set was constant the molar ratio of p-dichlorobenzene to the solute was greatest for the most dilute solution and could show the 'sorting effect' to the greatest extent. On this basis the extrapolation to infinite dilution might give the solute polarization in the solvent mixture of greatest polarizability. In neither case is this found, \( P_2 \) for p-buty1 chloride and methyl cyanide being higher in the mixed solvents than in either carbon disulfide or tetralin although the dielectric constants of these materials are lower than that of p-dichlorobenzene (ca. 2.03 at 25°C).

The effect of the addition of p-dichlorobenzene is considerably more marked with than carbon tetrachloride, its presence in the latter solvent decreasing \( P_2 \) by about 0.3 only. In view of the isotropic nature of the carbon tetrachloride molecule this would effect any, in part, be due to 'sorting' although the molar ratio of solute to p-dichlorobenzene was not very high; methyl cyanide having the greater amount would have been expected to be more susceptible with chlorine the presence of p-dichlorobenzene may result in a decrease
in the hydrogen bonding thereby giving a decrease in the apparent $P_2^\infty$ which would be considerably greater than that due to any 'saturating effect'. Here again the varying molar ratio of $n$-dichlorobenzene to solute is against the accurate evaluation of its effect on the $P$-bonding because if we assume that in all solutions the molar ratio of chlorine to solute is such that the possible hydrogen bonding effect is as great as for the solute in pure chlorine the extrapolation to $P_2^\infty$ is taken through points for which the effect of the $n$-dichlorobenzene will be increasing. Therefore the value of $P_2^\infty$ found is that corresponding to the weakest solutions and may bear no direct relationship to obtaining at the higher concentrations. The effect of $n$-dichlorobenzene can also be explained by van Arkel and Sted's hypothesis of 'dissociating power' for, although $n$-dichlorobenzene was found ineffective, 3:1 chlorine, being of more neutral and having two dipolar ionizing smaller atoms than chlorine, should have 'dissociating power' even greater than benzene. This is supported by methyl cyanide having the highest molecular polarization in chlorine and this being lowered by the addition of $n$-dichlorobenzene but it is more probable that hydrogen bonding between the oxygen atoms of the chlorine and the methyl hydrogen atoms of the solute, with the resulting modification of the charge distribution, is responsible for the modification of the polarization. That this may be so has been pointed out by Leibner (72) who states "there is considerable evidence for a very appreciable contribution to the dielectric constant of hydrogen-bonded liquids by the 'atomic polarization' of the proton in the hydrogen bond ..........In addition hydrogen-bond formation lengthens the X - H bond distance.
but this effect should not be an significant as the contribution from the proton polarizations. It is difficult to see how pure atomic polarization effect can account for the increased molecular polarization arising from hydrogen bonding, particularly the large difference observed by Fox and Smith for aniline in benzene and 1,2-dimethoxyethane (72) or Cleland and Smith results for alcohols in the presence or small amount of pyridine (113). It is noted that there is a greater extinction of the polarisation with methyl cyanide than \( p \)-butoyl chloride which is in accord with the Martius' work on the connection between hydrogen-bonding and viscosities (75). These authors showed that the hydrogen-bonding tendency of methyl groups is increased by polar groups, \(-\text{Cl}\) being > -Cl, in effect both in the compound E II e and HCl₂.

In the case of \( p \)-butoyl chloride, if the vapour phase polarization is correct, there is undoubtedly a positive solvent effect with the majority of the solvents used, a fact that does not seem to have been realized by observers since the publication of vapour-phase data by Shull and Smith in 1941. In this connection it is of interest to note the high distortion polarization obtained by Shull and Domine for solutions in 1,4-dioxane, these authors obtaining \( \delta P_2 = 0.4 \) as = 1.5 as \( \delta P_1 \) (22). If the methyl groups are the major contributions to the distortion polarization, it is possible that the axis of maximum polarizability is at right angles to that of the permanent moment in which case the theoretical considerations of Eggle, Nigoni and Fauci.
indicate that the result found in solution may be greater than that in
the vapour phase (see later).

3. THE AROMATIC HYDROCARBONS

Polarizations calculated from the solution measurements for
both 

butyl chloride and isobutyl chloride show a decrease with
increasing concentration and the polarizations at infinite dilution are
very dependent on the solvent. These effects have often been regarded
as distinct and the solvent effect taken as the variation obtaining in

\[ \frac{P}{T_2} \]

at infinite dilution it being assumed that by this procedure the
concentration variable has been eliminated. There is, however, no
reason why the two effects should be considered as separate, indeed all
concentrations of solute may be looked upon as lower concentrations of
solute in a mixed solvent of solute and solvent and on this basis a
derived polarization should be considered in conjunction with the
polarization for which it was derived. This basis was used by Beglin
(50) who suggested that a dipole in solution could be regarded as
surrounded by an atmosphere of dipoles of opposite sign produced partly
by induction and partly by orientation of adjacent permanent dipoles.
As a result the measured polarization would appear to be less than the
true value and the correction for the opposing dipole atmosphere should
be a function of the value polarization of the solution \( \frac{P_{\infty}}{P_{\infty}} - 1 = \Pi_{12} \)

\[ \frac{P}{T_2} = \frac{P_{\infty}}{T_2 (ga)} - K \Pi_{12} \]

For the plot of \( \frac{P}{T_2} \) against \( \Pi_{12} \), the intercept at \( \Pi_{12} = 1 \)
(i.e. \( \epsilon = \infty \)) should be \( \frac{P}{T_2} \) and the difference between the
intercepts at \( \text{I} = 0 \) and \( \text{I} \) should be \( \mu P_2 \), while if the plot is linear then the slope is equal to \( \mu P_2 \) (i.e. \( K = \mu P_2 \)). Some of the results have been plotted on this basis in Figure 13 and within experimental error straight lines are obtained, the intercepts and slopes for all the solutions being as follows:
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant of Solvent</th>
<th>Intercept at $\Pi_2 = 1$</th>
<th>Slope of $\Pi_2$</th>
<th>Intercept at $\Pi_2 = 1$</th>
<th>Slope of $\Pi_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dioxane + $\mu$-dichlorobenzene</td>
<td>2.373</td>
<td>+33</td>
<td>-37</td>
<td>+3</td>
<td>-32</td>
</tr>
<tr>
<td>Dioxane</td>
<td>2.394</td>
<td>+30</td>
<td>-36</td>
<td>+32</td>
<td>-32</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.373</td>
<td>+33</td>
<td>-37</td>
<td>+3</td>
<td>-32</td>
</tr>
<tr>
<td>Tetrachloroethane</td>
<td>2.783</td>
<td>+33</td>
<td>-33</td>
<td>+73</td>
<td>-22</td>
</tr>
<tr>
<td>Carbon tetrachloride + $\mu$-dichlorobenzene</td>
<td>2.235</td>
<td>+73</td>
<td>-33</td>
<td>+73</td>
<td>-22</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>2.235</td>
<td>+73</td>
<td>-33</td>
<td>+73</td>
<td>-22</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>2.235</td>
<td>+73</td>
<td>-33</td>
<td>+73</td>
<td>-22</td>
</tr>
<tr>
<td>$\mu$-krypton</td>
<td>1.621</td>
<td>+87</td>
<td>-47</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\mu$-xylene</td>
<td>2.073</td>
<td>+95</td>
<td>-30</td>
<td>-37</td>
<td>-33</td>
</tr>
</tbody>
</table>

$
\begin{align*}
\frac{\Delta P_2}{\Delta T} \text{ from } P_2/T &= 33 (22) \quad \text{or } 103 (23) \\
\mu P_2 \text{ from } P_2(\text{vap}) - \frac{\Delta P_2}{\Pi_2} &= 83 \quad \text{or } 33 (using e)
\end{align*}
$

$\theta = 1.3 \sqrt{\left[ \varepsilon \right]_D}.$

The numerical values of the slopes of the lines are of the same order for all the measurements on each solute and are of the same order as the orientation polarization in the vapor phase but the intercepts at $\Pi_2 = 1$ are far removed from $\frac{\Delta P_2}{\Pi_2}$. This is in part agreement with Guggenheim's original proposal but the relationship must be changed to the form

$$
\frac{\Delta P_2}{\Pi_2} = A + \frac{P_2(\text{vap})}{\Pi_2} - \left( \frac{\mu P_1 + B}{\Pi_2} \right) \Pi_2.
$$
before it can be applied to each combination of solute and solvent as was later realized by Justice. The constants \( A \) and \( B \) must be correctly chosen since they are not of universal application. It should be noted that an accurate value for the orientation polarization of methyl cyanide in the vapour phase is not available for comparison and the value given in the above table has been calculated assuming

\[
P_2 = 1.05 \left( \frac{R}{
u} \right)_D = 11.7 \text{ cc.}
\]

Data have been published by Lewis and Smyth (20) for solutions in toluene at various temperatures and although these authors did not evaluate \( P_2 \), examination of their results gives about 110 cc. but in view of the unreasonable interpolation of their results by these authors to find \( P_2 \) = 280 cc. at 293 and their treatment of results for methyl cyanide in benzene (1811) it is felt that little weight can be attached to the figure. It is therefore considered preferable to take \( P_2 \) as 1.05 \( \left( \frac{R}{
u} \right)_D \) in which case methyl cyanide is in line with \( t \)-butyl chloride in that the numerical slopes of the \( \sqrt{P_2} \) plot are of the same order as the vapour phase orientation polarizations. However, it has been pointed out by Jenkins (70) that moment calculated from the slope of the \( P_2^{1/4} \) line are frequently too small owing to change of dielectric constant of the solvent with temperature and therefore this method may also lead to high values for \( P_2 \). In addition, it is difficult to determine accurately the slope of the line when it is large (i.e. when the material has a large amount) as in the case with methyl cyanide. In spite of this, points the value of \( P_2 = 210 \) cc. still seems very high especially as \( P_2 \) for propionitrile has been reported as 40 cc. (61) and although it is known that the first member of a homologous series is frequently anomalous in many properties this does not usually apply to dielectric polarization.
The basis for the suggestion (Sugden) that the difference in the intercept at $\eta = 0$ and $1 (\epsilon = 1 \text{ or } \infty)$ respectively should be $\mu^2$ was that at $\epsilon = \infty$ the dipole atmosphere would neutralise the permanent dipole and only the distortion polarization should remain (Sugden realized that this did not hold in practice and introduced a correction constant) while at $\epsilon = 1$, gas phase conditions should hold and the total polarization be effective. There are two objections to the extrapolation to $\epsilon = 1$, 1) the extrapolation is through a section in which no experimental work has been done as solvents are not available with $\epsilon < \text{ca.} 1.5$ and 2) the transition from liquid to vapour is in doubt in view of the work of Hansen and Hansen (77) who found that the dielectric constant of a liquid and saturated vapour at the critical temperature are not identical.

