DIELECTRIC ABSORPTION

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THE purpose of this article is to review some of the studies made in recent years (up to September, 1953) of the dielectric behaviour, at high frequencies, of systems of chemical interest. The principal features observed are associated with the rotations of polar molecules in the solid or the liquid state which are induced by alternating electric fields.[1] In almost all the cases yet studied, the absorption of energy which occurs is due to the non-quantised motion of individual molecules. Especially for the liquid state where clear indications as to molecular configurations and motions are not readily obtained, the study of dielectric absorption may well provide considerable insight into molecular-kinetic behaviour. The interactions between polar molecules and their neighbours are revealed : the effective viscosity of the medium for molecular motion can be determined : the influence of polar or ionic solutes upon the dielectric behaviour of the solvent is measurable, as is the freedom of motion of polar groups in the solid state : and, in the case of resonance absorptions, the possibility arises that effective collision numbers in the liquid state can be studied.

After a summary of the simple relations used in analysing the experimental data, the account deals in turn with the properties of water, ice, and aqueous ionic solutions ; then the general features of non-aqueous solutions are described with some reference to pure organic liquids. Selected aspects of the behaviour of solids and polymer systems are reviewed.

General Features

If alternating electric fields of frequency from 0 to, say, 10^6 cycles per second are applied to a dielectric liquid containing simple polar molecules the latter are well able to follow, by their rotation, the oscillations of the imposed potential. When there is no lag between the orientation of the molecules and the variations of the alternating voltage, it follows that the displacement current in the dielectric will be exactly 90° out of phase with the voltage, the former leading the latter. In simple terms this results from the fact that rotation of the dipoles will be most rapid when the voltage changes most rapidly, *i.e.*, when it passes through the instantaneous value of zero (Fig. 1). In a phase diagram (Fig. 2*a*) it is seen that there is no component of the current in step with the e.m.f., so the Joule heating in the system, measured by the product $e \times i$, is zero. If the frequency of the applied e.m.f. is continuously increased up to microwave values

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[1] Debye, " Polar Molecules ", Reinhold Publ. Corp., New York, 1929 ; Fröhlich, " Theory of Dielectrics ", Oxford Univ. Press, London, 1949 ; Böttcher, " Theory of Electric Polarisation ", Elsevier, Amsterdam, 1952.

The reader seeking an introduction to the basic relations in this field could well consult §§42, 43, 55 *et seq.* of Professor Böttcher's book : and ref. 12.

($f = 3 \times 10^{11}$ c./s. at $\lambda = 1$ mm.) the rotation of the molecules will, at some stage, begin to lag behind the voltage oscillations and for all but the smallest molecules in a liquid they will be completely unable to follow the field at frequencies of 10^{10} c./s., *i.e.*, 10,000 Mc./s. Two important effects accompany this lag: first, owing to the phase displacement (δ, Fig. 2*b*) in the dipole rotations the current acquires a component ($i \times \sin \delta$) in step with the voltage and dissipation of energy, as Joule heating, occurs in the medium; secondly, owing to the inability of the dipoles to follow the field, the dielectric constant falls to that of a non-polar material which arises solely from the atomic and electronic polarisabilities. It is the former feature which gives rise to the term "dielectric loss", and the latter to the dispersion of the dielectric constant. The situation is, essentially, entirely analogous to the dispersion of the refractive index in optical systems which invariably arises from the occurrence of absorption at some not-too-distant frequency, usually in the ultra-violet.

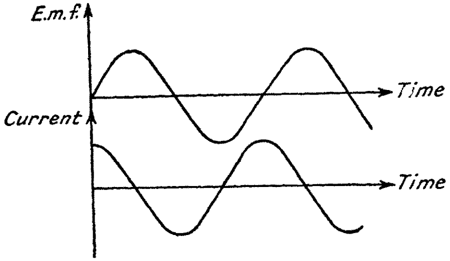

FIG. 1

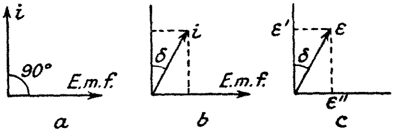

FIG. 2

The behaviour of the dielectric constant can also be represented by a phase diagram (Fig. 2*c*), in which the total dielectric constant, or permittivity (ε), has two components at those frequencies for which loss occurs in the medium: this is represented by

$$\varepsilon = \varepsilon' - j\varepsilon'' \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where ε' is the real dielectric constant, ε'' is the loss factor and is a measure of the conductance of the medium, and j is the operator representing rotation through 90° in the phase diagram; $j^2 = -1$. Clearly $\varepsilon''/\varepsilon' = \tan \delta$ and this is known as the dissipation factor; the closely related $\sin \delta$ is the power factor. It is frequently convenient to express the complex ε in terms of the real dielectric constant ε', and the conductance (in e.s.u.), σ; or, alternatively, by a refractive index n, and an absorption index r. These relations are

$$\varepsilon = \varepsilon' - 2j\sigma/f \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

$$\varepsilon = (n - jr)^2 \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

where f is the frequency in c./s. $= \omega/2\pi$.

Now $\varepsilon'' = 2\sigma/f = 1{\cdot}80 \times 10^{12}\kappa_f/f$, where κ_f is the specific conductance at frequency f in ohm^{-1} cm.$^{-1}$.

And, necessarily, $\varepsilon' = (n^2 - r^2)$; $\varepsilon'' = 2nr$.

If the absorption of radiation of wave-length λ cm. by a layer d cm. thick of the medium is represented by $I = I_0.\mathrm{e}^{-\alpha d}$, then the absorption coefficient $\alpha = 2\pi r/\lambda$.

The variation of the dielectric factors with frequency can be represented in a large number of cases by the equations

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/(1 + x^2) \qquad . \quad . \quad . \quad (4)$$

$$\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty)x/(1 + x^2) \qquad . \quad . \quad . \quad . \quad (5)$$

Here ε_0 is the static dielectric constant ($f = 0$) ; ε_∞ is the value on the high-frequency side of the dispersion region, and $x = \omega\tau$; $\omega = 2\pi f$ and τ is a characteristic relaxation time for the medium which represents the time variation of the polarisation (P) in the medium, so that if the electric field is instantaneously removed when $t = 0$, $\mathrm{d}P/\mathrm{d}t = -P/\tau$; or $P = P_0.\mathrm{e}^{-t/\tau}$. Böttcher [2] has pointed out that while the above are often referred to as Debye's equations, they were first put forward by Pellat.[3] Debye's particular advance was to relate τ for the medium with the intrinsic relaxation time, τ^*, for individual dipole molecules in the medium and for this he gave $\tau^* = (\varepsilon_\infty + 2)\tau/(\varepsilon_0 + 2)$. It appears that equations of precisely the forms (4) and (5) will apply in so far as the internal field in the dielectric is a linear function of the polarisation. With Onsager's modification [4] of this internal field factor it transpires that the correction $(\varepsilon_\infty + 2)/(\varepsilon_0 + 2)$ is not needed but rather that $\tau = \tau^*$, at least to a good approximation,[5] and a semi-empirical correction can be applied when greater precision is justified.

With $x = \omega\tau$, the maximum loss factor (ε''_m) occurs for $\omega_m\tau = 1$, and $f_c = \omega_m/2\pi$ is called the critical frequency. At this frequency $\varepsilon'_m = (\varepsilon_0 + \varepsilon_\infty)/2$; $\varepsilon''_m = (\varepsilon_0 - \varepsilon_\infty)/2$. Many methods can be applied to check whether a particular system follows equations (4) and (5). If ε_0 and ε_∞ are known the whole dispersion curve, usually drawn as a plot of ε' or ε'' against $\log_{10} f$, can be constructed from one measurement of either factor within the dispersion range, or, alternatively, from a chosen value of τ. Cole and Cole [6] introduced the plot of ε'' against ε'. Combination of equations (4) and (5) leads to

$$(\varepsilon'')^2 + [\varepsilon' - (\varepsilon_0 + \varepsilon_\infty)/2]^2 = [(\varepsilon_0 - \varepsilon_\infty)/2]^2 \qquad . \quad . \quad (6)$$

from which the Cole–Cole plot should be a semicircle of radius $(\varepsilon_0 - \varepsilon_\infty)/2$, meeting the abscissa at $\varepsilon' = \varepsilon_\infty$ and $\varepsilon' = \varepsilon_0$. This plot is of very general value as it remains almost a strictly circular arc in many cases where the dispersion cannot be adequately represented in terms of one relaxation time. This condition is not unusual in liquids or viscous solutions where the restraints on dipole rotation can vary markedly with changes in the

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[2] Bottcher, *op. cit.*, pp. 348—351.

[3] Pellat, *Ann. Chim. Phys.*, 1899, **18,** 150 ; *J. Physique*, 1900, **9,** 313.

[4] Onsager, *J. Amer. Chem. Soc.*, 1936, **58,** 1486.

[5] Cole, *J. Chem. Phys.*, 1938, **6,** 385 ; Bolton, *ibid.*, 1948, **16,** 486 ; Mandel, *Bull. Soc. chim. Belg.*, 1951, **60,** 301 ; and see especially Powles, *J. Chem. Phys.*, 1953, **21,** 633, and O'Dwyer and Sack, ref. 7, who give $\tau^* = (2\epsilon_0 - \epsilon_\infty)/3\epsilon_0.\tau$.

[6] Cole and Cole, *ibid.*, 1941, **9,** 341.

immediate surroundings of the molecule. The dispersion curves then become much flatter than corresponds to equations (4) and (5) owing to the "spectrum" of τ values involved. There is still uncertainty as to the precise representations of the different distributions of relaxation times found in practice,[7] but at least two empirical factors can be used to express the departures from a single τ value. Fuoss and Kirkwood [8] write

$$\varepsilon'' = \varepsilon''_m . \mathrm{sech}[\beta \ln (\omega/\omega_m)] \qquad \text{where } 0 < \beta < 1 \,;$$

and Cole and Cole start from

$$\varepsilon_{\mathrm{total}} = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/[1 + (j\omega\tau_0)^n] \qquad \text{where } 0 < n < 1.$$

Both β and n can be evaluated readily from the experimental data, the latter most simply from the displacement of the centre of the arc in the plot of ε'' against ε' below the abscissa. For β the relation $\varepsilon''_m = \beta . (\varepsilon_0 - \varepsilon_\infty)/2$ applies. Poley [9] has shown that the two representations are related as, to a sufficient approximation, $\beta = n/[\sqrt{2} \cos (n\pi/4)]$. The factors β and n are each unity for a single relaxation time. It should be noted that a molecule will be characterised precisely by one relaxation time only if its dipole vector is along one of its rotational axes.[10]

For dilute solutions of polar molecules both the Debye and the Onsager treatment lead to the relation :

$$\frac{\Delta \tan \delta}{c} = \text{molar loss tangent} = \frac{\varepsilon_0 + 2}{\varepsilon_0} . \frac{\Pi N_0 \mu^2}{6750\boldsymbol{k}T} . \frac{\omega\tau}{1 + \omega^2\tau^2} \quad . \qquad (7)$$

Here c is the molar concentration, N_0 Avagadro's constant, $\boldsymbol{k}$ the Boltzmann constant, and μ the dipole moment. An approximation is involved in using ε_0, the static dielectric constant of the solvent, for ε', the real part of the complex permittivity of the solution ; and $\Delta \tan \delta$ is the increase in that factor above its value for the non-polar solvent occasioned by the presence of the solute. Writing equation (7) as

$$\frac{\omega c}{\Delta \tan \delta} = \frac{\tau}{B}\omega^2 + \frac{1}{B\tau}$$

where

$$B = \frac{(\varepsilon_0 + 2)^2}{\varepsilon_0} . \frac{\Pi N_0 \mu^2}{6750\boldsymbol{k}T}$$

an important check of its applicability and the evaluation of μ and τ can be made by plotting $\omega c/\Delta \tan \delta$ against ω^2. Positive slopes and positive intercepts are required for the simple conditions envisaged.

