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Dielectric Relaxation as a Chemical Rate Process

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THIRTY years ago, Debye[1] showed that the polarization of a dielectric medium in an electric field might arise from the partial orientation of permanent molecular dipoles by the field as well as from the distortion of electronic orbits in the molecules. This suggestion has since proved to be of very great value in dielectric research and in the study of the structures of molecules and of the natures of the solid and liquid states.[2–7] For our present purposes it is sufficient to remark that when the dielectric constant of a liquid or solid is much greater than about $2\frac{1}{2}$ or 3, permanent molecular dipoles almost certainly play an important part in determining the dielectric properties of the medium. For a substance such as water, with a dielectric constant of about 80, dipoles clearly play a dominant role; this is also true of a great many commercially important dielectrics. Since much will be said about dipoles on these pages, it may be helpful to remind the reader that the actual magnitudes of the permanent dipoles typically found on "polar" molecules (H_2O, CH_3Cl, CH_3OH, etc.) is such as would result from the separation of an electron from a neutral atom by a distance of the order of magnitude of a quarter of that usually observed between adjoining atoms in a molecule.

Relaxation may be defined as the time lag in the response of a system to a change in the

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[1] P. Debye, Physik. Zeits. **13**, 97 (1912).

[2] P. Debye, *Polar Molecules* (The Chemical Catalogue Company, 1929).

[3] C. P. Smyth, *Dielectric Constant and Molecular Structure* (The Chemical Catalogue Company, 1931).

[4] H. A. Stuart, *Molekülstruktur* (Julius Springer, Berlin, 1934) Chap. 5.

[5] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford, 1931).

[6] R. J. Le Fevre, *Dipole Moments* (Methuen, 1937).

[7] E. Bergmann and A. Weizmann, Chem. Rev. **29**, 553 (1941).

physical forces to which it is subjected. From thermodynamics we know that processes are most efficiently carried out when they proceed under conditions of thermodynamic reversibility. Relaxation phenomena prevent the attainment of these conditions and thus give rise to energy waste which it is frequently highly desirable to reduce. A knowledge of the mechanisms of relaxation phenomena may therefore often be of great practical use.

Relaxation rates are, of course, the rates at which a system comes into equilibrium with its surroundings when various physical aspects of its surroundings (temperature, electric field, magnetic field, stress, etc.) are changed. These rates may be arranged in two more or less distinct groups, depending on how rapidly they change with the temperature. In one group we have those rates which depend on such properties as the thermal conductivity, the electrical conductivity of metallic conductors, and the velocities of sound and light, which do not vary markedly with the temperature. In the other group we have those rates which do change considerably with the temperature; the rate at which the portion of the dielectric polarization arising from the orientation of permanent molecular dipoles comes into equilibrium with an applied field belongs to this class. This is evident from Fig. 1, which shows that the frequency above which the contribution of dipolar orientations to the dielectric constant becomes negligible changes very rapidly with the temperature for a typical dielectric. This frequency is obviously closely related to the relaxation rate. Figure 1 also illustrates that in the region of the greatest irreversibility, the energy dissipation during each process of polarizing the dielectric is a maximum.

The fact that these *dielectric relaxation rates* depend markedly on the temperature is a very significant one insofar as an understanding of the detailed physical nature of the process is concerned. Whenever the rate of a process depends markedly on the temperature, it is quite certain that at some stage in the process a molecule or other unit involved is forced to wait until it has acquired, by thermal fluctuations, a considerable amount of energy in excess of the average thermal energy in the medium. Now the factors which govern the rate of acquiring large amounts of energy through thermal fluctuations have long been the object of study by chemists in their investigations of the very similar problem of the rates of chemical reactions. At the present time fairly complete ideas about these factors have been developed, so that it is natural to apply these notions to dielectric relaxation rates with a view toward obtaining a better understanding of their fundamental mechanisms. Such an application will be the basic purpose of the present paper.

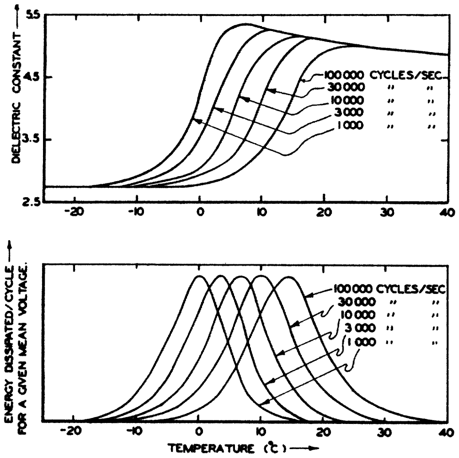

FIG. 1. Temperature dependence of dielectric relaxation rates for a chlorinated diphenyl [from A. H. White and S. O. Morgan, J. Frank. Inst. **216**, 635 (1933)].