Considering the figures in the above table, if the distortion polarization for methyl cyanide is taken as the molecular refraction for the liquid = 11.1 cc. then the orientation polarization has its maximum possible value (for the vapour phase) of $(503.1 - 11.1) = 392$ cc. and is lower than any of the numerical values of the $\frac{P_2}{\eta^2}$ slopes found. For $\gamma$-butyl chloride $\mu^2 (\text{gas}) = 33 \text{ cc.}$ and is $\geq$ the numerical value of the $\frac{P_2}{\eta^2}$ slopes except for solutions containing chlorine when the slope is a maximum at 95. This is in line with the known anomalous behaviour of chlorine which is also shown with methyl cyanide when the $\frac{P_2}{\eta^2}$ slope is a minimum.

Examination of the slope of the lines relative to the solvent shows that for $\gamma$-butyl chloride they are in the order $1,4$-dichloro benzene $> \text{toluene} > \text{carbon tetrachloride} > \text{carbon disulphide} > \mu$-heptane $> \mu$-hexane while for methyl cyanide almost exactly the reverse order
results. It is of interest to note that this order reflects the order of their molecular shapes of the solvents, long thin molecules like hexane and carbon disulfide at one end of the series, carbon tetrachloride of spherical form in the centre and the disc-like tetralin and benzene at the other end.

Extending the concept of Suck’s relationship it should relate the polarization at infinite dilution and the volume polarization of the solvent for a series of solvents. On this basis it predicts that plot of $\frac{P_2}{P_2^0}$ against $\Pi_1$ for various solvents should be linear, with the slope equal to $\mu_2$, as before. Data are plotted in Figure 16 but there is obviously no relationship between these quantities and it must be accepted that while the relation is of the right form for a solute in one solvent at one temperature it is doubtful if any simple significance can be attached to the constants.

If molecular interaction were responsible for the solvent effects observed with the polarization it might be expected that they would be reflected in the apparent specific volumes of the solutes. The figures below include the molecular polarization and specific volume of the solutes both at infinite dilution (the latter being calculated assuming that $V_1$ is equal to that of the pure solvent) and expressed as a percentage of that for the pure solute.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>n-Butyl chloride</th>
<th>Methyl cyanide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\frac{P_2}{P_2\text{gas}} \times 100$</td>
<td>$\frac{(V_1+\beta)}{V_2} \times 100$</td>
</tr>
<tr>
<td>Toluene</td>
<td>60.5</td>
<td>97.3</td>
</tr>
<tr>
<td>Mixture + p. Dichloro-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzenes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixture</td>
<td>103.9</td>
<td>97.9</td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tetrachloride + p. Dichloro-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>104.5</td>
<td>93.8</td>
</tr>
<tr>
<td>tetrachloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>101.5</td>
<td>90.6</td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dichloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Heptane</td>
<td>103.0</td>
<td>101.1</td>
</tr>
<tr>
<td>p-Heptane</td>
<td>103.9</td>
<td>101.0</td>
</tr>
</tbody>
</table>

There is no connection between the two quantities but the apparent specific volume shows the influence of both solute and solvent. The effect of the solvent is almost identical for both solutes (i.e. $V_1+\beta$ is almost the same percentage of $V_2$ for both n-butyl chloride and methyl cyanide in any one solvent) although for methyl cyanide the effect is slightly greater; the normal paraffins again show unexpectedly large differences from the other solvents. The differences between the two solutes in each and cannot be attributed directly to the shape since for n-butyl chloride there is a smaller external field due to the lower amount of the spherical nature of the molecule.
which will result in lower intermolecular forces in the pure material and therefore a smaller effect of a non-polar solvent on the apparent specific volume. The assumption, however, that the specific volume of the solvent in solution is the same as that of the pure material may be in error as values calculated from simultaneous equations set up from any set of experimental data show, e.g. \( \beta \)-butil chloride in carbon tetrachloride:

\[
\nu_{12} = \omega_1 \nu_1 + \omega_2 \nu_2
\]

\[
0.63114 = 0.00302 \nu_1 + 0.000576 \nu_2
\]

\[
0.63433 = 0.003043 \nu_1 + 0.00034 \nu_2
\]

whence \( \nu_1 = 0.6250 \) (pure solvent 0.6311)

\( \nu_2 = 1.2205 \) (pure solute 1.1200)

Although this indicates that the apparent specific volume in solution can differ from those of the pure components the figures thus calculated may be in error since the values for both solvent and solute probably vary with the concentration.

A similar order of solvents is given by consideration of the values of \( \nu_1 + \beta \) or the slopes \( \frac{d\beta}{d\nu_{12}} \) and it is possible that a relationship could be derived connecting these two quantities. If the molecular polarization of the solute is expressed as an apparent volume polarization \( \Pi \) and writing the volume polarization of the solution:

\[
\Pi_{12} = \Pi_1 \nu_1' + \Pi_2 \nu_2'
\]

where \( \nu_1' \) and \( \nu_2' \) are the volume fractions of the solvent and solute respectively and assuming \( \Pi_1 \) constant then the value of \( \Pi_{12}\infty \) can be calculated as \( \frac{V_{22}}{(\nu_1(\beta))M_2} \pi_1 \) while its value at any finite concentration will be given by.
\[ \Pi_2 = \Pi_1 + \frac{P_{12} - \Pi_1 V_{12}}{\omega_2 (V_1 + \beta)}. \]

Calculation of the values of \( \Pi_2 \) for some of the series of solutions has been made and are given in Table 23 and plotted in Figure 14 but it is found that the change of \( \Pi_2 \) with \( \Pi_1 \) also differs from solvent to solvent. Thus if molecular interaction is responsible for the solvent effects it does not lead to a parallel effect with the specific volume. This implies that, assuming the polarisation equations are correct, the interaction must be one that either alters the amount of the solute molecule without a corresponding change in its volume (4) (73) or more likely there is a change in both solute and solvent molecular volume as indicated above making it impossible to evaluate the specific volume of either.

4. CONTINUOUS MORTALITY CHAIN AND ANTHROPOMORPH

The present two series of investigations have shown that in each case the values of \( \frac{P_2}{X} \) for solutions in carbon dimethyl and tetralin are appreciably lower than the values for solutions in solvents of lower \( \epsilon_1 \), but with neither solute does the order of the \( \frac{P_2}{X} \) values follow that of the dielectric constants of the solvents. This fact and the low polarisations found in the normal paraffins invalidate all the proposed solvent effect corrections based only on the dielectric constant of the solvent, for these cannot predict the different values of \( \frac{P_2}{X} \) (or \( \frac{\mu P_2}{X} \)) for one value of solvent dielectric constant as has been found.
Each equation includes that due to:-

\[
\begin{align*}
\text{Jardim's} & \quad \mu P_2 \quad (or \quad \frac{\mu P_2}{T_1^2}) \quad \text{linear with} \quad \frac{\nu}{e_1} \quad (\text{44}) \\
\text{Sugden} & \quad \mu \quad \frac{e-1}{e+2} \quad (\text{52}) \\
\text{Huller} & \quad \mu \quad \frac{e-1}{e+2} \quad (\text{7}) \\
\text{Le Page} & \quad \mu \quad \frac{1}{e+2} \quad (\text{70})
\end{align*}
\]

As pointed out by these authors, quite good correlation is obtained for certain solvents and solutes but in some cases they break down completely and in any case the experimental results are never predicted exactly. From early work it was obvious that \( e_1 \) is a factor in the solvent effect but it was also realised that other constants of both the solvent and solute were important. The problem has been approached from this viewpoint by several authors including fern and Krishnam (57), Veity (53), Mignari (63) and Franks (61). To simplify the mathematics the molecular shape is sometimes generalised, e.g. to an ellipsoid of revolution by Mignari, and the polarisabilities along three mutually perpendicular axes are considered. The theory of fern and Krishnam was the first development from these fundamental principles and it is now considered in connection with the present solutes and solvents.

These authors pointed out that molecules are not optically isotropic, i.e. equally polarizable in all directions and hence the Delya Moestri Clausius relationship is not strictly applicable. For the case of a pure liquid they derived a relation which can be written in the form

\[
\frac{\Pi}{T_1} = \left( \frac{e-1}{e+2} \right) M \frac{N}{d} = \frac{4\pi}{3} N \left( \frac{\Xi}{3} + \frac{\mu^2}{3kT} \right) + \left( \frac{e-1}{e+2} \right) N \left( \psi + \frac{\varphi}{3kT} \right),
\]

where \( \Xi \) is the sum of the polarisabilities \( \alpha_1 + \alpha_2 + \alpha_3 \) along three axes at right angles, \( \psi = \frac{1}{3} (\alpha_1 s_1 + \alpha_2 s_2 + \alpha_3 s_3) \).
\[ \theta = \sum \mu_i^2 s_i + \sum 2 \mu_i \mu_j q_{ij} \]  

the \( \theta \) terms denoting the constants of the static polarization field and the \( s_i \) terms being given by expressions of the type

\[ q_{ij} = \frac{1}{2} \mu_i \mu_j \]  

\( \psi \) and \( \theta \) depend on the geometry of the solute molecule and involve the effect of the anisotropy of the solvent on the induced and orientation polarization respectively.

The theory has been extended to liquid mixtures by Sabharwala (53) and simplified by Iau (55) for solutions in non-polar solvents to give

the expression for the true value of \( \tau_{P_2} \):

\[ \tau_{P_2}(q_{ab}) = \frac{1}{2} \left( \frac{\Pi_0 M_{12}}{d_{12}} - \frac{d_1}{d_{12}} \right) - N \psi \int_{f_2}^{f_1} \left( \Pi_{i2} - \Pi_i \right) - \Pi_{12} N \left( \psi_2 + \frac{\theta_2}{3 \kappa T} \right) \]

where the second and third terms on the right hand side are corrections to the Lissotti-Clusius expression for \( \tau_{P_2} \). Iau pointed out that by considering the limiting case as \( f_2 \rightarrow 0 \) the first term on the right hand side:

\[ \frac{1}{2} \left( \frac{\Pi_{12} M_{12}}{d_{12}} - \frac{d_1}{d_{12}} \right) \]

becomes the uncorrected \( \tau_{P_2}^0 \) and writing

\[ \epsilon_\infty = \epsilon_i + \frac{d \epsilon}{df_2} f_2 \]  

the second term becomes

\[ N \psi \int_{f_2}^{f_1} \left[ \left( \frac{\epsilon_i + \frac{d \epsilon}{df_2} - 1}{(\epsilon_i + \frac{d \epsilon}{df_2} + 2)} \right) - \left( \frac{\epsilon_i - 1}{\epsilon_i + 2} \right) \right] \]

\[ = N \psi \int_{f_2}^{f_1} \left[ \frac{3 \frac{d \epsilon}{df_2} f_2}{(\epsilon_i + \frac{d \epsilon}{df_2} + 2)^2} \right] \]

\[ = N \psi \int_{f_2}^{f_1} \frac{3 \epsilon \Pi_{12}}{(\epsilon_i + 2)^2 M_1} \]

where

\[ \epsilon = \frac{d \epsilon}{df_2} = \frac{d \epsilon}{d \omega_2} \]
Hence \( \frac{P_2}{P_2^\infty} = N\psi_1 \frac{3\alpha M_2}{(e_1 + 2)M_1} - \pi_1 N\left(\psi_2 + \frac{\psi_3}{3M_1} + \frac{\Theta_2}{3M_1}\right) \) (VII)

\( \psi_1 \) applying to the homogeneous solvent and \( \psi_2 \) and \( \Theta_2 \) to the solute molecule in an infinitely dilute solution.