A great variety of methods is available for the experimental study of the dielectric dispersion. The variation arises in the first instance from the frequency range being studied. From the lowest frequencies to roughly 10^8 c./s. ($\lambda = 3$ m.) conventional bridge or resonant circuit methods can

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[7] Garton, *Discuss. Faraday Soc.*, 1946, **42,** *A*, 56 ; Kauzmann, *Rev. Mod. Physics* 1942, **14,** 12 ; Macdonald, *J. Chem. Phys.*, 1952, **20,** 1107 ; see also O'Dwyer and Sack, *Austral. J. Sci. Res.*, 1952, **5,** 647.

[8] Fuoss and Kirkwood, *J. Amer. Chem. Soc.*, 1941, **63,** 385.

[9] Bottcher, ref. 1, p. 371.

[10] Perrin, *J. Phys. Radium,* 1934, **5,** 497 ; Oncley, *Chem. Reviews,* 1942, **30, 433.**

be used. Essentially because the dimensions of the circuit-connections are of the same order as the wave-length of the radiation, at frequencies higher than 10^8 sec.$^{-1}$, new methods characterised by wave-guide techniques are necessary.[11] It is not intended to review any of these experimental methods here. A further differentiation arises in practice according to the factors chosen for measurement. In the simplest systems it will be clear from what has already been outlined that the measurement either of the real dielectric constant (ε') or of the loss factor (ε'') over a sufficiently wide frequency range would suffice to characterise the dispersion process. It must be emphasised, however, that only by the simultaneous measurement of both factors can systems not following the simple relations be adequately studied. The same applies if, as is frequently done in the centimetre range, the factors measured correspond to the refractive index n and the absorption index r. Small losses such as arise in dilute solutions of polar molecules in non-polar solvents correspond to negligibly small changes in ε' (or n). It is then imperative to measure the loss factor (or absorption) directly. This can be done in at least three ways ; first, from the width of the resonance curve for a circuit in which the dielectric medium forms one element ; secondly, by the measurement of the percentage energy transmitted through an appropriate layer of the medium ; and, thirdly, by a direct (calorimetric or dilatometric) determination of the energy absorbed by the material. One of the simplest wave-guide methods is that of Potapenko and Wheeler[11] which used a precisely corrected Lecher-wire system to measure the dielectric constant and the coefficient of anomalous absorption for dilute solutions in dioxan. Frequency is the most important factor to vary in these studies : a range of several decades may be needed to cover properly one dispersion region. Roughly equivalent in the simplest cases—although much less generally satisfactory—is the study of the changing loss factor or dielectric constant as the temperature is varied at one frequency in the dispersion range. Increasing the temperature causes an exponential decrease in τ, and so the factor $\omega\tau = 2\pi f\tau$ can be greatly changed. The dispersion curves described by equations (4) and (5) can be traversed in this fashion.

Water

Surprisingly enough, in the matter of dielectric loss, liquid water shows a relatively simple behaviour, a survey of which provides data of exceptional interest. Until 1947 only a few measurements on water had been reported below 10 cm. wave-lengths and these, together with others above 10 cm. were vitiated by insufficient purity in the radiation used. As the critical

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[11] Lamont, " Wave guides ", Methuen and Co., London, 1942 ; Montgomery, " Technique of Microwave Measurements ", McGraw-Hill Book Co. Inc., New York, 1948 ; Willis Jackson, *Discuss. Faraday Soc.*, 1946, **42**, *A*, 91, and many other papers in the same volume ; Collie, Hasted, and Ritson, *ibid.*, p. 129 ; *Proc. Phys. Soc.*, 1948, **40,** 71 ; Bleaney, Loubser, and Penrose, *ibid.*, 1947, **39,** 185 ; Roberts and Hippel, *J. Appl. Phys.*, 1946, **17,** 610 ; Dakin and Works, *ibid.*, 1947, **18,** 789 ; Surber, *ibid.*, 1948, **19,** 514 ; Surber and Crouch, *ibid.*, p. 1130 ; Heston, Franklin, Hennelly, and Smyth, *J. Amer. Chem. Soc.*, 1950, **72,** 3443 ; Potapenko and Wheeler, *Rev. Mod. Physics*, 1948, **20,** 143.

wave-length at 20° is quite near 1 cm. and almost the whole of the dispersion occurs between 10 cm. and 0·1 cm., no reliable account of this process was available until Saxton and Lane's measurements appeared. These authors made systematic measurements of the absorption (r) and reflection (leading to the refractive index, n) by free-wave methods at 0·89, 1·24, and 1·58 cm.,[12] and by wave-guide methods at 0·62, 1·24, and 3·21 cm.[13]

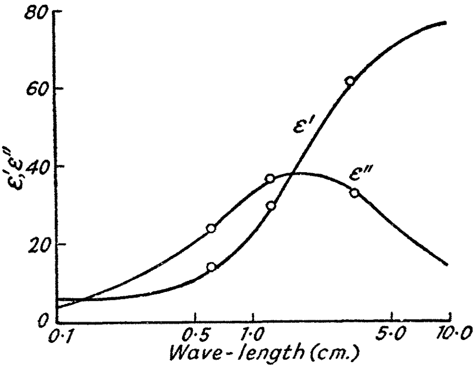

FIG. 3

The dielectric properties of water at 20° C.

[Reprinted, by permission, from Saxton, *Proc. Roy. Soc.*, 1952, *A*, **213**, 478.]

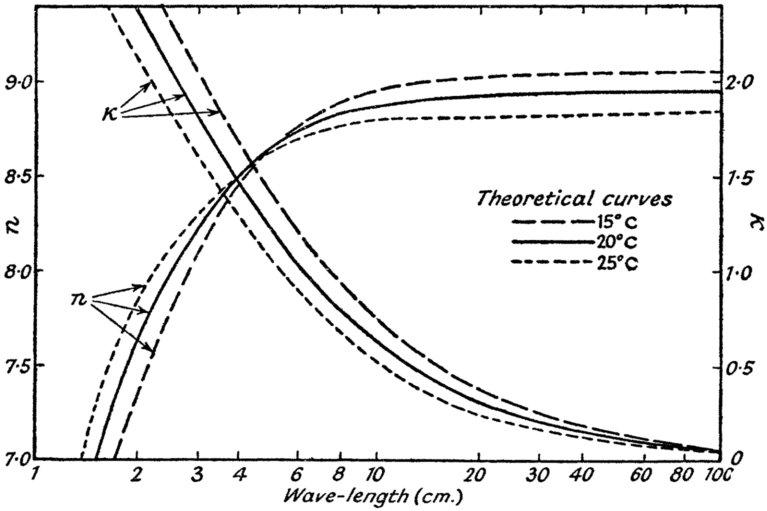

FIG. 4

Dielectric properties of water in the wave-length range 1 cm. *to* 1 m.

[Adapted, by permission, from Saxton, *Wireless Engineer*, 1949, **26**, 2.]

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[12] Saxton and Lane ; and Saxton, Phys. and Royal Meteorol. Soc. Report, 1947, pp. 273—325.

[13] Lane and Saxton, *Proc. Roy. Soc.*, 1952, *A*, **213**, 400.

Substantial agreement is found between their results and those obtained almost simultaneously at 1·27, 3·21, and 10·0 cm. by Collie, Hasted, and Ritson.[14]

The behaviour of the components ε' and ε'' at 20° is shown in Fig. 3, a summary of the directly measured n and r values at various temperatures from 15° to 25° being given in Fig. 4. The numerous experimental results now available closely follow the curves shown. The latest results give n and r correctly to about $\pm$ 1%. Saxton and Lane's results [13] extended from $-$ 8° (for supercooled water) to 50°, and Table 1 gives a summary of the essential factors.

TABLE 1. *Liquid water :* $\varepsilon_{\infty} = 4{\cdot}9$

Temp. :	− 10°	0°	10°	20°	30°	40°	50°
ϵ_0	92·3*	88·2	84·2	80·4	76·7	73·1	69·8
$10^{12}\tau$ (sec.) . .	27·5*	18·7	13·6	10·1	7·5	5·9	4·7

* Extrapolated values.

A conclusion of major significance is that all the reliable measurements can be accounted for at any one temperature by the assumption of a single relaxation time. In view of the molecular complexity usually ascribed to liquid water, this is surprising. The Onsager values of τ (which are quoted in Table 1) may be combined with Debye's evaluation of this factor for a simple sphere of radius a whose rotation is opposed by the macroscopic viscosity of the medium, η ; *i.e.*, $\tau = 4\pi\eta a^3/\boldsymbol{k}T$. It is well known that this expression leads to unacceptable a values for polar molecules in non-polar solvents because, it has been thought, the effective molecular viscosity is markedly different from (*i.e.*, smaller than) the macroscopic value (see below). However, use of $\tau = 10{\cdot}1 \times 10^{-12}$ sec. at 20° leads to $a = 1{\cdot}46$ Å. If the Cole–Van Vleck correction [5] of the Onsager treatment is applied in evaluating τ from x in equations (4) and (5), the modified value of $\tau = 15{\cdot}4 \times 10^{-12}$ sec., whence $a = 1{\cdot}68$ Å. The kinetic-theory value of the effective radius is usually given as $\sim$ 1·35 Å.[15] The agreement is much better than would have been expected. It has been pointed out recently [16] that in solutions the correct viscosity factor is that for the solute–solvent interactions and not simply that of the medium, but for the solvent molecules themselves this difference does not arise. Even so, it may well be that the above agreement on the effective radius of the water molecule is a coincidence.