The suitability of the approach to dielectric relaxation rates from the standpoint of chemical rate theory was first pointed out by Eyring.[8] Applications to isolated problems in dielectrics have been made by Frank,[9] Stearn and Eyring,[10] and Baker and Smyth.[11] In this paper a more general attack will be carried out. We shall begin by outlining a general theory of dielectric relaxation in terms of the frequency of discontinuous molecular reorientations (hereafter called "jumps"). The more common quantities (such as the loss factor) used in describing the behavior of dielectrics in oscillating fields will be formulated in terms of the quantities appearing in the theory. This treatment is closely similar to that already given by Debye[12] in terms of rotatory

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[8] H. Eyring, J. Chem. Phys. **4**, 283 (1936).

[9] F. C. Frank, Trans. Faraday Soc. **32**, 1634 (1936).

[10] A. Stearn and H. Eyring, J. Chem. Phys. **5**, 113 (1937).

[11] W. Baker and C. P. Smyth, J. Chem. Phys. **7**, 574 (1939).

[12] P. Debye, Physik. Ber. **15**, 777 (1913) and reference 2.

Brownian motions, but it will be shown that the fundamental picture of molecular motions used by Debye is probably inaccurate, or at best ill-suited to the study of most dielectrics of practical interest. Before applying the theory to actual data, a brief review of the principles of chemical kinetics will be presented. Eyring's general rate theory will be stressed here, it being particularly well adapted to the problems likely to be encountered. Finally, the available data on dielectric relaxation will be considered and the general features of the phenomenon as well as some more specific details will be investigated with a view to understanding the mechanism of the relaxation process in terms of molecular dynamics.

I. THEORY

A. Derivation of the Differential Equation for the Relaxation of the Dielectric Polarization

1. *Continuous Distribution of Dipoles over Different Directions in Space*

In common with the usual methods of calculating dielectric properties, let us consider a medium containing N_0 dipoles per cubic centimeter, each possessing a dipole moment μ pointing in a direction having a polar angle θ and longitude φ with respect to some fixed set of axes. (Usually $\theta=0$ will be taken as the direction of the applied field, when there is a field.) Then there will be at any time t a distribution of the dipoles among the various directions in space such that the number of dipoles out of one cubic centimeter whose directions are included in an element of solid angle $d\Omega$ around the direction θ, φ will be given by

$$N(\theta,\ \varphi,\ t)d\Omega,$$

the function N being normalized such that

$$\int N(\theta,\ \varphi,\ t)d\Omega=N_0. \tag{1}$$

At any time the polarization along the direction $\theta=0$ contributed by the dipoles will be

$$P(t)=\mu\int N\cos\theta d\Omega. \tag{2}$$

Our problem is to find P as a function of the time from a knowledge of the details of the motion of the individual dipoles. The latter are most easily described in terms of transition probabilities defined as follows: Suppose that a molecule has an orientation θ, φ. The probability that it will move to a new position, θ', φ', within a solid angle $d\Omega'$ in an interval of time dt will be $\mathbf{k}(\theta,\ \varphi\rightarrow\theta',\ \varphi')dtd\Omega'$. Now it is practically universally observed that the rate of decay of the polarization in condensed phases (or properties dependent upon this decay rate) is very strongly dependent on the temperature. This indicates that the transition probability is governed by the rate of thermal activation of the dipoles. That is, the rate of reorientation is proportional to the Boltzmann factor $e^{-E/kT}$, where E is the energy which must be furnished before the dipoles can dissolve the bonds which hold them in one position and re-establish themselves in another. Even in the simplest molecules in condensed phases, E is of the order of 10 kT at room temperature, but it is often much greater, as we shall see, so that this factor must be of dominant importance in any consideration of dielectric relaxation. This fact forces us to the conclusion that the dipoles change their directions, not continuously, but in a series of sudden jumps. The transition probability, $\mathbf{k}(\theta,\ \varphi\rightarrow\theta',\ \varphi')dtd\Omega'$, may then be regarded as the probability that a *jump* will occur in an interval of time dt resulting in the indicated change of orientation.