For the solutes in the present investigation the constants \( \psi_2 \) and \( \Theta_2 \) are not available but for a given solute if equation (VII) is correct then \( \frac{P_2}{P_2^\infty} = N\psi_1 \frac{3\alpha M_2}{(e_1 + 2)M_1} \) should be a linear function of \( \pi_1 \) and equal to the total molecular polarization in the gas phase at \( \pi_1 = 0 \) i.e. \( \epsilon = 1 \), as would be expected.

The following tables give values of \( s \) and \( \alpha \) for the solvents shown taken from the data of Rou (53) together with the \( N\psi_1 \) values deduced from them and the corrected values of \( \frac{P_2}{P_2^\infty} \).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( s_1 \times 10^3 )</th>
<th>( s_2 \times 10^3 )</th>
<th>( s_3 \times 10^3 )</th>
<th>( \alpha_1 \times 10^3 )</th>
<th>( \alpha_2 \times 10^3 )</th>
<th>( \alpha_3 \times 10^3 )</th>
<th>( N\psi_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>-1.73</td>
<td>0.63</td>
<td>0.63</td>
<td>1.44</td>
<td>1.07</td>
<td>1.07</td>
<td>-1.53</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>-2.09</td>
<td>1.0</td>
<td>1.0</td>
<td>1.05</td>
<td>1.22</td>
<td>1.22</td>
<td>-2.47</td>
</tr>
<tr>
<td>Carbon</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>tetrafluoride</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>-1.21</td>
<td>-1.21</td>
<td>2.42</td>
<td>1.41</td>
<td>1.41</td>
<td>0.71</td>
<td>-5.63</td>
</tr>
<tr>
<td>Carbon</td>
<td>-0.01</td>
<td>0.43</td>
<td>0.43</td>
<td>1.43</td>
<td>0.59</td>
<td>0.59</td>
<td>-1.53</td>
</tr>
<tr>
<td>disulfide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>( \Pi_1 ) for solvent</td>
<td>( \bar{D}_2 ) (cm)</td>
<td>( \frac{3\alpha \cdot M_2}{N \Pi_1 (e_1 + e_2)^2 \cdot M_1} )</td>
<td>( \bar{D}_2 ) corrected for solvent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>--------------------------</td>
<td>----------------------</td>
<td>---------------------------------</td>
<td>----------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Heptane</td>
<td>0.2302</td>
<td>122.9</td>
<td>-0.93</td>
<td>123.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0.2307</td>
<td>122.6</td>
<td>-1.02</td>
<td>123.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>0.2331</td>
<td>122.6</td>
<td>0</td>
<td>122.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>0.2373</td>
<td>119.9</td>
<td>-1.54</td>
<td>118.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>0.5227</td>
<td>109.6</td>
<td>-1.77</td>
<td>111.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \Pi_1 ) for solvent</th>
<th>( \bar{D}_2 ) (cm)</th>
<th>( \frac{3\alpha \cdot M_2}{N \Pi_1 (e_1 + e_2)^2 \cdot M_1} )</th>
<th>( \bar{D}_2 ) corrected for solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Heptane</td>
<td>0.2374</td>
<td>233.9</td>
<td>-2.51</td>
<td>231.3</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>0.2331</td>
<td>251.5</td>
<td>0</td>
<td>251.5</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.2373</td>
<td>257.7</td>
<td>-0.23</td>
<td>257.0</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>0.5233</td>
<td>221.6</td>
<td>-5.13</td>
<td>226.7</td>
</tr>
</tbody>
</table>

In the case of 2-butylnyl chloride the corrections do lead to almost equal values of \( \bar{D}_2 \) for the solvents of lower dielectric constant (i.e. approximately equal values of \( \Pi_1 \)) but carbon disulfide appears to be quite anomalous. Data are not available to permit a similar calculation for tetrachlorobenzene but this again would need a very large anisotropy factor to bring it in line with the other solvents. With methyl cyanide, however, the corrected values of \( \bar{D}_2 \) are much less satisfactory and
again carbon disulphide shows the greatest discrepancy. In neither case is the plot of corrected $\mu^\infty$ linear with $\Pi_1$.

It has been shown by Smith (60) that the relationship proposed by Selden, van Arkel and Snook (75), and Weigle can be deduced from that due to Eaman and Krishnan and since the latter does not predict the experimental data it is not surprising that the others are not obeyed. However, although these theories do not predict the dielectric constants found, that of Eaman and Krishnan and also that due to Higasi relate the polarisabilities along different axes to the polarisations calculated in solution and the vapour phase (13). From these considerations the solvent effect can be positive or negative according as the ratio of polarisabilities along and at right angles to the dipole axis is less or greater than unity (i.e. if the Kerr constant is negative or positive). It is obvious for methyl cyanide that the axis of maximum polarisability is that of the dipole but with 4-buty1 chloride the converse might be true and would thereby explain the positive solvent effect observed with most of the solvents. Eaman (50) has also pointed out that the extrapolation usually employed to find $\mu^\infty$ may be incorrect due to the variation of $\Pi_1$ with concentration of the solute. This was shown in the Eaman and Krishnan relation as modified by Eaman and has been realised and allowed for by Coas (63). The latter author made use of an intercept method first proposed by Orr and Butler (61) who stated that the intercepts at $f_2 = 0$ and 1 of the tangent to the plot at $f_2 = x_0$ gave the values of $\Pi_1$ and $\Pi_2$ respectively. This does not however give the correct values of $\Pi_1$ and $\Pi_2$ if they both vary with $\epsilon_1$ (i.e. $f_2$ ). Similarly, it is often assumed that the change of $\Pi_1$ with $\epsilon_1$ is eliminated by extrapolation to
infinite dilution but that this is not so may readily be shown as follows (30). $P_2$ at finite dilution is calculated as $P_1 + \left( \frac{P_{12} - P_1}{f_2} \right)$ assuming $P_1$ is that of the pure solvent. Hence, if both $P_1$ and $P_2$ are a function of $f_2$ and have values $P_1^o$ and $P_2^o$ at $f_2 = 0$, then at a finite concentration $f_2$:

$$P_1^o + \int_0^{f_2} \frac{dP_1}{df_2} \cdot df_2; \quad P_2^o = P_1^o + \int_0^{f_2} \frac{dP_2}{df_2} \cdot df_2 + \left( \frac{P_{12} - P_1^o}{f_2} \right) \int_0^{f_2} \frac{dP_2}{df_2} \cdot df_2$$

as $f_2 \to 0$ this becomes $P_2^o = P_1^o + \lim_{f_2 \to 0} \left( \frac{P_{12} - P_1^o}{f_2} \right) - \frac{dP_1}{df_2}$

The value of $P_1$ is of course correct but the value of $P_2^o$ as usually calculated is not $P_2^o$ but $P_2^o + \left( \frac{dP_1}{df_2} \right)_{f_2 = 0}$ and as it is not possible to evaluate the limiting value of $dP_1/df_2$ the correct polarization of the solute at infinite dilution, $P_2^o$, cannot be found. The Onnes and Krishnan treatment however shows that the polarization of an isotropic solvent, such as carbon tetrachloride, should not vary with $\varepsilon_{12}$ (or $f_2$) and therefore $P_2^o$ measured in this material should be free from this "solvent effect". The problem of the influence of the molecular shape of the solute and the relationship of the field in which it is situated to that of the applied field still remains.

5. DETERMINATION OF THE DURELL FIELD EQUATION

Considerations so far have been based on the Debye treatment starting from the Lorenz expression $E_0 = E + 4\pi I$ with the Isotti-Clausius assumptions for the local field acting on a molecule. This gives an expression which holds moderately well for almost all non-polar materials (when $\varepsilon = n^2$) but it fails in many respects for polar liquids.
In particular, the prediction of an electric 'Curie Point', as shown below:

\[ \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \leq \sqrt{\left( \chi + \frac{2}{3}\mu^2 \right)} \]

\( \varepsilon \) being the concentration of molecular/\( \varepsilon_0 \), the summation being extended over all the species present. \( \chi \) calculated from this formula will decrease as \( \varepsilon \) of the solution rises (i.e., the temperature falls) due to the function \( \frac{\varepsilon - 1}{\varepsilon + 2} \) which cannot exceed unity.

For any dielectric \( \frac{4\pi}{3} \left( \chi + \frac{2}{3}\mu^2 \right) \leq \) molecular volume and the point of equality is known as the electric 'Curie Point' characterised by an infinite dielectric constant. Beyond the 'Curie Point' the theory predicts a stable state of permanent electric polarization.

Such effects have been observed only in the case of certain solids (e.g., Rochelle salt) and consequently other treatments have been developed including drastic modifications of the fundamental theory.

Hart and Ward (23) have re-examined the internal field hypothesis with particular reference to that used by Lorentz and Debye and decided that the Lorentz-Debye specific refraction equation is correct for a single material.

\[ \frac{n-1}{d} = \text{const.} \]
\[ \frac{\varepsilon - 1}{d} = \text{const.} \]

In a later paper however (Aden, 207) these authors showed that the Ryzien equation (22) \( \left( \frac{n^2 - 1}{n^2 + 0.4^2} \right) \frac{1}{d} = \text{const.} \), \( \left( \frac{\varepsilon - 1}{\varepsilon + 0.4^2} \right) \frac{1}{d} = \text{const.} \) gave better agreement for the effect of temperature and pressure on \( n \) and \( \varepsilon \) for non-polar materials. Although neither of these equations were put forward originally for mixtures, it is known that molecular refractions are additive and it was considered sufficiently interesting to examine the present data assuming the two equations applicable to mixtures.

These two expressions can be used without requiring elaborate calculations.
if limiting conditions are imposed:

Hentry form - \((e-1)V_M = 4\pi N(\alpha + \frac{\mu^2}{3kT})\)

or to give the polarisation the same significance as the Clausius

Nozotti form - \(\frac{(e_{12}-1)}{3} V_{12} = P_{12} = P_1 \omega_1 + P_2 \omega_2\).

Since

\[ P_2 = P_1 + \frac{P_{12} - P_1}{\omega_2}; \quad \tau P_2^\infty = P_1 + \left(\frac{dP_{12}}{d\omega_2}\right)_{\omega_2 = 0}\]

\[ \frac{dP_{12}}{d\omega_2} = \frac{V_{12} d\epsilon_{12}}{3} \frac{d\epsilon_{12}}{d\omega_2} + \frac{\epsilon_{12}-1}{3} \frac{dV_{12}}{d\omega_2} \]

And

\[ \tau P_2^\infty = \frac{\epsilon_1-1}{3} (v_1 + \beta) + \alpha v_1 \quad \text{where} \quad \alpha = \left(\frac{d\epsilon_{12}}{d\omega_2}\right)_{\omega_2 = 0}; \quad \beta = \left(\frac{dV_{12}}{d\omega_2}\right)_{\omega_2 = 0}\]

Einstein form - \(\left(\frac{e-1}{\epsilon e + 0.4}\right) \frac{V}{3} = \tau P\)

Which as above

\[ \tau P^\infty = \frac{1}{3} \left(\frac{\epsilon_1-1}{\epsilon_1 e + 0.4}\right) (v_1 + \beta) + \frac{\alpha v_1}{6} \left(\frac{e_1 + 1 + 0.8n^2\epsilon_1}{(\epsilon_1 e + 0.4)^2} \frac{\epsilon_1}{V_T}\right)\]

An empirical relation for the total molecular polarisation has also been

put forward by Horder (91) who gives:

\[ \tau P = \frac{(e-1)(e+4)}{(8e+7)} V\]

and states that \(e\) should

be \(< 20\) and the concentration \(< 30\%\) mol.