The correlation between τ and η may be taken further. Collie, Hasted, and Ritson,[14] from their own data, showed that τ and η/T were almost linearly related for both water and deuterium oxide, a logarithmic plot

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[14] Collie, Hasted, and Ritson, *Proc. Phys. Soc.*, 1948, **40,** 145. Refs. 12 and 14 give bibliographies of the earlier determinations.

[15] Stuart, " Die Struktur des Freien Moleküls ", Springer Verlag, Berlin, 1952, p. 88.

[16] (Miss) N. E. Hill, *Nature*, 1953, **171,** 836 ; *Proc. Phys. Soc.*, 1954, **67,** *B*, 149.

giving the power as 0·97. From this the relaxation time can be determined for any temperature at which η is known. Further $\tau_{D_2O}/\tau_{H_2O} = \eta_{D_2O}/\eta_{H_2O}$ within the experimental uncertainty. Saxton emphasises the same conclusion by using the expressions from reaction-rate theory,[17]

$$\eta = \frac{hN_0}{V} \exp (\Delta F_\eta/RT) ; \quad \tau = \frac{h}{kT} \exp (\Delta F_\mu/RT)$$

Here, apart from universal constants, V is the molar volume and the ΔF's are the free energies of activation for viscous flow and dipole rotation. Without resolving the latter into their heat and entropy terms, some interdependence can confidently be expected for them. The precise relation will depend upon the detailed molecular mechanism of the processes, *e.g.*, a difference might be expected as ΔF_η would appear to involve translational terms as well as the rotational ones in ΔF_μ. However, Saxton found that the results could be quantitatively represented by $\Delta F_\mu = 1{\cdot}11 \Delta F_\eta$. It transpires that the ΔH term in ΔF_μ is about 5 kcal./mole at 0° and it appears to fall with increasing temperature. The hydrogen-bond energy between water molecules is given [18] as $5{\cdot}5 \pm 0{\cdot}4$ kcal./mole. The fact that the dipole rotation can be represented at each temperature by a single relaxation time shows that the change between the various structures suggested in the well-known Bernal and Fowler picture [19] is continuous.

The ε_∞ value for water is, within the uncertainty in its evaluation, independent of temperature and has the surprisingly high value of 4·9. This means that the atomic polarisation term is approximately $4{\cdot}9 - (1{\cdot}33)^2 = 3{\cdot}1$. The unusualness of this value is seen when it is recalled that for gaseous molecules the ratio of atomic to electronic polarisations rarely exceeds 0·40 and an average value of about 0·20 has frequently been used for this ratio.[20a] Harris and Alder [20b] have suggested that this feature in water arises from the bending mode of the O–H···O group of the hydrogen bridge whose frequency is sufficiently low for it to be appreciably excited even at 273° K. (The same factor accounts for the anomalously high atomic polarisation term deduced for the carboxylic acid dimers.[20c]) Whilst the polarisation due to this deformation mode will certainly contribute to the observed atomic term for frequencies up to infra-red values, no quantitative calculations of it have yet been reported.* There also remains the general possibility that protonic resonance of the type O–H···O $\rightleftharpoons$ O···H–O may be involved in some circumstances, although it must be emphasised that this process has not yet been localised in any particular instance.

Amongst the many other abnormalities of water for which its association is responsible one of immediate relevance is that from the dielectric constant of water (80) the Onsager equations lead to a dipole moment for water of 1·5 D : the vapour-phase value is 1·87 D. Usually the Onsager relations

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[17] Glasstone, Laidler, and Eyring, "Theory of Rate Processes", McGraw-Hill Book Co., New York, 1941.

[18] Ref. 15, p. 49.

[19] Bernal and Fowler, *J. Chem. Phys.*, 1933, **1**, 515.

[20] (*a*) Ref. 15, pp. 294—295 ; (*b*) Harris and Alder, *J. Chem. Phys.*, 1953, **21**, 1031 ; (*c*) Coop, Davidson, and Sutton, *ibid.*, 1938, **6**, 905 ; Hobbs, Gross, *et al.*, *ibid.*, 1941, **9**, 408, 415.

* But see ref. 25.

are such good approximations that the vapour dipole moment can be calculated from the dielectric constant of the liquid to within a few per cent.[21]

This anomaly has been the source of further significant calculation of major interest. On the basis of a liquid-water structure whose details were arrived at in terms of molecular-orbital theory, Pople [21a] calculated dielectric-constant values within about 20% of those observed for water. Using a statistically deduced extension of the Kirkwood–Fröhlich relations in which precise evaluation of the distortion polarisation term is made, Harris and Alder [20b] have now refined Pople's results until the agreement between calculated and observed values is within 2% for water and deuterium oxide from 0° to 83°. With the original Onsager treatment, which is equally successful for non-associating liquids, these quantitative deductions must be regarded as one of the most convincing molecular interpretations of "medium effects", *i.e.*, solvent properties, yet available in the physico-chemical field.

Ice.—A definitive account of the dielectric properties of ice (and solid deuterium oxide) appeared [22] in 1952. Disagreement in the earlier results, *e.g.*, ε_0 values at 0° ranging from 70 to 95, was shown to be due to two principal troubles, namely, voids or flaws in the solid dielectric, and the presence of conducting impurities. These factors were controlled and measurements made from 20 c./s. to 100,000 c./s. and temperatures from $-65°$ to $-0{\cdot}1°$. Again, all the observations are precisely represented by the equations (4) and (5) for a single relaxation time. The data are summarised in Table 2.

TABLE 2. *Ice* (H_2O)

Temp. :	$-0\ 1°$	$-10\ 8°$	$-20\ 9°$	$-32\ 0°$	$-44\ 7°$	$-56\ 8°$	$-65\ 8°$
ϵ_0	91·5	95·0	97·4	100	104	114	133
ϵ_∞	3·10	3·08	3·10	3·00	3·10	3·1	3·1
$10^5\tau$ (sec.) . .	2·2	6·0	16·4	57	252	1200	4500

The relaxation times are now very much longer than in the liquid phase, reaching 0·05 second at $-66°$. Such values made the lowest bridge frequency (20 c./s.) too high for reliable measurement and recourse was had to the direct observation of the time-dependence of the polarisation. The temperature variation could be fitted, as for an unimolecular reaction-rate constant, by the expression

$$1/\tau = A\exp(-E/RT)$$

For water : $A = 1{\cdot}89 \times 10^{15}$ sec.$^{-1}$; $E = 13{\cdot}25$ kcal./mole : for deuterium oxide, $A = 1{\cdot}30 \times 10^{15}$ sec.$^{-1}$; $E = 13{\cdot}4$ kcal./mole. Although definitely larger values of τ for deuterium oxide than for water at the same temperature are established, no quantitative significance can be attached to the small

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[21] Bottcher, *Rec. Trav. chim.*, 1943, **62,** 119 ; and ref. 1, p. 323 *et seq.*

[21(a)] Pople, *Proc. Roy. Soc.*, 1951, *A*, **205,** 163.

[22] Auty and Cole, *J. Chem. Phys.*, 1952, **20,** 1309.

differences between the individual A and E parameters. The simple version of absolute reaction-rate theory predicts identical A values. On Pauling's estimate [23] for the solid, the activation energy E corresponds to the rupture of three hydrogen bonds. Whether or not this is structurally significant (see below), it is certain that some hydrogen bonds are broken in the activation process. The almost precise identity of the E values for water and deuterium oxide shows that quantum-mechanical protonic resonance makes no significant contribution to the energy of these bonds as such a contribution would be much smaller in the case of deuterium oxide.

A statistical calculation of the dielectric constant of ice has been made by Powles [24] on the basis of Pauling's model for the solid, and for a refinement of the latter taking into account the energy differences of the various arrangements of the hydrogen bonds between the tetrahedrally-disposed oxygens. For 0° the values so arrived at are 77 and 103 respectively. These theoretical values bracket the observed $\varepsilon_0 = 91{\cdot}5$ quite closely when the approximations of the point-charge electrostatic model are remembered, but they have been greatly improved upon by a later evaluation.[20b]

A knowledge of the molecular mechanism of the dielectric loss in ice would be of particular interest. Auty and Cole [22] write as follows :

" In an ideal lattice, displacements by proton shifts from one bond to another, no matter how devised, either have improbable energy requirements or lead to no net polarisation. If instead one supposes that the displacements occur by proton shifts from one oxygen atom to another, as considered in some detail by Latimer,[25] equally serious difficulties with energy requirements, absence of net polarisation, or the improbable consequence of a space-charge type of polarisation are encountered.

" The difficulties with various such mechanisms have been examined in detail by Schellman,[26] who proposes, as a way out of the difficulty, that actually one has missing [hydrogen] bonds between a few of the oxygen atoms from lattice defects or vacancies, and that molecular reorientations through the lattice are then made possible by propagation of the missing bonds."

This picture, involving essentially the attainment of freedom for molecular rotation in the lattice, is not in conflict with the high activation energy (13 kcal./mole) owing to the large energy of the hydrogen-bond interactions. It is the magnitude of the latter, too, which is almost certainly responsible for the simplicity of the dielectric dispersion in both water and ice. The restrictions imposed on all the small rigid molecules by these interactions result in dipole rotations' being possible only after an activation step of appreciable energy and thus lead to a well-defined single relaxation time. The latter is by no means typical of the behaviour of liquids.

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[23] Pauling, " The Nature of the Chemical Bond ", Cornell Univ. Press, Ithaca, N.Y., 1939, p. 284.

[24] Powles, *J. Chem. Phys.*, 1952, **20,** 1302.

[25] Latimer, *Chem. Reviews*, 1949, **44,** 59.

[26] Schellman and Kauzmann, *Phys. Review*, 1951, **82,** 315 ; Schellman, Thesis, Princeton Univ. Press, 1951.

Aqueous Ionic Solutions.—It has already been pointed out that the loss factor ε'' corresponds to a conductance in the medium : the relation between them is

$$\varepsilon'' = 2\sigma/f = 1{\cdot}80 \times 10^{12}\kappa_f/f$$

where σ is the conductance in e.s.u. and κ_f that in practical units (ohm^{-1} cm.$^{-1}$). In the latter units, the absorptive (or dispersive) conductance of water at 20° is, of course, markedly dependent on wave-length (Table 3).