The total number of molecules in a solid angle $d\Omega$ about the direction θ, φ which *leave* that direction in an interval dt will be

$$Adt=\int_{\Omega'} N(\theta,\ \varphi,\ t)\mathbf{k}(\theta,\ \varphi\rightarrow\theta',\ \varphi)dtd\Omega d\Omega', \tag{3}$$

where the integration is over Ω', the directions *into* which the dipoles jump. Similarly, the number of dipoles *entering* the same solid angle $d\Omega$ from other directions will be

$$Bdt=\int_{\Omega'} N(\theta',\ \varphi',\ t)\mathbf{k}(\theta',\ \varphi'\rightarrow\theta,\ \varphi)dtd\Omega d\Omega'. \tag{4}$$

The net rate of change in the probability function N is thus

$$\begin{aligned} dN(\theta,\ \varphi,\ t)/dt&=B-A\\ &=\int[N(\theta',\ \varphi',\ t)\mathbf{k}(\theta',\ \varphi'\rightarrow\theta,\ \varphi)\\ &\qquad -N(\theta,\ \varphi,\ t)\mathbf{k}(\theta,\ \varphi\rightarrow\theta',\ \varphi')]d\Omega'. \end{aligned} \tag{5}$$

The two sides of this equation may be multiplied by $\mu \cos\theta$ and integrated over all θ, φ, and we find, remembering Eq. (2),

$$\begin{aligned} dP(t)/dt &= B' - A' \\ &= \mu \int\int \cos\theta [N(\theta', \varphi', t)\mathbf{k}(\theta', \varphi' \rightarrow \theta, \varphi) \\ &\quad - N(\theta, \varphi, t)\mathbf{k}(\theta, \varphi, \theta', \varphi')] d\Omega d\Omega'. \end{aligned} \tag{6}$$

This equation, which gives the time rate of change of the macroscopic polarization in terms of the motions of the individual dipoles, cannot be further reduced unless we make simplifying assumptions concerning the dependence of the transition probabilities on direction; a very complex result is possible if this dependence is not simple, but usually considerable simplification will be possible, as will be shown below. In general, too, $\mathbf{k}$ will depend upon the applied field which may in turn vary with the time, so that $\mathbf{k}$ may also be a function of the time. This will be a factor when we apply Eq. (6) to the calculation of the properties of the dielectric in alternating fields.

2. *Dipoles Distributed among Discrete Orientations*

The above treatment is best suited to media, such as liquids, in which there is a certain amount of over-all homogeneity. In crystalline solids, on the other hand, another treatment will usually be more suitable. Here we must realize that, in many cases at least, each dipole can point only in certain general directions, giving rise to a discrete series of possible orientations. The distribution function is now written as

$$N_i = N(\theta_i, \varphi_i, t), \tag{7}$$

which gives the number of dipoles in unit volume which have an orientation i. The transition probabilities may be written as $\mathbf{k}_{i\rightarrow j}$, or more simply as $\mathbf{k}_{ij}$, $N_i\mathbf{k}_{ij}dt$ being the number of molecules in unit volume whose position changes from that of state i to that of state j in an interval dt. For the net polarization along the axis, $\theta = 0$,

$$P(t) = \mu \textstyle\sum_i N_i \cos\theta_i; \tag{8}$$

for the net rate of change of the number of dipoles in orientation i,

$$dN_i/dt = \textstyle\sum_j (N_j\mathbf{k}_{ji} - N_i\mathbf{k}_{ij}); \tag{9}$$

and for the rate of change of the polarization,

$$\begin{aligned} dP(t)/dt &= \mu \textstyle\sum_i \cos\theta_i \cdot (dN_i/dt) \\ &= \mu \textstyle\sum_{i,j} (N_j\mathbf{k}_{ji} \cos\theta_i - N_i\mathbf{k}_{ij} \cos\theta_i). \end{aligned} \tag{10}$$

Equation (10) is the counterpart of Eq. (6) for the case of discrete orientations.

3. *Simplifying Assumptions*

a. Assumption of jump probabilities independent of the sizes of the jumps; no field.—Suppose that in Eq. (6) $\mathbf{k}(\theta, \varphi \rightarrow \theta', \varphi')$ depends only on ϑ, the polar angle measured from the direction θ, φ, and not on the particular value of θ and φ. That is, suppose (as may frequently be the case) that the probability of a jump depends only on how far away the final position is from the initial position. This, of course, implies that neither external nor internal fields act on the dipoles. Then we may write Eq. (6) as

$$\begin{aligned} \frac{dP(t)}{dt} &= -2\pi P(t) \int_0^\pi \mathbf{k}(\vartheta) \sin\vartheta d\vartheta \\ &\quad + \mu \int\int \cos\theta N(\theta', \varphi', t)\mathbf{k}(\vartheta) d\Omega d\Omega'. \end{aligned} \tag{11}$$

The first term here arises from term A' of Eq. (6) because the two integrations there may now be carried out independently.