Treating this as above gives

\[ \tau P^\infty = \frac{(e-1)(e+4)}{(8e_1 e + 7)} (v_1 + \beta) + \frac{\alpha v_1}{6} \left(\frac{8e_1 e + 14 e_1 + 53}{(8e_1 e + 7)^2}\right)\]

Kirkwood has proposed (25) that for pure liquids

\[ \tau P = \left(\frac{e-1}{qe1}\right) M V = \frac{4\pi N}{3} \left(\alpha + \frac{q^2 \mu^2}{3kT}\right) \]

where \(q^2 \mu^2\) is the actual moment associated with the dipole of the

molecule in the liquid. We may examine the expression (if applied to

mixtures) in a similar manner to those above obtaining:

\[ \tau P^\infty = \frac{(e-1)(2e-1)}{qe_1} (v_1 + \beta) + \frac{\alpha v_1}{qe_1^2} (2e_1^2 + 1)\]

The molecular polarisations at infinite dilution thus calculated are given

below together with the vapour phase values for methyl cyanide calculated.
from the data of Groves and Suyden. Similar calculations for the vapour
phase with 1-butyl chloride are not possible as the authors (Hewitt and
Suyden) do not quote any pressures or densities. To facilitate comparison
of the results from each equation a second table is given in which the
polarizations are expressed as a percentage of that found in carbon
tetrachloride. Expressing the results as a percentage of that in one
particular solvent is not as sound as using the mean value as the base
but the latter is not justifiable since in this case taking a mean would
assure that the variations were distributed in a random manner over the
solvents used. Carbon tetrachloride was chosen because of its isotropic
character with the result that it does not lead to extreme values for the
percentages.
<table>
<thead>
<tr>
<th>Solvent (in order of increasing $C_i$)</th>
<th>$P_2^\infty$</th>
<th>$\text{HCl}$</th>
<th>$\text{HBr}$</th>
<th>$\text{HNO}_3$</th>
<th>$\text{HClO}_4$</th>
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<td>Solvent</td>
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<td>115.3</td>
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<td>92.3</td>
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</table>
For any given solvent/solute combination the various equations lead, not unexpectedly, to different values for the total molecular polarization and always in the order Recin > Kizimod > Enquiries > Massetti ceramics > Ryman, while the polarizations calculated for 4-butyldichloride show smaller variations from solvent to solvent than found for methyl cyanide. In all cases the polarizations measured in diatom or solutions containing diatom are a minimum which is very strong evidence that this compound produces an exaltation of the total molecular polarization. Since the molecular refraction, for both solutes, as judged by the Lorentz-Lorenz function is the same for the pure liquids and in solution, it must be concluded that the orientation polarization is the only one affected - a conclusion reached by Miller from consideration of the solvent effect in general (7). This means that the 'complex' formed with diatom must be sufficiently stable to maintain its form during the oscillations in the applied field, or, as proposed by Latimer (74), the hydrogen bonding must result in the greatly increased polarizability of the proton due to increased mobility of the electrons. If this latter case is true it would be expected to be shown in the distortion polarization but since this is not so it is possible that the 'optical field' is not strong enough to effect a proportional displacement of the hydrogen-bond electrons, i.e. the field applied for dielectric constant measurement must result in the electrons passing through an energy barrier. This is not a convincing theory and it must be concluded that the electronic mobility is not greatly altered by hydrogen-bonding.
Returning to the various equations used above it will be seen that neither Houten's nor Eifwood's give low values for the polarizations in carbon disulphide or tetralin but they fail to bring the figures for the normal paraffins in line with the other solvents.

In was pointed out earlier that polarizations measured in the vapour phase should be used as criteria for the liquid phase. In cases where there is obvious interaction between solute and solvent as with dioxan it is to be expected that there will be poor agreement but also in cases where this is absent it would be fortuitous if the resultant field acting on a molecule is the same in the vapour phase as it is in the liquid state or in dilute solution in a solvent. It might then be expected that the vapour phase polarizations as calculated by one equation would show agreement with those from solution measurements using another equation. As will be seen only the Lipman equation gives a value for the vapour phase polarization different from the others which are the same as obtained with the Hosotti-Clusius and since it is generally accepted that the latter is correct for gases at low pressure it is considered as the reference polarization. With methyl cyanide Eifwood's equation gives fair agreement between solution and vapour values but in no case is this found for n-butyl chloride which is surprising in view of the symmetry of the molecule, but the method of computing the polarization of the solute may also be at fault due to neglecting the term $\frac{d\mu}{dt}$ (i.e. assuming it to be zero).
6. ALTERNATIVE APPROACH TO THE INDUCED DIPOLAR POLARIZATION

Further treatments of the problem have involved drastic modifications of the fundamental theory. Under the conditions normally used for the measurement of polarizations in solution, i.e. high dilution and non-polar solvents, Debye (28) has suggested that it is possible to avoid the use of the Koehl-Einstein relationship. Approaching the problem from the same basic as the Debye-Friedel theory, considering the solute molecule spherical and regarding the solvent as a continuous medium, he obtains

\[ \frac{(\varepsilon_{\infty} - \varepsilon_1) - (n_{\infty}^2 - n_1^2)}{\varepsilon_{\infty}/\varepsilon_2} = \frac{4\pi \mu^2}{3kT} \]

where \( \varepsilon_{\infty} \) is the number of solute molecules per cm of the solution and \( \mu \) is defined as the total electric moment between the plates of a large parallel-plate condenser filled with solvent and containing a single solute molecule with its polar axis normal to the plates.

Hence

\[ \varepsilon_{\infty}/\varepsilon_2 = \omega_2 N/\varepsilon_2 M_2 \]

and therefore we can write

\[ \frac{4\pi N \mu^2}{3kT} = \mu \mathcal{P}_{\infty} = \left[ \frac{(\varepsilon_{\infty} - \varepsilon_1) - (n_{\infty}^2 - n_1^2)}{\omega_2} \right] \varepsilon_{\infty} \frac{M_2}{3 \varepsilon_1} \]

which in the limit becomes:

\[ \lim_{\omega_2 \to 0} \mu \mathcal{P}_{\infty} = (\alpha - \gamma) \frac{M_2}{3 \varepsilon_1} \]

whence \( \gamma = \lim_{\omega_2 \to 0} \frac{(n_{\infty}^2 - n_1^2)}{\omega_2} \).

permitting quick and simple evaluation of the orientation polarization at infinite dilution. This author's model indicates that the orientation polarization varies from one solvent to another according to the relation:

\[ \mu \mathcal{P}_{\infty} \left( \varepsilon_1 + \frac{\varepsilon_2}{2} \right)^2 = \text{const}. \]
At about the same time这样才能 publish a similar treatment of the
diffusion (87) but taking into account the reaction field as distinct
from the cavity field treated by Lorenz and Pohl.

He obtained for a pure polar liquid
\[
\frac{(1-\eta^2)(2\eta+\eta^2)}{\eta (\eta^2+2)^2} = 4\pi N \frac{\mu_0^2}{kT}
\]
(where \(\mu_0\) is the permanent moment in vacuo) and for dilute solutions
of a polar solute in a non-polar solvent
\[
\epsilon_{12} - n_{12}^2 = \frac{4\pi N V_2}{3kT} \mu^2 \left[ \frac{n_1^2(n_2^2+2)}{2n_1^2+n_2^2} \right]
\]

Assuming that the molecules are spherical and \(n_1^2 = \epsilon_1\),
Cagner states that since \(\mu_2^2\) is small the theory gives results little
different from that due to Bocchi and Clausius but it does not predict
a Curie point. He also shows that the moment in solution is not the
same as that in the vapour phase, the two being related by the
expression
\[
\frac{\mu (\text{vap})}{\mu (\text{g})} = \frac{(2n_1^2+1)(n_2^2+2)}{3(2n_1^2+n_2^2)}
\]

i.e. \(\mu_2^2 (\text{vap}) = \mu_2^2 (\text{g}) \left[ \frac{3(2n_1^2+n_2^2)}{(2n_1^2+1)(n_2^2+2)} \right]^2\)

To apply the present results Cagner's equation may be treated as
follows: since \(V_2 = \omega_2 N / M_2 V_{12}\)
\[
\left( \epsilon_{12} - n_{12}^2 \right) M_2 V_{12} = \frac{4\pi N}{3kT} \mu^2 \omega_2 \left[ \frac{n_1^2(n_2^2+2)}{2n_1^2+n_2^2} \right]^{2}
\]

Differentiating with respect to \(\omega_2\)
\[
\left( \frac{d\epsilon_{12}}{d\omega_2} - \frac{d n_{12}^2}{d\omega_2} \right) M_2 V_{12} + \left( \epsilon_{12} - n_{12}^2 \right) M_2 \frac{dV_{12}}{d\omega_2} = \frac{4\pi N \mu^2}{3kT} \left[ \frac{n_1^2(n_2^2+2)}{2n_1^2+n_2^2} \right]^{2}
\]
in the limit \( \omega_1 \to 0 \)

\[
M_2[(\alpha - \gamma) v_i + (\epsilon_1 - n_i^2) \beta] = \frac{4 \pi N \mu^2}{kT} \left[ \frac{n_i^2(n_i^2 + 2)}{2n_i^2 + n_i^2} \right]^2
\]

or

\[
\frac{\mu_2^2}{\mu_2^2} = \frac{4 \pi N \mu^2}{kT} = \frac{M_2}{3} \left[ (\alpha - \gamma) v_i + (\epsilon_1 - n_i^2) \beta \right] \left[ \frac{2n_i^2 + n_i^2}{n_i^2} \right]^2
\]

The polarizations at infinite dilution calculated from these two equations are as follows:

<table>
<thead>
<tr>
<th>Solvent (in order of increasing ( \epsilon_1 ))</th>
<th>( \frac{\mu_2^2}{\mu_2^2} )</th>
<th>( \frac{4 \pi N \mu^2}{kT} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Dioxane</td>
<td>29.7 (Cugnati)</td>
<td>29.7 (Cugnati)</td>
</tr>
<tr>
<td>p-Hexane</td>
<td>33.5 (Oster)</td>
<td>33.5 (Oster)</td>
</tr>
<tr>
<td>Dioxan</td>
<td>23.7 (Cugnati)</td>
<td>23.7 (Cugnati)</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>23.0 (Cugnati)</td>
<td>23.0 (Cugnati)</td>
</tr>
<tr>
<td>Carbon tetrachloride + p-Dichlorobenzene</td>
<td>34.9 (Oster)</td>
<td>34.9 (Oster)</td>
</tr>
<tr>
<td>Dioxan + p-Dichlorobenzene</td>
<td>23.6 (Cugnati)</td>
<td>23.6 (Cugnati)</td>
</tr>
<tr>
<td>Benzenes</td>
<td>23.0 (Oster)</td>
<td>23.0 (Oster)</td>
</tr>
<tr>
<td>Toluene</td>
<td>23.3 (Oster)</td>
<td>23.3 (Oster)</td>
</tr>
</tbody>
</table>

In all cases the solvent of highest dielectric constant gives a low polarization and for p-butyl chloride values calculated from Cugnati's expression are in the reverse order of the solvent dielectric constants.
Onager's equation gives a maximum value for both solutes in dioxan and dioxan-containing solutions. Both authors predict that the moment will vary from solvent to solvent and therefore $\mu_2^\infty$ will not be constant.