TABLE 3. *Water at 20°*

λ (cm.)	100	10	1·0
κ_f (ohm^{-1} cm.$^{-1}$) . .	0·00019	0·019	0·53

The critical wave-length (*i.e.*, for ε'' maximum) is 1·8 cm. At the same temperature and low frequencies, the specific conductance of N-sodium chloride solution is 0·08 ohm^{-1} cm.$^{-1}$, this ionic conductance being approximately proportional to the salt concentration. Thus, in studying the dielectric dispersion, the ionic conductance must be allowed for and, furthermore, its possible frequency dependence must be considered. The latter variation will arise from the relaxation time of the ionic atmosphere and its order of magnitude, at least, can be predicted from Falkenhagen's evaluation [27] of the Debye–Hückel parameters. For normal aqueous univalent electrolytes the ionic-atmosphere effect is at most 20% of the total ionic conductance : at wave-lengths near 1 cm. the latter will itself be less than 20% of the dispersive conductance of the medium. Thus no serious error arises by assuming that the ionic conductance is independent of frequency when measurements of the dispersion factors for the solvent in the medium can be made to only about ± 1%. This approximation has been made in the treatments [28] by Saxton and Lane, and of Hasted, Ritson, and Collie. Even if, owing to the ionic atmosphere or other effects, the ionic conductance of N-sodium chloride increased by 15% over its low-frequency value at $\lambda = 1$ cm., allowance for this maximum forseeable effect would give $\varepsilon_s = 60$; $\tau = 8{\cdot}3 \times 10^{-12}$ sec., compared with $\varepsilon_s = 63$ and $\tau = 9 \times 10^{-12}$ sec. obtained when it is neglected.[29]

Saxton and Lane have reported results for sodium chloride solutions measured at 0·62, 1·24, and 3·21 cm. over the temperature range 0°—50°. These are again all adequately represented by the single relaxation-time equations (4) and (5), with ε_∞ at the same value as for the pure solvent (4·9) but ε_s, the dielectric constant of the solvent in the solution, and τ significantly different from the solvent values. Table 4 is taken from reference 28*a*.

These results give an explicit measure of the influence of the electrolyte

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[27] See Falkenhagen, " Electrolytes ", translated by R. P. Bell, Oxford Univ. Press, London, 1934, p. 211 *et seq.*

[28] (*a*) Lane and Saxton, *Proc. Roy. Soc.*, 1952, *A*, **214,** 531 ; (*b*) Hasted, Ritson, and Collie, *J. Chem. Phys.*, 1948, **16,** 1.

[29] Saxton, personal communication.

TABLE 4. *Dielectric properties of water in sodium chloride solutions*

c (g.-equiv./litre) :	0		1·0		2·0		3·0	
Temp.	ε_s	$10^{12}\tau$ (sec.)	ε_s	$10^{12}\tau$ (sec.)	ε_s	$10^{12}\tau$ (sec.)	ε_s	$10^{12}\tau$ (sec.)
0°	88	18·7	69	16·4	56	14·4	46	13·0
10	84	13·6	66	11·8	54	10·9	43	10·3
20	80	10·1	63	9·0	51	8·3	41	7·6
30	77	7·5	60	7·1	49	6·7	39	6·2
40	73	5·9	58	5·6	47	5·4	37	5·2

upon one of the most important of the solvent properties. Qualitatively the influence can be described as equivalent to a rise in temperature : thus a 0·5N-sodium chloride solution at 0° has solvent dielectric properties closely similar to that of water at 30°. The breaking-down of the co-ordinated structure suggested in this way conforms to X-ray results.[30] The limitations of this interpretation are seen in that the ε_s and τ values lead to slightly different " effective temperatures ". Saxton and Lane suggest that the change in τ provides the structurally more significant estimate. Essentially similar although less precise results have been obtained by Hasted *et al.*,[31] mostly measured at 3 cm. and 10 cm. wave-lengths and at 25°. These authors make an ambitious attempt at a detailed analysis of the data, but even the deduction of the number of water molecules bound by the individual ions involves some very doubtful assumptions. They emphasise that the departures of ionic solutions at medium concentrations from the Debye–Hückel relations involve at least four factors : (i) a van der Waals co-volume correction ; (ii) the breaking of the water structure by the ions ; (iii) a Bjerrum-type ion association ; (iv) the change in the dielectric constant of the medium. The unravelling of these contributions from, say, the measurement of activity coefficients is, at least, a very difficult task. Hückel computed the influence of (iv), after prior allowance for the finite ionic radii [32] on the basis of the linear variation of dielectric constant with concentration, $\varepsilon_{\text{solution}} = \varepsilon_{\text{solvent}} - 2\delta c$. For 0—3N-sodium chloride Saxton and Lane deduce from the activity values : d = mean effective ionic diameter = 4 Å ; $\delta = 12{\cdot}5 \pm 1$. Although the observed concentration dependence is not strictly linear, the latter factor provides a not unreasonable fit to the measured values : *e.g.*, at 20° and 2N the measured $\varepsilon_{\text{solution}}$ is 51, whilst $\delta = 12{\cdot}5$ gives 55. In support of the significance of this agreement (as quantitative evaluation of all the factors is as yet impossible) it must suffice to indicate that in the present instance factors (ii) and (iii) above are of opposite sign to (i). Clearly, important contributions to electrolyte theory should be forthcoming from the development of these studies.

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[30] Morgan and Warren, *J. Chem. Phys.*, 1938, **6**, 666 ; Stewart, *ibid.*, 1939, **7**, 869 ; 1943, **11**, 72.

[31] Ref. 28*b* and *ibid.*, 1951, **20**, 1452.

[32] Hückel, *Physikal. Z.*, 1925, **26**, 93.

Solutions in Non-polar Solvents

A considerable accumulation of data has already taken place in the field of polar organic molecules and their liquids, and only some of the interesting findings can be reported here.

The most significant and reliable results are again those obtained by

TABLE 5. *Some relaxation times of simple molecules in solution*

Solute	Solvent	Temp.	$10^{12}\tau$ (sec.)	$\mu_{\text{obs.}}$*	$\mu_{\text{lit.}}$	Method †	Ref. 33
Chlorobenzene	Benzene	19° ± 2°	7·5	1·52D	1·52—1·69D	1	*a*
,,	,,	18·5 ± 1	10·8	1·51	,,	1	*b*
,,	,,	23	10·6	—		2	*c*
Bromobenzene	Benzene	19 ± 1	10·5	1·64	1·35—1·58	3	*d*
,,	,,	19 ± 2	10	1·51	,,	1	*a*
Chloroform .	Benzene	19 ± 1	7·7	1·13	1·20	3	*d*
,, .	*n*-Heptane	20	3·1	1·09	,,	3	*a*
,, .	Benzene	23	8·4	—		2	*c*
Acetone . .	Benzene	19 ± 1	3·3	(2·74)	2·74	3	*d*
,, . .	,,	19 ± 2	3·2	2·58	,,	1	*a*
,, . .	,,	23	3·3	—		2	*c*
Benzophenone	Benzene	19 ± 1	16·4	3·04	2·98	3	*d*
,,	Nujol	19 ± 1	295	—		3	,,
,,	Benzene	18·5 ± 1	18·1	2·81	,,	1	*b*
,,	,,	23	20·4	—	,,	2	*c*
Nitrobenzene	Benzene	19 ± 1	11·6	3·96	3·98	3	*d*
,,	,,	18·5 ± 1	13·0	3·88	,,	1	*b*
1-Bromo-naphthalene	*n*-Heptane	20	13·0	1·55	1·5—1·6	3	*a*
,,	,,	20	16·0	1·66	,,	1	,,
Toluene . .	Toluene	20	6·4	0·32	0·38	3	,,
,, . .	,,	19 ± 2	7·7	0·32	,,	1	,,
Camphor . .	*n*-Heptane	20	6·5	2·99	2·95	3	,,
,, . .	,,	20	7·1	2·98	,,	1	,,
Methyl acetate	Benzene	18·5 ± 1	3·7	1·58	1·67	1	*b*
Methyl benzoate	Benzene	19 ± 2	12	1·69	1·84	1	*a*
Formic acid .	Dioxan	Room temp.	17·1	1·98	1·82—2·07	4	*e*
Propionic acid	,,	,, ,,	28·5	1·50	1·68—1·75	4	,,

* μ_{obs} = dipole moment deduced from dielectric loss measurements ; μ_{lit} = literature value of dipole moment (Debye units). † (1) Temperature variation ; (2) dilatometric (calorimetric) method ; (3) frequency variation ; (4) Lecher-wire.

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[33] (*a*) Whiffen and Thompson, *Discuss. Faraday Soc.*, 1946, **42***A*, 114, 122, and 166 ; (*b*) Cripwell and Sutherland, *ibid.*, p. 149 ; (*c*) Fischer, *Z. Naturforsch*, 1949, **4**a, 707 ; (*d*) Willis Jackson and Powles, *Discuss. Faraday Soc.*, 1946, **42***A*, 101 ; (*e*) Potapenko and Wheeler, ref. 11.

an adequate study of the frequency-dependence of dielectric behaviour. Only with radar sources and wave-guide techniques has the dipole-dispersion region for simple organic molecules become directly accessible and some of the first studies were reported at the Faraday Society Discussion in 1946. Table 5 shows a selection of such results in addition to those obtained by less certain methods, *e.g.*, from observations at only two frequencies: from the temperature variation of ε'' at one frequency; and from the heating effect in solutions at one frequency ($\sim 5 \times 10^7$ c./s.; $\lambda \sim 6$ m.), at least two decades from the critical value in most instances. The agreement between the different methods is satisfactory in view of the known experimental uncertainties. It is particularly striking that the simple dilatometric (heating effect) method provides reasonably good values in straightforward cases. However, it must be emphasised that, except in the frequency-variation method, it is necessary to assume in evaluating the observations that the theoretical Debye equation (7) for the molar loss tangent is obeyed. (For dilute solutions the Onsager treatment reduces to precisely the same form.) One limitation thus imposed is that the presence of two or more distinct critical frequencies (*i.e.*, loss processes) or a distribution of relaxation times would not necessarily be recognised in the results and some mean "effective relaxation time" would be deduced.

Molecular Size and the Viscosity Factor.—Perhaps the first deduction from these results is, in fact, the general adequacy of the Debye relation in reproducing the form of the dispersion curve, *i.e.*, for the examples quoted the observations conform to a single relaxation time. This is probably related to the fact that the great majority of the solutes represent virtually rigid dipole structures. Even so, the careful study by Jackson and Powles shows that for benzophenone in the viscous medium provided by medicinal paraffin the loss is far broader than the Debye type, the factor β in the Fuoss–Kirkwood representation being 0·68. Whiffen has suggested [34] that such departures from a single relaxation time can be expected in highly viscous media and, it may be added, the molecular–kinetic appreciation suggests it would be the more likely the less rigid the dipole molecule. The variable restraint on molecular rotations in a liquid phase resulting from thermal fluctuations has been treated explicitly by Kauzmann [7] who shows that the distribution of relaxation times characteristic of many liquids can readily be understood in this way.

Among Debye's contributions [1] to this subject was the calculation of the relaxation time for a sphere of radius a in an uniform medium of viscosity η. By using Stokes's relation the result deduced was

$$\tau = 4\pi\eta a^3/kT \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In an early test [35] of this for the polar molecule *o*-dichlorobenzene in six solvents with viscosities differing by a factor of seven, the ratio τ/η varied from 1·4 to $5{\cdot}5 \times 10^{-10}$ c.g.s. units, the mean value corresponding to $a = 1{\cdot}2$ Å. These results are typical of the quantitative inadequacy of

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[34] Whiffen, *Discuss. Faraday Soc.*, 1946, **42***A*, 156.

[35] Debye, *Trans. Faraday Soc.*, 1934, **30**, 679; *Physikal. Z.*, 1934, **35**, 101.

equation (8), which nevertheless often gives the correct order of magnitude for a and appropriately emphasises the relation between τ and η, frequently seen in their almost identical temperature coefficients.

One certain limitation to the relation (8) is that a single relaxation time can at best be expected only when the dipole axis of a rigid molecule coincides with one of its principal axes of inertia. The general case of the rigid molecule for which three rotational relaxation times can be expected has been treated by Perrin.[10] An important practical example of these relations provided by the protein zein in aqueous-alcoholic solutions was studied by Elliott and Williams.[36] Their analysis showed relaxation times characteristic of rotation about the different axes and they were able to deduce both the particle molecular weight (*viz.*, 38,000, in good agreement with other determinations) and the ratio of the minor to the major axis (1 : 7) for the ellipsoidal particle. Fischer [37] has taken cognisance of these geometrical factors in a systematic attempt to find under what conditions a modified Debye relation might apply. Fischer uses

$$\tau = 4\pi\eta(abc).s/\boldsymbol{k}T \qquad . \quad . \quad . \quad . \quad (8a)$$

where a, b, and c are the semi-axes of the rotational ellipsoid for accurate Stuart models of the molecular structure and s is a small numerical factor (1·5—2·0) taking account of the direction of the dipole axis with respect to the axes of inertia.[38] Even so the calculated relaxation time for chlorobenzene in benzene at 23° is 4·3 times as large as the observed value. With the further application of this numerical factor, however, Fischer obtains sensible agreement for solutes conforming to the model in the same solvent (Table 6).

TABLE 6

	$10^{12}\tau_{\text{obs}}$ (sec.)	$10^{12}\tau_{\text{calc}}$ (sec.)		$10^{12}\tau_{\text{obs}}$ (sec.)	$10^{12}\tau_{\text{calc}}$. (sec.)
Acetone . . .	3·3	3·6	Nitrobenzene . . .	13·2	10·8
Chloroform . .	8·4	7·0	Benzonitrile . . .	12·8	11·8
Bromobenzene .	12·3	12·7	1-Chloronaphthalene .	15·7	14·6
o-Dichlorobenzene	10·4	10·2	2-Chloroanthraquinone	25·2	27·1

This apparently satisfactory, albeit empirical, representation of the results is lost when the solvent is varied. In this connection some precise data due to Whiffen may be cited.[39]

The interest of these τ values and their interpretation in terms of molecular structure and solvent properties is considerable: not only should they help to provide an intimate picture of the motion of the solute particle and its interaction with the solvent but, for non-rigid molecules, they can provide indications of the configurations favoured in solution. Thus,

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[36] Elliott and Williams, *J. Amer. Chem. Soc.*, 1939, **61,** 718.

[37] Fischer, *Z. Physik*, 1949, **127,** 49; see also refs. 39.

[38] Budo, Fischer, and Miyamoto, *Physikal. Z.*, 1939, **40,** 337.

[39] Whiffen, *Trans. Faraday Soc.*, 1950, **46,** 130. See also many data by Spernol and Wirtz, *Z. Naturforsch.*, 1953, **8**a, 522; Gierer and Wirtz, *ibid.*, p. 532.

amongst other studies, some results of Smyth *et al.*[40] deserve mention. They found, in contrast to equation (8), that the relaxation times of nearly spherical molecules are much less dependent upon the viscosity of the medium than are those of unsymmetrical molecules, the rotation of which requires displacement of the surrounding molecules. Again, for the nearly spherical *tert.*-butyl chloride molecule the relaxation time in the pure liquid was almost twice that in Nujol although the viscosity of the latter was greater by 200-fold. This is interpreted as a clear indication of restriction of the rotational motion by dipole interactions in the liquid. Another example of this character is probably provided by the greater relaxation times for a number of molecules in carbon tetrachloride compared with the same solutes in *cyclo*hexane, both solvents having the same viscosity. It is suggested here that the local C—Cl dipoles of the carbon tetrachloride interact with those of the solutes. Again, in comparison with aliphatic hydrocarbons benzene shows appreciably larger values of τ/η for individual solutes : this is attributed to the greater polarity of the C–H aromatic units, for which there is much independent evidence.[41] Such interesting deductions could (and should) be further checked by determination of the activation energies for the rotational processes.

It is clear from the foregoing examples that the macroscopic solvent viscosity only poorly represents the viscous drag on the rotating solute molecule. It is in fact certain that what is needed is a frictional coefficient measuring the interaction between the solute and the solvent molecules. (Miss) N. E. Hill [16] has now shown one method by which this may be obtained. For a very dilute solution the expression

$$\tau = A\,.\eta_{AB}/2\boldsymbol{k}T \quad . \quad . \quad . \quad . \quad (9)$$

is deduced. In this, A is a function of the moments of inertia and masses of the solvent (A) and solute (B) molecules and of the intermolecular distances ; η_{AB} is the " mutual viscosity " of these species, which can be found from the viscosity of their mixtures expressed as

$$\eta\sigma = N_A^2.\eta_A\sigma_A + N_B^2\eta_B\sigma_B + 2N_AN_B\eta_{AB}\sigma_{AB} \quad . \quad . \quad (10)$$

Here the N's are mole fractions, the σ's are intermolecular distances in the pure liquids and their mixtures, and the terms on the left refer to the mixture. Equations (9) and (10) are derived by using Andrade's model of a liquid.[42] A comparison of the Debye relation and equation (9) is shown by Figs. 5 and 6. In the former the points for each solute should fall on straight lines through the origin. Whilst no approach to this condition is found in Fig. 5, much greater regularity appears in Fig. 6. The deviations from a straight line in the latter instance may be interpreted as not unreasonable variations of the factor A in the various cases. Although the instances chosen for this first analysis are of a somewhat random character, it is clear that a great advance has been made in treating the viscosity factor.

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[40] Curtiss, McGeer, Rathmann, and Smyth, *J. Amer. Chem. Soc.*, 1952, **74,** 645.

[41] Cole and Thompson, *Trans. Faraday Soc.*, 1950, **46,** 103 ; see also Staveley, Jeffes, and Moy, *ibid.*, 1943, **39,** 5.

[42] Andrade, *Phil. Mag.*, 1934, **17,** 497.

As already indicated in the case of water, the temperature coefficients of η and τ can be very similar. This is readily understood on the basis

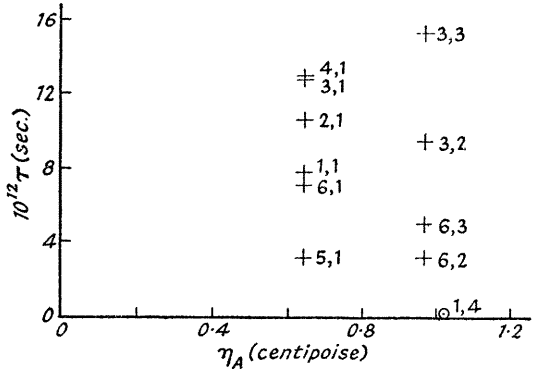

FIG. 5

Relaxation time and solvent viscosity for various polar-non-polar solutions. The numbers indicate solute, solvent :

Solutes : 1, C_6H_5Cl ; 2, C_6H_5Br ; 3, $C_6H_5{\cdot}NO_2$;
4, $C_2H_5{\cdot}CO_2C_6H_5$; 5, $CH_3{\cdot}CO{\cdot}CH_3$; 6, $CHCl_3$.
Solvents : 1, C_6H_6 ; 2, C_6H_{12} ; 3, CCl_4 ;
4, Medicinal paraffin.

For the point marked by a circle, both scales should be multiplied by 200.

of Debye's relation, or, more generally, from the reaction-rate theoretical expressions for these factors. The latter provide the more realistic picture of the interconnection of η and τ when the plausible assumption is made that the activation energies for the two processes will be closely related

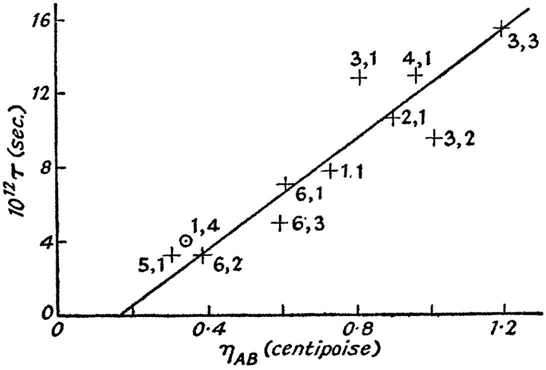

FIG. 6

Relaxation time and mutual viscosity. The solutions are numbered in the same way as in Fig. 5. For the point marked by a circle, both scales should be multiplied by 10.

[Figs. 5 and 6 are reproduced, by permission, from Hill, *Proc. Phys. Soc.*, 1954, **67**, *B*, 149.]

although not necessarily identical. The observed temperature coefficient of τ shows that rotation of the polar molecule is normally only possible after an activation process in which it acquires an excess of energy which varies from about $5kT/2$ to $50kT/2$ according to the solvent.

The use of the Eyring equation, written as for a reaction-rate coefficient,

$$\frac{1}{\tau} = \frac{kT}{h} \exp(\Delta S/R) \exp(-\Delta H/RT) \quad . \quad . \quad . \quad (11)$$

where ΔS and ΔH are the entropy and heat content increases for rotational activation, was examined by Whiffen and Thompson.[33] In a number of low-viscosity solvents they found for typical simple polar molecules $\Delta H \sim 1{\cdot}5$ kcal./mole, and small negative values of $\Delta S \sim -4$ cal./mole/°K. The concurrence of numerically small ΔH and ΔS values recalls the many instances in which these factors are proportionally related,[43] and is readily appreciated here in molecular terms as, if the rotation can occur for small excess energies (ΔH), then it is likely to involve the minimum of molecular reorganisation (ΔS) in the solvent (see Fig. 7). Levi has indicated a similar parallelism in diffusion processes and emphasised the occurrence of negative entropies of activation.[44] Doubt has been expressed as to the physical reality of such negative values [45] but there seems to be no *a priori* reason for rejecting them and only an activated state showing an increased order (*e.g.*, mutual alignment of the molecules) is needed to account for them.