It is possible to calculate the corresponding vapour phase value from the relationships given below:

Guggenheim

$$\mu_2^\infty (e_1 + e_2) = \text{const.}$$

$$\mu_2^{\text{(vap)}} = \mu_2^\infty \left(\frac{e_1 + e_2}{1 + \frac{e_2}{2}}\right)^2$$

and as shown above Onager relates

$$\mu_2^{\text{(vap)}} = \mu_2^\infty \left[\frac{3(2n_1^2 + n_2^2)}{(2n_2^2 + 1)(n_2^2 + 2)}\right]^2$$

The polarisations thus calculated are as follows taking the dielectric constant at 20°C of p-butyl chloride as 2.40 interpolated (22) and methyl cyanide as 32.0 (29).
<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \mu P_a ) (vapour phase)</th>
<th>( \mu P_a ) (vapour phase)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \mu ) Dibutyl chloroide</td>
<td>( \mu ) Dibutyl chloroide</td>
</tr>
<tr>
<td></td>
<td>( \mu ) Ethyl cyanoide</td>
<td>( \mu ) Ethyl cyanoide</td>
</tr>
<tr>
<td>p-Dioxane</td>
<td>115.2</td>
<td>234.5</td>
</tr>
<tr>
<td></td>
<td>85.7</td>
<td>135.7</td>
</tr>
<tr>
<td>p-Heptane</td>
<td>115.9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>85.4</td>
<td>-</td>
</tr>
<tr>
<td>Dioxane</td>
<td>125.4</td>
<td>232.1</td>
</tr>
<tr>
<td></td>
<td>85.6</td>
<td>222.7</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>125.2</td>
<td>243.0</td>
</tr>
<tr>
<td></td>
<td>85.0</td>
<td>233.0</td>
</tr>
<tr>
<td>Carbon tetrachloride + p-Dichlorobenzene</td>
<td>125.6</td>
<td>243.9</td>
</tr>
<tr>
<td></td>
<td>85.7</td>
<td>233.8</td>
</tr>
<tr>
<td>Dioxane + p-Dichlorobenzene</td>
<td>124.7</td>
<td>233.5</td>
</tr>
<tr>
<td></td>
<td>85.7</td>
<td>233.4</td>
</tr>
<tr>
<td>Benzene</td>
<td>123.7</td>
<td>234.0</td>
</tr>
<tr>
<td></td>
<td>85.2</td>
<td>233.3</td>
</tr>
<tr>
<td>Tetrolin</td>
<td>112.9</td>
<td>211.2</td>
</tr>
<tr>
<td></td>
<td>74.6</td>
<td>203.9</td>
</tr>
</tbody>
</table>

For the derivation of his equation, Czegar treated the solute molecule as a cavity of dielectric constant equal to the square of the optical refractive index of the pure liquid and its environment as a structureless continuum of uniform dielectric constant equal to that of the liquid in bulk. Towards the end of his paper Czegar states, "Incidentally our 'refractive index' should include the 'atomic polarization' due to elastic displacement of the atomic nuclei by the electric field" and since we are using non-polar solvents it is therefore preferable to use \( \varepsilon_1 \) in place of \( \eta_1^2 \) in his relationships. This has already been done by Latimer for the calculation of the moment of the molecule as a gas from that in solution (74) and applying it here the equation becomes:
\[
\mu P_2^\infty = \frac{M}{3} \left[ (\alpha - \gamma) \nu_1 + (\varepsilon_1 - \eta_1) \beta \right] \left[ \frac{2 \varepsilon_1 + \eta_1^2}{\varepsilon_1 (\eta_1^2 + 2)} \right]^2
\]

\[
\mu P_2(\nu \rho) = \mu P_2^\infty \left[ \frac{3(2 \varepsilon_1 + \eta_1^2)}{(2 \varepsilon_1 + 1)(\eta_1^2 + 2)} \right]^2
\]

In the first of these the term \((\varepsilon_1 - \eta_1) \beta\) has been left, although it is zero if \(\eta_1\) is replaced by \(\varepsilon_1\). The significance of this term is not known but for the present evaluation its effect on \(\mu P_2^\infty\) is neglected since its inclusion only raises the calculated polarisation by ca. one percent for \(\eta\)-butyl chloride and ca. 0.3 percent for methyl cyanide.

The recalculated polarisations are as follows:

<table>
<thead>
<tr>
<th>Solvent (in order of increasing (\varepsilon_1))</th>
<th>Butyl chloride</th>
<th>Methyl cyanide</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mol.)</td>
<td>(gass)</td>
<td>(\mu P_2^\infty)</td>
</tr>
<tr>
<td>p-Dioxane</td>
<td>96.9</td>
<td>61.0</td>
</tr>
<tr>
<td>p-Dinitrobenzene</td>
<td>97.1</td>
<td>62.3</td>
</tr>
<tr>
<td>Dioxane</td>
<td>102.1</td>
<td>63.9</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>102.0</td>
<td>61.9</td>
</tr>
<tr>
<td>Carbon tetrachloride + p-dichlorobenzene</td>
<td>102.5</td>
<td>61.8</td>
</tr>
<tr>
<td>Dioxane + p-dichlorobenzene</td>
<td>100.9</td>
<td>63.5</td>
</tr>
<tr>
<td>Benzene</td>
<td>93.5</td>
<td>70.4</td>
</tr>
<tr>
<td>Toluene</td>
<td>87.3</td>
<td>66.7</td>
</tr>
</tbody>
</table>

To simplify the comparison of these results with those previously calculated the polarisations have been expressed as a percentage of that found in carbon tetrachloride.
### Orientation Polarization as a Function of that in Carbon Tetrachloride

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Benzyl chloride</th>
<th>( \mu_2^\infty ) (soln.)</th>
<th>( \mu_2^\infty ) (vap.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>p-Butane</td>
<td>93.5</td>
<td>102.6</td>
<td>93.1</td>
</tr>
<tr>
<td>p-Heptane</td>
<td>93.2</td>
<td>102.6</td>
<td>93.3</td>
</tr>
<tr>
<td>Eicoen</td>
<td>100.3</td>
<td>100.9</td>
<td>100.3</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>+ p-Dichlorobenzene</td>
<td>93.5</td>
<td>93.9</td>
<td>100.1</td>
</tr>
<tr>
<td>Eicoen</td>
<td>93.1</td>
<td>93.3</td>
<td>100.6</td>
</tr>
<tr>
<td>Benzen</td>
<td>93.1</td>
<td>97.8</td>
<td>95.6</td>
</tr>
<tr>
<td>Tetrafluoroisoxylylene</td>
<td>101.6</td>
<td>103.0</td>
<td>95.6</td>
</tr>
<tr>
<td>Vapour phase *</td>
<td>94.4</td>
<td>94.4</td>
<td>100.6</td>
</tr>
<tr>
<td>Maximum loss</td>
<td>9.1</td>
<td>4.4</td>
<td>10.6</td>
</tr>
<tr>
<td>Minimum t</td>
<td>94.4</td>
<td>94.4</td>
<td>100.6</td>
</tr>
<tr>
<td>Actual value in</td>
<td>92.5</td>
<td>93.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

### Ethyl Cyanide

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ethyl cyanide</th>
<th>( \mu_2^\infty ) (soln.)</th>
<th>( \mu_2^\infty ) (vap.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>p-Butane</td>
<td>93.4</td>
<td>93.3</td>
<td>93.4</td>
</tr>
<tr>
<td>p-Heptane</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Eicoen</td>
<td>107.3</td>
<td>107.3</td>
<td>100.7</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>+ p-Dichlorobenzene</td>
<td>93.6</td>
<td>93.9</td>
<td>100.4</td>
</tr>
<tr>
<td>Eicoen</td>
<td>104.0</td>
<td>105.0</td>
<td>107.3</td>
</tr>
<tr>
<td>Benzen</td>
<td>103.7</td>
<td>103.8</td>
<td>103.8</td>
</tr>
<tr>
<td>Tetrafluoroisoxylylene</td>
<td>90.3</td>
<td>92.5</td>
<td>97.6</td>
</tr>
<tr>
<td>Vapour Phase *</td>
<td>102.8</td>
<td>102.8</td>
<td>102.8</td>
</tr>
<tr>
<td>Maximum loss</td>
<td>13.2</td>
<td>12.0</td>
<td>23.5</td>
</tr>
<tr>
<td>Minimum t</td>
<td>94.4</td>
<td>94.4</td>
<td>100.6</td>
</tr>
<tr>
<td>Actual value in</td>
<td>91.3</td>
<td>91.3</td>
<td>92.9</td>
</tr>
</tbody>
</table>

**Pict.:**

- A: Lorentz-Loewenstein equation
- B: Guggenheim equation
- C: Gouy equation
- C': Gouy equation correcting to vapour phase
- C': Gouy equation correcting to vapour phase
The spread for \( \beta \)-butyl chloride is less than that for methyl cyanide but it is surprising to find that in spite of tetralin being polar and dixana interacting with the solute, both these solvents give reasonable polarizations with certain of the equations. With both solvents Guggenheim's equation leads to the least spread but the use of \( C_1 \) instead of \( \eta_1^2 \) in Guggen-geim's equation gives the closest agreement of any then corrected to the vapour phase. In all cases Guggen-geim's relationships require a positive solvent effect and Guggenheim a negative but neither nor are these lead to the same calculated vapour values \( \Lambda \) near those given by vapour measurements using the boschti Clausius equation. Considering the simplification of the molecular model used by these two authors the results obtained are fair but explain the need for a detailed treatment of each solution using the modified field equations as a basis. In this connection it has been pointed out by Frank (83) that the nockstti Clausius field model is correct for a dipole-free substance only and that the components of the electrical field acting on a dipole in a liquid are:

(a) That arising from the field applied for measurement.

(b) The field due to the permanent moment of the central molecule which polarizes the surrounding medium thereby producing a reacting field on the molecule.

(c) The resultant field arising from neighbouring polar molecules which will not, in general, be zero even when we are...
considering a non-polar central molecule.