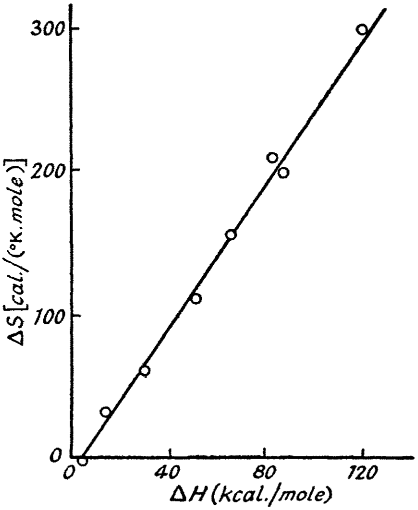

FIG. 7

Relation between entropy (ΔS) *and energy* (ΔH) *of activation for dielectric relaxation. Data from Table* 1 (*p.* 153), *ref.* 44.

Intramolecular Motions in Polar Molecules.—In relation to molecular structure the studies of Fischer and his collaborators offer aspects of especial

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[43] See, for instance, Butler, " Chemical Thermodynamics ", Macmillan, London, 1951, p. 393 *et seq.*

[44] Levi, *Discuss. Faraday Soc.*, 1946, **42***A*, 152.

[45] Gee, *ibid.*, p. 161 ; Pelzer, *ibid.*, p. 164.

interest. Their earlier results have been summarised.[33, 37] It must be recalled that Fischer's measurements were made by the dilatometric method,[46] and it is assumed that the Debye equation (7) applies in the dilute solutions examined. This means that the dipole moment of the solute in solution must be known beforehand and only an "effective relaxation time" can be deduced from the observations. This limitation is important when freely-rotating groups can contribute their own absorption to the measured effect. Fischer shows that in such cases the effective relaxation time becomes

$$\tau_{\text{eff}} = \Sigma \mu_i^2/\mu^2 . \tau_i$$

where μ_i and τ_i are the component moments and their individual relaxation times ; also $\mu^2 = \Sigma \mu_i^2$.

For many benzene derivatives such as phenol or benzyl chloride the resultant polar moment is not along a symmetry axis but it can be represented by two components (Fig. 8), namely, μ_f which is along the axis and can reorientate only with the whole molecule, and μ_p perpendicular to that axis which rotates with the frequency of the group rotation. In this case

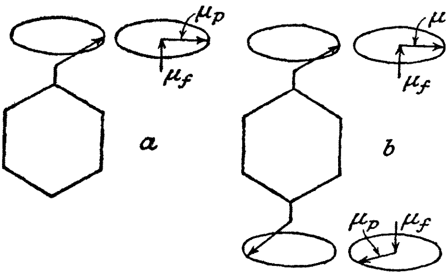

FIG. 8

$$\tau_{\text{eff}} = (\mu_f^2/\mu^2)\tau_f + (\mu_p^2/\mu^2)\tau_p \; ; \quad \mu^2 = \mu_f^2 + \mu_p^2$$

As τ_f the relaxation time for the effectively rigid molecule can be adequately estimated—with the aid of the empirical factor 4·3 for benzene at 23° in the expanded version of Debye's equation, (8*a*), or for benzyl chloride, say, by reference to toluene—this relation in principle allows τ_p to be deduced from τ_{eff}, *i.e.*, from the relaxation time deduced from dilatometric observation. For his qualitative conclusions, however, Fischer merely compares τ_{eff} with τ_f and where the former is markedly smaller he deduces that rotation is possible for the substituted group. A comparison of these two factors for a number of relevant cases is given in Table 7.

Of these examples it will be noted that benzaldehyde, acetophenone, and ethyl benzoate behave as rigid molecules. They are all of the structure (I), and presumably the conjugation of the carbonyl double bond with the phenyl nucleus gives the carbon bond to the ring sufficient double-bond character to

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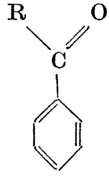
[46] Debye, ref. 35 ; Fischer and Frank, *Physikal. Z.*, 1939, **40**, 345 ; for a full account of this method see also Sharbaugh, Schmelzer, Eckstrom, and Kraus, *J. Chem. Phys.*, 1947, **15**, 47.

TABLE 7. *Relaxation times at 23° in dilute benzene solutions*

	$10^{12}\tau_{\text{eff.}}$(obs.) (sec.)	$10^{12}\tau f$(calc.) (sec.)		$10^{12}\tau_{\text{eff}}$ (obs) (sec)	$10^{12}\tau f$(calc.) (sec.)
Benzaldehyde	10·9	10·1	Aniline	6·7	9·0
Acetophenone	12·2	11·3	*o*-Toluidine	8·5	10·0
Ethyl benzoate	11·4	12·7	*p*-Toluidine	5·8	11·5
Anisole	7·6	9·4	*p*-Phenylenediamine	1·5	9·7
Benzyl chloride	9·9	11·0	Benzidine	1·5	15·1
p-Xylylene dichloride	5·0	13·1	1-Naphthylamine	9·8	13·5
p-Xylylene dibromide	9·4	14·5			

prevent rotation about it in times appreciably less than τ_f. Anisole probably shows the occurrence of group rotation. This conclusion might not be regarded as established beyond doubt in benzyl chloride, but with the two *para*-substituted groups of the xylylene dichloride the presence of rotation is certainly established. The *para*-position of the groups (Fig. 8*b*) gives a resultant μ_f of zero, and the measured τ_{eff} shows that the dipole reorientation takes place more rapidly than could possibly correspond to rotation of the whole molecule.



(I)

For the aromatic amines particularly interesting observations have been made. In the case of the monoamines the presence of a low τ_p value is reasonably certain, and this is directly established for the *p*-phenylenediamine and 4 : 4′-diaminodiphenyl (benzidine) where the reported τ_{eff}'s are maximum values. These results appear to dispose of the suggestion that the aniline molecule, for instance, is in a strictly planar form.[47] However, they do not necessarily mean that the low τ_p values correspond to rotational motion about the C_{aromatic}–N bond : the high-frequency loss process in these instances could possibly be due to the inversion of the non-planar configuration of the nitrogen bonds. This would be the analogue of the well-known resonance absorption in ammonia at 3×10^{-10}sec.$^{-1}$. Fischer has sought evidence on this possibility by examining diphenylamine in solution, and for it he found $\tau_{\text{eff}} = 8{\cdot}0 \times 10^{-12}$ sec. It is perhaps difficult to account for this low value (cf. benzophenone $= 20{\cdot}4 \times 10^{-12}$ sec., aniline $= 6{\cdot}7 \times 10^{-12}$ sec.) by reference to the free rotation of the bulky $-NH{\cdot}C_6H_5$ group (or one half of the molecule) about the other C_{aromatic}–N bond, and Fischer suggests that it is probably due to the inversion mechanism, which, of course, reverses the dipole direction. Unfortunately, the calorimetric method gives no indication of the form of the dielectric absorption, *i.e.*, of the dependence of ε'' upon frequency : this can be quite different for such a resonance absorption from a Debye-type curve and the use of the

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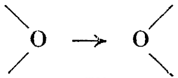
[47] Pauling, ref. 23, p. 192 ; Coulson, " Valence ", Oxford Univ. Press, London, 1952, p. 246 ; Ingold, " Structure and Mechanism in Organic Chemistry ", Bell and Sons Ltd., London, 1953, p. 103.

Debye dipole relaxation equations to evaluate τ_{eff} in these cases would not necessarily be justifiable. Again, an even lower " effective relaxation time " deduced for diphenyl ether, $\tau_{\text{eff}} = 2{\cdot}8 \times 10^{-12}$ sec., cannot be explained —unless it is due to an oxygen " inversion " (II).



(II)

In a recent paper by Hase [47a] an attempt is made to extend and refine such conclusions for some intramolecular rotations. Interesting though the deductions appear to be, they must be accepted with caution as the absorptions are measured at only one frequency and that so far from the peak values that detailed quantitative analysis is scarcely justified.

What is certainly a resonance absorption has been found by variable frequency measurements of dielectric loss for triethylamine, both in Nujol solution and in the pure liquid.[48] It corresponds to a characteristic frequency of $1{\cdot}4 \times 10^8$ sec.$^{-1}$. This absorption shows precisely the same form of $\varepsilon'' \sim$ frequency dependence as that for ammonia gas at pressures above 10 cm. pressure, the absorption contours for which have been calculated from two different treatments with essentially the same result by Fröhlich,[49] and by Van Vleck and Weisskopf.[50] No plausible explanation other than that it is the inversion frequency for the NR_3 structure is available. Compared with that for ammonia the frequency is, not surprisingly, lower by a factor of a hundred.

A wide topic for future study is that of molecular and ionic aggregation in non-aqueous solutions. Fischer has commenced both the theoretical and experimental study of dielectric absorption in relation to molecular association for such cases as phenol in carbon tetrachloride and for acetone–chloroform mixtures.[50a] By measurements in dilute hydrocarbon media Kraus and his co-workers [51] have examined the process of ion-association for a number of alkylammonium salts. Some of the deductions referring to instances where single relaxation times were found for the solute are given in Table 8.

TABLE 8. *Ion-pair characteristics determined from dielectric loss*

Solute	Solvent	$10^{10}\tau$ (sec.)	μ (D).
Dibutyldioctadecylammonium octadecyl sulphate	Benzene	1·1	27·6
Tri*iso*amylammonium picrate . . .	Benzene	2·8	12·7
,, ,, . . .	Diphenylmethane	15	12·5

In other instances, *e.g.*, tetrabutylammonium thiocyanate, ion-association

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[47a] Hase, *Z. Naturforsch.*, 1953, **8**a, 695.

[48] Davies and Price, Réunion Internationale de Spectroscopie Moléculaire, Paris, June 29, 1953 : *J. Physique*, 1954, **15**, 307.

[49] Ref. 1, p. 98 *et seq.*

[50] Van Vleck and Weisskopf, *Rev. Mod. Physics*, 1945, **17**, 227.

[50a] Fischer, *Z. Naturforsch.*, 1951, **6**a, 446 ; 1953, **8**a, 168 ; (with R. Fessler), *ibid.*, p. 177 ; see also Klages, *Z. Physik*, 1953, **136**, 480.

[51] Sharbaugh, Eckstrom, and Kraus, *J. Chem. Phys.*, 1947, **15**, 54.

first produces an ion-pair whose appearance is followed by that of increasingly complex aggregates as the concentration increases. The results confirm and extend previous deductions from low-frequency (electrolytic) conductance and osmotic measurements.[52]

Amongst other electrolyte solutions examined are those of some salt solutions in methyl alcohol, and one conclusion may be quoted : " Existing theories of electrolyte solutions suggest that departures from the ideal limiting laws occur at even lower concentrations in methyl alcohol than in water. The results of the present work indicate that one contributing factor in this effect is the larger fractional change in ε in methyl alcohol compared with that in water." [28a]

Organic Liquids.—Many of the factors discussed in the preceding paragraphs with reference to dilute solutions recur in precisely the same qualitative form when the loss processes in pure liquids are examined. A recent paper by Branin and Smyth [53] provides extensive and accurate data for a large number of liquid alkyl (and some aryl) halides. Molecules not far from spherical in shape such as those of *iso*propyl, *iso*-, *sec.*-, and *tert.*-butyl bromide have loss functions defined by a single relaxation time. The straight-chain molecules on the other hand, show increasingly broad distributions both of relaxation times and of free energies of activation for rotation. As increasing chain-length in flexible molecules leads to increasing numbers of configurations and greater probability of entanglement with neighbours—each condition associated with its own free energy of activation for dipole orientation—the general picture is sufficiently clear. A parallelism between the free energies and entropies involved in the dielectric loss and in viscous flow is again established, with some negative values for the entropy terms. As, however, only a mean relaxation time can be determined in most of these cases and such mean values do not necessarily refer to the same molecular process at the different temperatures, caution is needed (as the above authors indicate) before accepting finally some of the numerical deductions. This uncertainty possibly accounts for the considerable scatter in the plot of ΔS against ΔH for the *n*-alkyl bromide dipole relaxation factors.

For a number of rigid, non-associating, dipole molecules (*e.g.*, chlorobenzene, 1-bromonaphthalene, benzonitrile) Fischer has shown that the Onsager treatment of the internal field consistently represents the dielectric loss relations from dilute solutions to the pure liquid state. This extends the previous similar agreement for total polarisation measurements at low frequencies. For the alcohols and other associating molecules departures from the simple relations occur which throw light on the aggregation processes. In addition to Saxton and Lane's study of methyl and ethyl alcohol,[13] Davidson and Cole have examined *n*-propyl alcohol and propylene glycol and glycerol over wide frequency and temperature ranges.[54] The

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[52] Cole and Strobel, *Ann. N.Y. Acad. Sci.*, 1949, **51**, 807.

[53] Branin and Smyth, *J. Chem. Phys.*, 1952, **20**, 1121. This paper summarises, at least in some respects, the details of an extended series of observations, references to which will be found in it.

[54] Davidson and Cole, *J. Chem. Phys.*, 1951, **19**, 1484 ; 1952, **20**, 1389.

results provide important data on relaxation time distributions. Other significant observations of dielectric relaxation in long-chain liquids, and in mixtures involving association, have been made by Schallamach.[55]

One recent study of exceptional interest relates to the identity of the dielectric and ultrasonic relaxation processes in glycerol.[56a] Both types of absorption were measured over a frequency range $7{\cdot}5$—$37{\cdot}5 \times 10^6$ c./s. from 20° to − 25°. Striking similarities are established between the two phenomena showing that molecularly they are intimately related. The detection of a number of other molecularly interesting ultrasonic resonant absorptions has been claimed in a brief note.[56b]

Solids and Polymers

The technical and economic importance of dielectric loss was first encountered in the use of solid or plastic insulators, and commercial materials have been extensively examined in this respect. In ionic solids an entirely new source of loss appears as the result of piezo-electric properties, but in this summary of some chemically well-defined systems only dipole phenomena are included.

Molecular Rotation in Solids.—It is generally to be expected that when a polar liquid is frozen the molecules will lose their rotational freedom and the dielectric constant should fall abruptly to values characteristic of non-polar media. This is what happens in the vast majority of systems, but if only for their intrinsic interest mention must be made of instances where this is not so. The hydrogen halides are perhaps the best-known examples but camphor and some of its derivatives are the most striking in dielectric terms. Fig. 9 shows the temperature-dependence of the dielectric constants for a number of camphor derivatives as measured by Morgan, Yager, and their collaborators at the Bell Telephone Laboratories.[57] The melting points are marked by heavy arrows and it is seen that in most cases not only is there no discontinuity at that point but that the dielectric constant continues to increase with falling temperature of the solid. At a temperature for camphor of about − 35°, *i.e.*, 210° below its melting point, the dielectric constant falls abruptly from 14 to 2·7 : this transition temperature has been termed " the rotational melting point ". It is not very sharply defined, in the sense that a hysteresis of up to 10° can occur between the transitions observed on cooling and on heating. The factors conducive to this behaviour are the occurrence of a localised dipole in a large molecule of spherical form. The bridge system in camphor provides an appropriately compact structure and the results show how the presence of a second polar and bulky substituent reduces the temperature range for rotational freedom in the solid : in bromocamphor rotation is possible only on melting.

The results shown in Fig. 9 are independent of frequency up to 10^5 c./s. Powles [58] has recently reported a dielectric loss study of camphor from

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[55] Schallamach, *Trans. Faraday Soc.*, 1946, **42**, 495 ; 1946, **42***A*, 180.

[56] (*a*) Litovitz and Sette, *J. Chem. Phys.*, 1953, **21**, 17 ; (*b*) Karpovich, *ibid.*, p. 1120.

[57] (*a*) Yager and Morgan, *J. Amer. Chem. Soc.*, 1935, **57**, 207 ; (*b*) *idem.*, *Ind. Eng. Chem.*, 1940, **32**, 1519.

[58] Powles, *J. Chem. Phys.*, 1952, **20**, 1648.

measurements at 10^{10} c./s. He was able to estimate the critical frequency, *e.g.*, at 40°, $f_c = 7{\cdot}9 \times 10^9$ c./s., and an energy of activation $\Delta E = 3{\cdot}2$ kcal./mole, and entropy of activation $\Delta S = 5$ cal./mole °c. A comparison of these values with similar data for a number of crystalline benzene derivatives [59] serves to confirm the interpretation of the camphor results already given. A number of accounts of the behaviour of the solid hydrogen halides have appeared.[60]

Another group of compounds showing similar properties are the fully substituted benzene derivatives $C_6Me_xCl_{6-x}$.[57b] In these the methyl and chloro-substituents have approximately the same volumes but differing dipole contributions. Related to their aspherical form and the presence of a number of polar units, these molecules show only a gradual onset of rotation in the solid, a range of approximately 50° being involved in the transition. This bespeaks a range of relaxation times, *i.e.*, a range of retarding potentials in the solid. It is worth mention that various chlorinated naphthalenes are used in the manufacture of insulators.

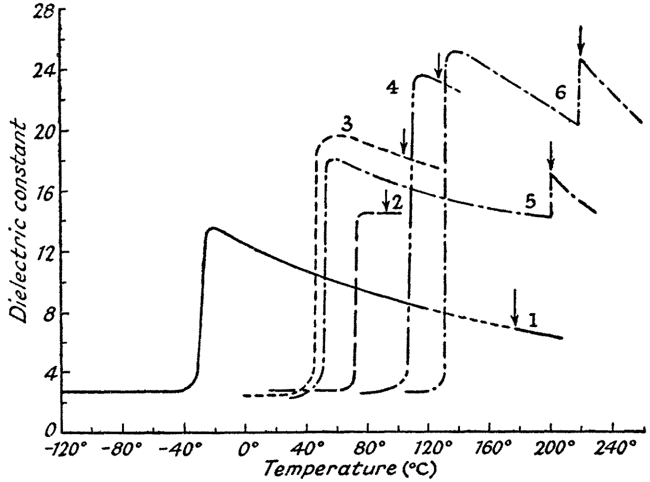

FIG. 9

Dielectric constant of camphor (1), *chlorocamphor* (2), *nitrocamphor* (3), *cyanocamphor* (4), *camphorquinone* (5), *and camphoric anhydride* (6). *Arrows indicate the melting points. Values are independent of frequency below* 10^5 c./s.

[Reproduced, by permission, from Morgan and Yager, *Ind. Eng. Chem* , 1940, **32**, 1519.]

As for the liquid state it might be expected that the most readily interpretable results for solids would be those for dilute solutions of polar molecules in non-polar media. This assumption is by no means necessarily correct but Willis Jackson certainly obtained practically important results by examining such systems as cetyl palmitate dispersed in paraffin wax and

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[59] White and Bishop, *J. Amer. Chem. Soc.*, 1940, **62**, 16.

[60] Brown and Cole, *J. Chem. Phys.*, 1952, **20**, 196 ; Swenson and Cole, *ibid.*, 1954, **22**, 284, and other refs. therein.

2-naphthol in polystyrene.[61] In the former instance the results were interpreted as showing that only a portion of the long ester molecule was able to follow the alternating field (10^5—10^7 c./s.) and that the " effective viscosity " of the solid was approximately the macroscopic value for castor oil. Polystyrene represented a far more rigid solid and two absorption peaks were found for the 2-naphthol. These were taken to represent the differing frequencies characteristic of rotation for the hydroxyl group and for the whole molecule. Further detailed analysis would be needed to establish the correctness of these plausible deductions.

The processes in crystalline solids cannot be clearly understood without reference to the molecular organisation obtaining there and it is certain that the application of concepts appropriate to the liquid state (such as " viscosity ") can at best lead to their qualitative appreciation. A fruitful approach to the study of crystals of organic polar molecules has been made by Hoffman, the treatment being in many respects a detailed analysis of the conditions in a number of models whose probable behaviours were explored by Frank.[62] For a long-chain compound terminated by a polar grouping the potential function is assumed to be of the form shown in Fig. 10. The deep energy well corresponds to antiparallel orientation of the polar groups which form opposite members in the dipole–dipole plane of a larger lattice, the larger number of equivalent positions of higher energy being those accessible to the molecule as it rotates about its long axis. Application of the Bragg–Williams treatment for a simple co-operative change leads to the prediction of a first-order transition between non-rotating and rotating states. Appropriate behaviour for the specific heat and entropy terms as well as for the dielectric constant changes due to the onset of rotation are

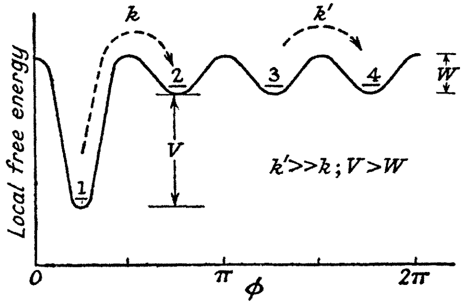

FIG. 10

Assumed local free-energy barrier as a function of angle of rotation (ϕ) for a single-axis rotator with four positions. k and k′ are the molecular transition probabilities for jumps over barriers of magnitude ($W + V$) and W, respectively.