(d) Possible non-electrostatic forces restricting molecular rotation, which can reduce the contribution of dipolar orientations to the dielectric constant. (This is equivalent to a microscopic viscosity).

Frank states further that the defect of Debye's theory is that he disregarded (b) while Onsager disregarded both (d) and the dielectric saturation which is the essence of the Debye theory.

7. COMMUTATOR RELATIONS AND THE INFLUENCE

No treatment has taken all the above components into account together with the effect of molecular shape, anisotropy and interaction between solute and solvent such as hydrogen bonding. As has been discussed above various authors have analysed the field acting on the molecule and have endeavoured to relate the polarisation to the dielectric constant of the solution. Others have made a more detailed study of the cavity occupied by the molecule or the molecular anisotropy and in particular the relationship for the latter due to唤 and Krishnan has been examined. These authors used the Busco-Cludo cavity field equation but it is possible to examine the corrections given by their relation using other expressions for the volume polarisation as shown below.

The treatments developed by Guggenheim and Onsager however are not suitable as they give only the orientation polarisation and the method has therefore only been applied to those due to Morton, Aylmer, Honigk and Krishnan.

It has been shown that for solutions in non-polar solvents the唤 and Krishnan expression reduces to:

\[
\tau_2^{\infty}(y_{\infty}) = \tau_2^{\infty} - N \psi_1 \left[ \frac{1}{\beta_2} \Pi_2 \Pi_1 \right]_{T=0} - \Pi_2 N \left( \psi_2 + \frac{\Theta_2}{3kT} \right)
\]
where \( \frac{f_1}{f_2} = \frac{\omega_1 M_2}{\omega_2 M_1} \) and \( \therefore \frac{f_0}{f_2} = \frac{1}{M_2} \left( \frac{d \Pi_2^\infty}{d \omega_2} \right) \omega_2 = 0 \)

and since the values of \( \left( \frac{d \Pi_2^\infty}{d \omega_2} \right) \omega_2 = 0 \) have been evaluated previously we can write down the four equations required:

\[
\begin{align*}
\text{Newton:} & \quad \Pi_2^\infty = \Pi_2^\infty - N \Psi_1 \alpha \frac{M_2}{M_1} \left( \frac{e_1 - 1}{3} \right) N \left( \Psi_2 + \frac{\Theta_2}{3 kT} \right) \\
\text{Redlich:} & \quad \Pi_2^\infty = \Pi_2^\infty - N \Psi_1 \alpha \frac{M_2}{M_1} \left( \frac{e_1 + q e_1^2 + 1}{(q e_1 + 1)^2} \right) \frac{e_1 - 1}{q e_1^2} N \left( \Psi_2 + \frac{\Theta_2}{3 kT} \right) \\
\text{Redlich:} & \quad \Pi_2^\infty = \Pi_2^\infty - N \Psi_1 \alpha \frac{M_2}{M_1} \left( \frac{e_1 - 1}{3} \right) \frac{e_1 - 1}{q e_1^2} N \left( \Psi_2 + \frac{\Theta_2}{3 kT} \right) \\
\text{Redlich:} & \quad \Pi_2^\infty = \Pi_2^\infty - N \Psi_1 \alpha \frac{M_2}{M_1} \left( \frac{e_1 - 1}{3} \right) N \left( \Psi_2 + \frac{\Theta_2}{3 kT} \right)
\end{align*}
\]

How \( \Psi_2 \) and \( \Theta_2 \) are not available for the solvents used but as was pointed out earlier, if the expressions are correct then \( \Pi_2^\infty = N \Psi_1 \alpha \frac{M_2}{M_1} \left( \epsilon_1 \right) \) should be linear with \( \Pi_1 \). The figures calculated, using the values of \( N \Psi_1 \) given previously, are as follows:

\begin{table}[h]
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
\textbf{Solvent} & \textbf{1-Butyl chloride} & \textbf{Methyl cyanide} & \textbf{Methyl cyanide} \\
& \textbf{1} & \textbf{2} & \textbf{3} & \textbf{1} & \textbf{2} & \textbf{3} \\
\hline
n-Heptane & 0.3035 & -0.7 & 107.9 & 200.4 & 0 & 493.1 & 493.1 \\
n-Heptane & 0.3035 & -2.7 & 107.9 & 200.4 & 0 & 493.1 & 493.1 \\
Carbon tetrachloride & 0.4607 & 0 & 227.3 & 227.3 & 0 & 469.0 & 469.0 \\
Benzene & 0.4231 & 0 & 225.4 & 225.2 & 0 & 459.6 & 459.6 \\
Carbon disulfide & 0.5445 & -1.2 & 232.3 & 232.3 & 0 & 512.3 & 512.3 \\
\hline
\end{tabular}
\end{table}
<table>
<thead>
<tr>
<th>Solvent</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Pentane</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.170</td>
<td>0.170</td>
<td>0.170</td>
<td>0.170</td>
<td>0.170</td>
<td>0.170</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.210</td>
<td>0.210</td>
<td>0.210</td>
<td>0.210</td>
<td>0.210</td>
<td>0.210</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>0.250</td>
<td>0.250</td>
<td>0.250</td>
<td>0.250</td>
<td>0.250</td>
<td>0.250</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Pentane</td>
<td>0.220</td>
<td>0.220</td>
<td>0.220</td>
<td>0.220</td>
<td>0.220</td>
<td>0.220</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.300</td>
<td>0.300</td>
<td>0.300</td>
<td>0.300</td>
<td>0.300</td>
<td>0.300</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>0.300</td>
<td>0.300</td>
<td>0.300</td>
<td>0.300</td>
<td>0.300</td>
<td>0.300</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.330</td>
<td>0.330</td>
<td>0.330</td>
<td>0.330</td>
<td>0.330</td>
<td>0.330</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>0.300</td>
<td>0.300</td>
<td>0.300</td>
<td>0.300</td>
<td>0.300</td>
<td>0.300</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
<th>n&lt;sub&gt;1&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Pentane</td>
<td>0.290</td>
<td>0.290</td>
<td>0.290</td>
<td>0.290</td>
<td>0.290</td>
<td>0.290</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.350</td>
<td>0.350</td>
<td>0.350</td>
<td>0.350</td>
<td>0.350</td>
<td>0.350</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>0.330</td>
<td>0.330</td>
<td>0.330</td>
<td>0.330</td>
<td>0.330</td>
<td>0.330</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.390</td>
<td>0.390</td>
<td>0.390</td>
<td>0.390</td>
<td>0.390</td>
<td>0.390</td>
</tr>
<tr>
<td>Carbon disulfide</td>
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\[
A = N \psi_1 \left( \frac{d \Pi_1}{d \omega_2} \right)_{\omega_2 = 0} \quad \quad B = \frac{\Pi_1}{\omega_2} - N \psi_1 \left( \frac{d \Pi_1}{d \omega_2} \right)_{\omega_2 = 0}
\]
Examination of these data show that the linearity of $\overline{P}_2^\infty \ (\text{corr.})$ with $\overline{\eta}$ is not better than when using the volume polarization as given by the Helviti Clusius expression although certain of the equations do show carbon disulfide as not being anomalous, e.g. Norton and Rahnwood.
CONCLUSIONS
Considering first the experimental work, it has been found that provided the data are of sufficient accuracy then the calculated polarization at infinite dilution is independent of the method of extrapolation used, but in general it is undoubtedly preferable to use the modified method of Helvelstall and Kudler. This allows direct assessment of the experimental results and does not require the use of derived functions which may contain cumulative errors. Particular attention must be given to the constants for the pure solvent as these have a direct bearing on the extrapolated values.

Differences between the behaviour of \( \delta \)-butylic chlorides and methyl cyanide attributable to differing molecular shapes are difficult, if not impossible, to differentiate from those arising from the difference in moments and are complicated by the association of methyl cyanide in solution. As has been pointed out by previous authors, the use of non-polar solvents gives a very limited range of dielectric constants and only by careful experimental work can it be definitely ascertained whether a given equation fits the data for different solvents or not. The overall result of the present work is that no equation can correlate all the data with any accuracy, Smagorinsky's expression gives the least spread for the orientation polarization but only when the square of the refractive index of the solvent is replaced by its dielectric constant.

If the vapour phase data are correct, there is a positive solvent effect for \( \delta \)-butoylic chlorides and a negative one for methyl cyanide (using the Debye-Einstein Clausius relationships) which is the only effect that may be directly attributable to molecular shape, implying that with \( \delta \)-butoylic chlorides the axis of maximum polarizability is at right angles...
to that of the dipole while for methyl cyanide the two are collinear. Contrary to expectation the normal paraffins are found to give unusual results, leading to low values for the total molecular polarizations at infinite dilution, an observation which is paralleled by the unexplained fact that for these compounds the square of the refractive index is greater than the dielectric constant.

The use of mixed solvents clearly indicates that the dielectric constant is not the only parameter connected with the solvent effect and the possibility of the existence of a sorting effect brought about by the solute is not proved. The latter issue is complicated in the case of methyl cyanide by its association in solution and with chlorine by the tendency of this compound to hydrogen bond formation resulting in an excitation of the orientation polarization only.

Calculated specific volumes of the solute at infinite dilution do not correlate with polarizations calculated by any of the methods but for both solutes they show a similar effect for each solvent, that with methyl cyanide being greater than that for 4-butoxy chloride. From the results however it is obvious that the calculated specific polarizations are in error due to the variation of that of the solvent with solute concentration.

The work as a whole indicates that none of the theories or equations examined can alone quantitatively predict the relationship between the physical constants of a solution and its components. Each solution must be treated as an individual problem (due to the effects operating bearing no relation to each other) if its behaviour is to be explained completely and quantitatively.
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3.

TABLES AND FIGURES


**t-Buty1 Chloride**

in n-Hexane at 25°C.

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### Table 2: t-Butyl Chloride in n-Heptane at 25°C

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**TABLE 3**

Butyl Chloride in heptane at 25°C

Interpolated from data by Smyth and Donets (22)

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Authors give \( \frac{P}{\omega_2} \) at 25°C as 126 cc.