[After Hoffman, ref. 63.]

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[61] Jackson, *Proc. Roy. Soc.*, 1935, *A*, **150,** 197 ; Frank and Jackson, *Trans. Faraday Soc.*, 1940, **36,** 440.

[62] (*a*) Frank, *Discuss. Faraday Soc.*, 1946, **42***A*, 24 ; (*b*) Hoffman, *J. Chem. Phys.*, 1952, **20,** 541 ; see also Hoffman and Decker, *J. Amer. Chem. Soc.*, 1933, **75,** 520.

predicted. Experimental data for *n*-octacosane, *n*-docosyl bromide, and *n*-triacontyl bromide show very satisfactory agreement with the calculations when the degeneracy of the upper levels (*i.e.*, the number of subsidiary minima per complete rotation) is taken as 12 ± 4 ; this is an acceptable value. In the original treatment [62b] it appeared that two distinct relaxation times measured for *n*-docosyl bromide in the rotationally frozen state could be adequately accounted for because of the asymmetry of the potential barrier. Whilst this may be the cause of multiple absorption centres—and certainly of a distribution of (unresolved) relaxation times—in the crystalline state, the high frequency loss peak in the docosyl bromide is probably due to a wagging motion of the C–Br dipole. A more detailed statistical evaluation of the behaviour to be expected has now been made : it is shown that the much-used relation $\tau = (\boldsymbol{h}/\boldsymbol{k}T) \exp (E/\boldsymbol{R}T)$ (which arises from consideration of an activated vibrator) can also be deduced in appropriate circumstances from the expression applicable to restricted rotation about a single axis,[63] $\tau = 2\pi(2\pi I/\boldsymbol{k}T)^{\frac{1}{2}} \exp (E/\boldsymbol{R}T)$.

Hoffman, Crowe, and Smyth [64] have studied the onset of molecular rotation in its influence upon the dielectric behaviour of long-chain crystalline esters. They have also found that, depending upon the time allowed for freezing, an ordered lattice in which the ester groups (unsymmetrically placed along the total molecular length) are in a plane can be disordered longitudinally by the reversal of some of the chain orientations. Such findings are typical of what may be expected from systematic dielectric studies. A number of substituted methane derivatives—some, such as *tert.*-butyl chloride, of approximately spherical form—have been examined [65] at 10^{10} c./s., whilst some of the special features arising from hydrogen bonding in the solid state have been amongst the findings of a group of Australian workers.[66]

Dielectric Loss in Plastic Polymers.—Not surprisingly in view of their extensive use in the electrical industry the dielectric absorptions of polymer systems have been studied in some detail. The non-polar materials such as polystyrene, Polythene, and polytetrafluoroethylene are remarkable for the low loss factors they show when free from impurities, ε'' values as low as 10^{-4} being found which are almost independent of frequency up to optical values ; the ε' values are equal to n^2 (*e.g.*, for Polythene 2·30 and for polystyrene 2·64). A polar linear polymer (such as polyvinyl chloride) in the plastic state often shows dielectric loss at very low frequencies : when plasticised with 20% of diphenyl, polyvinyl chloride at 40° shows a maximum in its absorption at 60 c./s. This maximum moves to higher frequencies (or higher temperatures if the frequency is maintained constant) as the

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[63] Hoffman, personal communication : Hoffman and Pfeiffer, *J. Chem. Phys.*, 1954, **22**, 132, 156.

[64] Hoffman, Crowe, and Smyth, *ibid.*, 1952, **20**, 550.

[65] Powles, Williams, and Smyth, *ibid.*, 1953, **21**, 136.

[66] Meakins and Sack, *Austral. J. Sci. Res.*, 1951, *A*, **4**, 213 ; *idem, Nature*, 1949, **164**, 798. For further valuable studies, mostly of crystalline long-chain compounds, see Meakins *et al.*, *ibid.*, 1949, *A*, **2**, 405 ; 1951, *A*, **4**, 213, 359, 365, 616 ; 1952, *A*, **5**, 135, 661, 671 ; *Austral. J. Chem.*, 1953, **6**, 27, 104.

plasticiser content is reduced. In this system the most probable relaxation time is proportional to the degree of polymerisation.[67] Loss-factor measurements provide most revealing information on the " lubricating " action of plasticisers. The losses observed are very broad, sometimes having a half-width of as many as six decades on the frequency scale ; such wide distributions of relaxation times conform to a flexible chain structure possessing many degrees of internal rotational freedom.[68] A striking confirmation of this picture and of the Onsager–Kirkwood treatment of the reaction field is seen in the deduction of the dipole moments of polymer units. Kirkwood's relations [69] involve the average value of the product of the moment of a molecule and the total moment formed by the vector sum of itself and the moments induced in the surrounding medium. When a linear polymer is composed of units possessed of a single dipole (as in polyvinyl chloride) this product can be calculated on the basis of the flexible chain model : the result is $\mu'' = \frac{\sqrt{3}}{2}.\mu_0$, where μ'' is the average value of the moment per monomer unit in an n-mer and μ_0 is the moment of the same atomic grouping in the gas phase.[70] By extrapolation of the loss-factor data a correct static dielectric constant, ε_0, for the polymer can be found with an accuracy sufficient to show very good agreement between the μ_0 value arrived at in this way and that calculated from gas data.[71]

The appropriateness of regarding a polymeric plastic as more akin to a highly viscous liquid than to a crystalline solid has been tested by Fuoss in an interesting way. He has compared the temperature coefficient of the most probable relaxation time in the polymer with the temperature coefficient for ionic mobilities in the same system : the latter is measured from direct-current conductances. Essentially identical activation energies are involved so that the processes are hydrodynamically similar. A direct verification of the liquid-like behaviour is seen in the fact that the direct-current conductance is the same for the same electrolyte content in different plasticiser–polymer systems for those temperatures at which the systems have their absorption maxima for a given frequency.[72] A feature of very general interest is that the static dielectric constants of polar polymers are usually very much larger than those of their monomeric liquids. This results from the inability of the individual polar units in the former to take up anti-parallel zero-moment configurations as frequently as is possible in the liquid.

The foregoing comments indicate the nature of some of the results for plastic polymers. Important and revealing changes in dielectric loss occur at the brittle-point which is encountered when such plastics are cooled. This transition temperature (or, rather, range of several degrees) is analogous

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[67] Fuoss, *J. Amer. Chem. Soc.*, 1941, **63**, 2401.

[68] Kirkwood and Fuoss, *J. Chem. Phys.*, 1941, **9**, 329.

[69] Kirkwood, *ibid.*, 1939, **7**, 911.

[70] Kirkwood and Fuoss, *J. Amer. Chem. Soc.*, 1941, **63**, 385.

[71] Fuoss, *ibid.*, p. 2410.

[72] *Idem, ibid.*, 1939, **61**, 2329 ; *Ann. N.Y. Acad. Sci.*, 1940, **40**, 429.

to an " internal melting point " and is characterised by local crystallisation on cooling, or crystallite disappearance on heating. Again, for the case of polyvinyl chloride, Fuoss finds the maximum loss factor for the unplasticised material at 100 c./s. to occur at 100°. Decreasing temperature at the same frequency results in a fall in ε'' from 1·2 at 100° to 0·004 at 70°, the brittle point for this pure polymer. Further temperature decrease shows that a distinct minimum in ε'' is located at 70° and is followed by a low broad maximum centred at about 0° and $\varepsilon'' = 0{\cdot}0063$. This subsidiary low-temperature absorption is certainly associated with chain interactions (*i.e.*, localised crystallisation) as it can be made to disappear by addition of plasticiser or by the introduction of substituent groups on the chain unit, either of which treatments tends to prevent the regular alignment of the chains which is involved in crystallisation.

In addition to Fuoss's systematic studies of a number of linear polar polymers, including polyvinyl acetate and chloroacetate,[73] polymethyl α-chloroacrylate, polymethyl methacrylate, polymethyl acrylate, and polychloroethyl methacrylate,[74] and copolymers of acrylonitrile and ethyl acrylate,[75] many other polymer systems have been studied.[76] Mention may be made of the results of Hartshorn and his collaborators for the dielectric loss in cross-linked (thermal setting) resins,[77] and of a model investigation of polyethylene terephthalate (" Terylene ") by Reddish.[78] The latter investigation covered the frequency range 10^2—10^7 c./s. from − 80° to + 180° and served to emphasise, amongst other points, the value of a wide frequency coverage. Two of the three loss processes revealed are characterised in terms of the equation

$$\frac{1}{\tau} = A \exp(-E/RT) = \frac{kT}{h} \exp(\Delta S/R) \exp(-\Delta H/RT)$$

by the parameters of Table 9.

TABLE 9. *Entropies and energies of activation in " Terylene "*

	A	ΔH (kcal./mole)	ΔS (cal./mole deg.)
Low-temperature process . . .	10^{15}	12·4	12
High-temperature process . . .	10^{54}	90·4	190

On the basis of a detailed analysis the low-temperature process is identified as arising from those terminal hydroxyl groups which are present in the amorphous regions of the polyester. The high-temperature loss process is

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[73] Mead and Fuoss, *J. Amer. Chem. Soc.*, 1941, **63,** 2832.

[74] *Idem, ibid.*, 1942, **64,** 2389.

[75] *Idem, ibid.*, 1943, **65,** 2067.

[76] See, for instance, Tuckett, *Trans. Faraday Soc.*, 1944, **40,** 448 ; Oakes and Richards, *Discuss. Faraday Soc.*, 1946, **42***A*, 197 ; Plessner and Richards, *ibid.*, p. 206 ; and a review of polymer dielectrics by Würstlin, *Kolloid Z.*, 1951, **120,** 84.

[77] Hartshorn, Megson, and Rushton, *Proc. Phys. Soc.*, 1940, **52,** 796 ; *J. Inst. Elect. Eng.*, 1938, **83,** 474.

[78] Reddish, *Trans. Faraday Soc.*, 1950, **46,** 459.

due to dipole reorientations' involving segments of the main polymer chain ; it is related to a number of important thermo-mechanical changes in the material. A low-frequency loss process observed at high temperatures arises from a species of ionic conductance, again probably limited to the amorphous polymer regions.

Ionic and Semi-conducting Solids.—Freymann and his collaborators are actively exploring another aspect of dielectric loss in solids by their measurements of ionic and semi-conducting systems, with suggestive indications relative to phase changes and lattice theory.[79]

The author acknowledges helpful guidance on the scope of this article from Professor F. S. Dainton.

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[79] M. Freymann and R. Freymann, *J. Chem. Phys.*, 1952, **20**, 1970, and other refs. there.