Recalculation by method of Halverstadt and Kusler gives \( \frac{P}{\omega_2} = 122.6 \) cc.
### t-Buty1 Chloride

in 1:4 Dioxan at 25°C

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TABLE 5  

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in Carbon Tetrachloride at 25°C
$t$-Butyl Chloride

in Carbon tetrachloride

and $p$-dichlorobenzene at 25°C

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* Interpolated

TABLE 8

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### Methyl cyanide

in 1:4 Dioxan at 25°C

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Methyl cyanide  
in Carbon tetrachloride at 25°C

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TABLE 13
### TABLE 14

**Methyl cyanide**

in Carbon tetrachloride and p-Dichlorobenzene at 25°C

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**Methyl cyanide**

**in 1:4 Dioxan and p-Dichlorobenzene at 25°C**

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**Note:** The table represents data for some chemical compound in benzene at 25°C.
Methyl cyanide

in Carbon disulphide at 25°C

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## Methyl cyanide

### in Tetralin at 25°C

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<td>0.021900</td>
<td>2.9801</td>
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<td>0.39760</td>
<td>1.03527</td>
<td>0.41163</td>
<td>194.0</td>
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<th>$(n_{12})_D$</th>
<th>$(r_{12})_D$</th>
<th>$(R_{2})_D$</th>
<th>$\Delta \epsilon / \omega_2$</th>
<th>$\Delta V / \omega_2$</th>
<th>$\Delta n^2 / \omega_2$</th>
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<td>28.55</td>
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<td>32.92</td>
<td>0.225</td>
<td>-0.710</td>
</tr>
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<td>0.32550</td>
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<td>32.89</td>
<td>0.222</td>
<td>-0.710</td>
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<td>0.32541</td>
<td>10.9</td>
<td>32.57</td>
<td>0.215</td>
<td>-0.781</td>
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<td>11.3</td>
<td>32.41</td>
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<td>32.32</td>
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<td>-0.745</td>
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<td>2.3744</td>
<td>0.32527</td>
<td>11.1</td>
<td>32.50</td>
<td>0.221</td>
<td>-0.764</td>
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### Table 19

**m-Dinitrobenzene**

in Benzene at 25°C

<table>
<thead>
<tr>
<th>( x )</th>
<th>( \omega_2 )</th>
<th>( \epsilon_2 )</th>
<th>( \delta_2 )</th>
<th>( f_2 )</th>
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</thead>
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<tr>
<td>0</td>
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<td>0.87340</td>
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<td>0.005927</td>
<td>0.002763</td>
<td>2.3295</td>
<td>0.87557</td>
</tr>
<tr>
<td>3</td>
<td>0.019512</td>
<td>0.009162</td>
<td>2.4609</td>
<td>0.88022</td>
</tr>
<tr>
<td>4</td>
<td>0.041322</td>
<td>0.019634</td>
<td>2.6789</td>
<td>0.88873</td>
</tr>
<tr>
<td>5</td>
<td>0.089177</td>
<td>0.043512</td>
<td>3.1772</td>
<td>0.90621</td>
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</table>

<table>
<thead>
<tr>
<th>( v_{12} )</th>
<th>( p_{12} )</th>
<th>( \frac{D}{\omega_2} )</th>
<th>( \frac{\Delta \epsilon}{\omega_2} )</th>
<th>( \frac{\Delta V}{\omega_2} )</th>
</tr>
</thead>
<tbody>
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<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>0.35972</td>
<td>332.4</td>
<td>9.62</td>
</tr>
<tr>
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<td>0.37203</td>
<td>324.5</td>
<td>9.66</td>
</tr>
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<td>0.40323</td>
<td>313.3</td>
<td>9.84</td>
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<td>1.1034</td>
<td>0.46402</td>
<td>289.2</td>
<td>10.15</td>
</tr>
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</table>

\( D_2^\infty \) from plot \( D_2 \) vs \( f_2 \) = 336 cc

\( D_2^\infty \) calcd. by method of Halverstadt and Kunler = 336.7 cc
### TABLE 20

#### u. Dinitrobenzene in Benzene at 25°C

*Williams and Schwingel (115)*

<table>
<thead>
<tr>
<th>$\omega_2$</th>
<th>$f_2$</th>
<th>$\epsilon_{12}$</th>
<th>$\delta_{12}$</th>
<th>$v_{12}$</th>
<th>$\bar{v}_{2}$</th>
<th>$\frac{\Delta \epsilon}{\omega_2}$</th>
<th>$\frac{\Delta v}{\omega_2}$</th>
</tr>
</thead>
<tbody>
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<td>0.8751</td>
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<td>-</td>
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<tr>
<td>2</td>
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<td>0.0154</td>
<td>2.60</td>
<td>0.8852</td>
<td>1.1296</td>
<td>318</td>
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<tr>
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<td>0.04252</td>
<td>0.0202</td>
<td>2.69</td>
<td>0.8890</td>
<td>1.1249</td>
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<td>4</td>
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<td>0.0418</td>
<td>3.16</td>
<td>0.9057</td>
<td>1.1041</td>
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<td>0.0614</td>
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<td>1.0861</td>
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<tr>
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<td>0.0837</td>
<td>4.03</td>
<td>0.9381</td>
<td>1.0660</td>
<td>257</td>
<td>10.63</td>
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</table>

*Higasi (116)*

<table>
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<tr>
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<th>$f_2$</th>
<th>$\epsilon_{12}$</th>
<th>$\delta_{12}$</th>
<th>$v_{12}$</th>
<th>$\bar{v}_{2}$</th>
<th>$\frac{\Delta \epsilon}{\omega_2}$</th>
<th>$\frac{\Delta v}{\omega_2}$</th>
</tr>
</thead>
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<tr>
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<td>2.275</td>
<td>0.87331</td>
<td>1.1451</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>0.001527</td>
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<td>0.87449</td>
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<td>10.06</td>
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<td>0.002103</td>
<td>2.321</td>
<td>0.87496</td>
<td>1.1429</td>
<td>366</td>
<td>10.62</td>
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<td>4</td>
<td>0.00736</td>
<td>0.003433</td>
<td>2.346</td>
<td>0.87593</td>
<td>1.1416</td>
<td>342</td>
<td>9.92</td>
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<td>0.007666</td>
<td>2.426</td>
<td>0.87872</td>
<td>1.1380</td>
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<td>10.17</td>
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<td>0.012404</td>
<td>2.533</td>
<td>0.88296</td>
<td>1.1326</td>
<td>322</td>
<td>9.76</td>
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<tr>
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<td>0.012596</td>
<td>2.533</td>
<td>0.88288</td>
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<td>2.771</td>
<td>0.89160</td>
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</table>

**Author gives** $\bar{v}_{2}^\infty = 338$ cc

**Author gives** $\bar{v}_{2}^\infty = 365$ cc
Aniline

in Benzene at 25°C

<table>
<thead>
<tr>
<th>( \omega_2 )</th>
<th>( f_2 )</th>
<th>( \epsilon_{12} )</th>
<th>( \delta_{12} )</th>
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<td>0.0</td>
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</tr>
<tr>
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<td>0.042773</td>
<td>2.4245</td>
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<tr>
<td>4</td>
<td>0.085962</td>
<td>0.073112</td>
<td>2.5370</td>
</tr>
<tr>
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<td>0.110065</td>
<td>0.093982</td>
<td>2.6163</td>
</tr>
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<td>0.146214</td>
<td>0.125594</td>
<td>2.7394</td>
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<td>0.153770</td>
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<table>
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<th>( V_{12} )</th>
<th>( P_{12} )</th>
<th>( \tau_2 )</th>
<th>( \Delta\epsilon_{\omega_2} )</th>
<th>( \Delta V_{\omega_2} )</th>
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<td>1.13568</td>
<td>0.35659</td>
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\( \tau_2^{\infty} \) from plot \( \tau_2 \) v \( f_2 \) = 77.9 cc

\( \tau_2^{\infty} \) calcd. by method of Halverstadt and Kummer = 77.8 cc
### TABLE 22

**Aniline**

*in Benzene at 25°C*

Le Fèvre and Le Fèvre (117)

<table>
<thead>
<tr>
<th>$\omega_1$</th>
<th>$f_2$</th>
<th>$\varepsilon_{12}$</th>
<th>$\delta_{12}$</th>
<th>$V_{12}$</th>
<th>$\frac{P}{T_2}$</th>
<th>$\frac{\Delta \varepsilon}{\omega_2}$</th>
<th>$\frac{\Delta V}{\omega_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>0.87380</td>
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<td>0.026826</td>
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<td>0.87807</td>
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<td>1.1368</td>
<td>77.5</td>
<td>3.01</td>
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</table>

Author gives $\frac{P^\infty}{T_2} = 78.4$ cc

Higasi (62)

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<th>$\omega_1$</th>
<th>$f_2$</th>
<th>$\varepsilon_{12}$</th>
<th>$\delta_{12}$</th>
<th>$V_{12}$</th>
<th>$\frac{P}{T_2}$</th>
<th>$\frac{\Delta \varepsilon}{\omega_2}$</th>
<th>$\frac{\Delta V}{\omega_2}$</th>
</tr>
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<td>1</td>
<td>0.0</td>
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<td>0.8731</td>
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<td>1.1374</td>
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Author gives $\frac{P^\infty}{T_2} = 80.0$ cc
### 1:4 Dioxane

**TABLE 23**

<table>
<thead>
<tr>
<th>Dielectric Constant</th>
<th>Density g/ml.</th>
<th>Boiling Point °C/760</th>
<th>Melting Point °C</th>
<th>Year of Publication</th>
<th>References</th>
</tr>
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<tr>
<td>2.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1930</td>
<td>(97)</td>
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<tr>
<td>2.256</td>
<td>1.0311</td>
<td>-</td>
<td>-</td>
<td>1931</td>
<td>(98)</td>
</tr>
<tr>
<td>2.20</td>
<td>-</td>
<td>-</td>
<td>11.7</td>
<td>1933</td>
<td>(99)</td>
</tr>
<tr>
<td>-</td>
<td>1.0286</td>
<td>-</td>
<td>11.6</td>
<td>1934</td>
<td>(100)</td>
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<td>2.181</td>
<td>-</td>
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<td>11.780</td>
<td>n</td>
<td>(101)</td>
</tr>
<tr>
<td>-</td>
<td>101.4</td>
<td>11.6</td>
<td>n</td>
<td>(102)</td>
<td></td>
</tr>
<tr>
<td>2.1009</td>
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<td>n^25°C 1.4049</td>
<td>11.73 ± 0.01</td>
<td>1936</td>
<td>(104)</td>
</tr>
<tr>
<td>-</td>
<td>1.02801</td>
<td>101.40</td>
<td>11.80</td>
<td>1937</td>
<td>(105)</td>
</tr>
<tr>
<td>2.2374</td>
<td>1.0272</td>
<td>-</td>
<td>12</td>
<td>1938</td>
<td>(106)</td>
</tr>
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<td>2.280</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1939</td>
<td>(107)</td>
</tr>
<tr>
<td>2.2027 to 2.21623</td>
<td>1.02803 to 1.02825</td>
<td>-</td>
<td>-</td>
<td>1940</td>
<td>(108)</td>
</tr>
<tr>
<td>2.2095</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1941</td>
<td>(109)</td>
</tr>
<tr>
<td>2.207 to 2.226</td>
<td>1.0262 to 1.0279</td>
<td>-</td>
<td>-</td>
<td>1942</td>
<td>(110)</td>
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<td>2.2023 to 2.2163</td>
<td>0.97361 to 0.97390</td>
<td>-</td>
<td>-</td>
<td>1943</td>
<td>(111)</td>
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<tr>
<td>2.211 to 2.223</td>
<td>1.0279 to 1.0280</td>
<td>-</td>
<td>-</td>
<td>1944</td>
<td>(112)</td>
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<tr>
<td>2.211 to 2.230</td>
<td>1.0262 to 1.0282</td>
<td>-</td>
<td>1945</td>
<td>(113)</td>
<td></td>
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<td>2.2118</td>
<td>1.0277</td>
<td>-</td>
<td>-</td>
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<td>(114)</td>
</tr>
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<td>-</td>
<td>1947</td>
<td>(115)</td>
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<tr>
<td>2.2040</td>
<td>1.0280</td>
<td>n^25°C 1.4201</td>
<td>11.73</td>
<td>1948</td>
<td>Author</td>
</tr>
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</table>
### Table 24: Polarizations, Apparent Specific Volumes of Solutes, and $\frac{d\epsilon_1}{d\omega_2}$ and $\frac{d\eta_1}{d\omega_2}$ at 25°C

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant of Solvent</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$ (R₁)</th>
<th>$v_1 + \beta$</th>
<th>$\alpha$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapour phase</td>
<td></td>
<td>118.2</td>
<td>(26)</td>
<td>25.76²</td>
<td>1.1946e</td>
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<td>n-Hexane</td>
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<td>122.7</td>
<td>123.1</td>
<td>25.5</td>
<td>1.2165</td>
<td>3.445</td>
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<tr>
<td>n-Heptane</td>
<td>1.910</td>
<td>122.7</td>
<td>(22)b</td>
<td>123.0</td>
<td>25.7</td>
<td>1.2140</td>
<td>3.607</td>
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<tr>
<td>Dioxane</td>
<td>2.204</td>
<td>125.8</td>
<td>125.9</td>
<td>125.8</td>
<td>26.0</td>
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<td>6.196</td>
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<td>2.226</td>
<td>123.2</td>
<td>123.7</td>
<td>123.4</td>
<td>26.2</td>
<td>1.1853</td>
<td>9.365</td>
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<tr>
<td>Carbon tetrachloride</td>
<td></td>
<td>115.3</td>
<td>(23)a</td>
<td>119.8</td>
<td>26.3</td>
<td>1.1869</td>
<td>5.005</td>
</tr>
<tr>
<td>+ 2,3-dichlorobenzene</td>
<td>2.267</td>
<td>123.0</td>
<td>123.1</td>
<td>123.1</td>
<td>25.7</td>
<td>1.1812</td>
<td>9.105</td>
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<tr>
<td>Benzene</td>
<td>2.272</td>
<td>119.8</td>
<td>119.9</td>
<td>120.0</td>
<td>26.3</td>
<td>1.1869</td>
<td>5.005</td>
</tr>
<tr>
<td>Dioxane + 2,3-dichlorobenzene</td>
<td>2.272</td>
<td>122.5</td>
<td>122.7</td>
<td>122.8</td>
<td>25.7</td>
<td>1.1894</td>
<td>6.480</td>
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<td>Carbon disulphide</td>
<td>2.634</td>
<td>109.5</td>
<td>109.6</td>
<td>109.7</td>
<td>-</td>
<td>1.2074</td>
<td>6.820</td>
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<tr>
<td>Tetralin</td>
<td>2.753</td>
<td>105.8</td>
<td>105.9</td>
<td>105.9</td>
<td>25.9</td>
<td>1.1612</td>
<td>5.210</td>
</tr>
</tbody>
</table>

Calculations based on Mosotti Clausius Equation. For notes see continuation of table.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant of Solvent</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>($R_1$) $\beta$</th>
<th>$V_1 + \beta$</th>
<th>$\alpha$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapour phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Hexane</td>
<td>1.876</td>
<td>240.0*</td>
<td>239.7*</td>
<td>240.0*</td>
<td>11.1$^f$</td>
<td>1.2875$^e$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Heptane</td>
<td>1.910</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dioxan</td>
<td>2.204</td>
<td>269.6</td>
<td>269.6</td>
<td>269.5</td>
<td>11.1</td>
<td>1.2628</td>
<td>37.58</td>
<td>-0.271</td>
</tr>
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<td>Carbon tetrachloride</td>
<td>2.226</td>
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<td>251.5</td>
<td>251.0</td>
<td>11.3</td>
<td>1.2744</td>
<td>54.30</td>
<td>-0.638</td>
</tr>
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<td>Carbon tetrachloride + n-dichlorobenzene</td>
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<td>248.6</td>
<td>250.4</td>
<td>250.7</td>
<td>10.8</td>
<td>1.2619</td>
<td>52.29</td>
<td>-0.796</td>
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<tr>
<td>Benzene</td>
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<td>255.0</td>
<td>257.7</td>
<td>257.7</td>
<td>11.1</td>
<td>1.2607</td>
<td>31.38</td>
<td>-0.523</td>
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<tr>
<td>Dioxan + n-dichlorobenzene</td>
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<td>262.9</td>
<td>263.2</td>
<td>263.3</td>
<td>10.8</td>
<td>1.2517</td>
<td>40.06</td>
<td>-0.444</td>
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<td>Carbon disulphide</td>
<td>2.634</td>
<td>221.6</td>
<td>221.6</td>
<td>221.7</td>
<td>-</td>
<td>1.3479</td>
<td>44.25</td>
<td>-</td>
</tr>
<tr>
<td>Tetralin</td>
<td>2.753</td>
<td>205.0</td>
<td>205.1</td>
<td>205.5</td>
<td>11.0</td>
<td>1.2546</td>
<td>33.05</td>
<td>-0.749</td>
</tr>
</tbody>
</table>

Calculations based on Mosotti Clausius Equation. For notes see continuation of table:
<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$\tau^\infty_P$ cc Extrapolated from plot $\tau_2 v f_2$;</td>
<td>f</td>
<td>Molecular refraction of the pure liquid.</td>
<td>f</td>
<td>f</td>
</tr>
<tr>
<td>B</td>
<td>$\tau^\infty_P$ cc Calculated by Method of Halverstadt and Kumler (52)</td>
<td>g</td>
<td>Dielectric constant of &quot;n-hexane&quot; used was 1.883 at 25°C.</td>
<td>g</td>
<td>g</td>
</tr>
<tr>
<td>C</td>
<td>$\tau^\infty_P$ cc Extrapolated from plot $H v \tau_P$</td>
<td>g</td>
<td></td>
<td>g</td>
<td>g</td>
</tr>
</tbody>
</table>

a. Calculated from data at 20°C.


c. Accuracy may be low. $\tau_P$ assumed 51.7 cc for this calculation from $\mu = 24.0$ D.

d. The data is unsatisfactory.

e. Specific volume of pure solute.
Values of Dipole Moments using Debye Relation

\[ \mu = 0.01282 \sqrt{\frac{\mu}{T}} \] Debye Units

(Calculations based on Mosotti Clausius Equation)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant of Solvent</th>
<th>t-Butyl Chloride</th>
<th>Methyl Cyanide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>Vapour phase</td>
<td>-</td>
<td>118.2</td>
<td>2.112</td>
</tr>
<tr>
<td>Dioxan</td>
<td>2.204</td>
<td>125.8</td>
<td>2.195</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>2.226</td>
<td>123.6</td>
<td>2.174</td>
</tr>
<tr>
<td>Carbon tetrachloride + ( p )-dichlorobenzene</td>
<td>2.267</td>
<td>123.1</td>
<td>2.165</td>
</tr>
<tr>
<td>Dioxan + ( p )-dichlorobenzene</td>
<td>2.272</td>
<td>122.7</td>
<td>2.164</td>
</tr>
<tr>
<td>( n )-Hexane</td>
<td>1.876</td>
<td>122.9</td>
<td>2.165</td>
</tr>
<tr>
<td>( n )-Heptane</td>
<td>1.910</td>
<td>122.8</td>
<td>2.164</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.272</td>
<td>119.9</td>
<td>2.132</td>
</tr>
<tr>
<td>Carbon disulphide</td>
<td>2.634</td>
<td>109.6</td>
<td>2.013</td>
</tr>
<tr>
<td>Tetralin</td>
<td>2.753</td>
<td>105.9</td>
<td>1.916</td>
</tr>
</tbody>
</table>

A  \( \frac{D}{T} \) cc.

C  \( \mu \) assuming \( \frac{D}{T} = 1.05M [\frac{\gamma_0}{\xi_0}]_D \) for pure solute.

B  \( \mu \) assuming \( \frac{D}{T} = M [\frac{\gamma_0}{\xi_0}]_D \) for pure solute.

D  \( \mu \) found by other authors.

* Recalculated by Li and Chu (30)
### E. Dutil Chloride:

**TABLE 26**

<table>
<thead>
<tr>
<th>Benzene</th>
<th>Carbon tetrachloride</th>
<th>Carbon disulphide</th>
<th>n-Hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image.png" alt="Image" /></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Methyl Cyanide:**

| ![Image](image.png) |

---

---
PLATINUM WIRE
FOR SUPPORT
ON BALANCE

ETCHED MARK
CAPILLARY TUBING

PYKNOMETER
FIG. 3
OSCILLATOR & WAVEMETER
(SEE FOLLOWING PAGE FOR COMPONENT VALUES)
### Oscillator and Miller

**Component Values**

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁</td>
<td>1 μF - 1000 V</td>
<td>9 turns, 22 Ω S.W.C.</td>
</tr>
<tr>
<td>C₃</td>
<td>4 μF - 2000 V</td>
<td>24 turns, 22 Ω S.W.C.</td>
</tr>
<tr>
<td>C₅</td>
<td>200 pF</td>
<td>1 turn, 22 Ω S.W.C.</td>
</tr>
<tr>
<td>C₆</td>
<td>See Fig. 4</td>
<td></td>
</tr>
<tr>
<td>C₇</td>
<td>(200 pF fixed, 150 pF variable) (preset)</td>
<td>All coils close wound on 1/8&quot; diameter &quot;Tarnolin&quot; formers.</td>
</tr>
<tr>
<td>C₈</td>
<td>1 μF - 1000 V</td>
<td></td>
</tr>
<tr>
<td>C₉</td>
<td>4 μF - 1000 V</td>
<td></td>
</tr>
<tr>
<td>C₂</td>
<td>25 pF</td>
<td></td>
</tr>
<tr>
<td>C₃</td>
<td>Crystal holder</td>
<td>capacity to earth</td>
</tr>
</tbody>
</table>

A and B: See Fig. 4.

R₁ = 100,000 Ω fixed
R₂ = 50,000 Ω variable (preset)
V₁ = Kleson 210 S.F.T.
V₂ = Laban S.F.T.

Q: Quartz Crystal

1000.0 kHz/sec.

H.F.C. High frequency choke 500-1000 mtrco.

μA: 0-500 micro-amps moving-coil meter.
Resonance

Condenser Readings

5000  6000  7000  7990  7995  8000  9000
Condenser cell for liquids

Top of silvering

Taut 20SWG platinum wire

20 mm

1.2 mm

This tube is at right angles to plane of figure

Water level

Condenser cell for liquids

Fig. 6
FRACTIONATING COLUMN FIG. 9
LEGEND

1. Butyl Chloride.
2. Methyl Cyanide
3. Dioxane.
4. Dioxane + 2-Dichlorobenzene
5. Benzene
6. Carbon Tetrachloride
7. Carbon Tetrachloride + 2-Dichlorobenzene
8. n-Hexane
9. n-Heptane
10. Carbon Disulphide
11. Tetralin.
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Dorothy E. Denyer