Next assume that $\mathbf{k}$ is not only independent of θ and φ, the original orientation of the dipole, but also of ϑ, the angular distance through which it jumps in a transition. Interpreted in the light of our previous remarks on the role of thermal activation, this is to say that whenever a molecule is activated sufficiently to allow reorientation, it is so completely disconnected from its former direction that all possible new directions are equally likely. We shall see in Section II that in the light of the experimental observations, such an assumption is quite reasonable for many substances.

Under these circumstances, the integral B' in Eq. (6) is zero, since $\int \cos\theta d\Omega = 0$; or more physically, this term must be zero since it gives the net amount of polarization re-established by jumps from other orientations, and due to the assumed equal probability of all jumps, no polarization can be established in this way. Then

$$dP(t)/dt = -4\pi\mathbf{k}P(t) = -\mathbf{k}_0 P(t). \tag{12}$$

This, of course, is the differential equation leading to an exponential decay of the polarization:

$$P(t) = P_0 e^{-\mathbf{k}_0 t}. \qquad (13)$$

Owing to the manner in which $\mathbf{k}$ was defined, $\mathbf{k}_0$ is the rate constant for the *activation* of dipoles, i.e., the *jump rate*, or the mean number of jumps made by a dipole in unit time. We may define a *relaxation time*, $\tau = 1/\mathbf{k}_0$, such that in this time the polarization will fall to $1/e$th of its initial value. This is the usual quantity used to describe the dielectric relaxation; in this paper, however, we shall make a point of using the *dipole relaxation rate* or the *jump rate*, $\mathbf{k}_0$ itself, in describing the relaxation, since this tends to emphasize the important similarity of the relaxation process to a chemical reaction.

The above assumption may also be applied to Eq. (10); if all of the $\mathbf{k}_{ij}$'s are equal to a constant, $\mathbf{k}$,

$$\begin{aligned} dP/dt &= -\mathbf{k}\mu\left(\textstyle\sum_i nN_i \cos\theta_i - N_0 \sum_i \cos\theta_i\right) \\ &= -n\mathbf{k}P(t) + N_0\mathbf{k}\mu \textstyle\sum_i \cos\theta_i, \end{aligned} \qquad (14)$$

where n is the total number of orientations allowed. If there is anything like a symmetrical arrangement of possible directions, the last term will vanish and again we will have that

$$dP/dt = -n\mathbf{k}P(t) = -\mathbf{k}_0 P(t). \qquad (15)$$

$\mathbf{k}_0$ is here again the frequency with which dipoles change their orientation in unit time.

b. Effect of an applied field.—All of the assumptions in the previous section imply that no electric field is acting on the dipoles. Now let us suppose that a field F is acting along the $\theta = 0$ direction. Let F be so small that $\mu F \ll kT$ (which is true for fields up to 10^5 volt/cm). Note that F is the field acting *on the dipole* and may not be the same as the externally applied field E either in direction (due to crystal anisotropy) or in magnitude (due to internal field effects such as that of Lorentz or of Onsager). The crystal anisotropy effect need not concern us here, though it might lead to very interesting considerations in the relaxation of single crystal dielectrics.

The assumption that the transition probabilities are independent of the nature of the jump will have to be modified in the presence of a field, since, starting with an unpolarized medium, jumps into the direction opposing the field will have to become less frequent, while those toward the field will have to become more frequent; otherwise there would be no way for an unpolarized medium to acquire polarization in the field. If we agree to the importance in dielectric relaxation of the role of energy barriers which are only occasionally overcome by thermal agitation, this is easily accounted for: If the dipole formerly, in the absence of a field, required an energy E_0 in order to change its orientation (E_0 being independent of the size of the jump), it will now need an additional energy $\mu F(\cos\theta - \cos\theta_{\theta\theta'})$, in order to move from a position with a polar angle θ to one with polar angle θ'. ($\theta_{\theta\theta'}$ is the polar angle of the dipole at the top of the energy barrier between the two positions.) Since $\mathbf{k} = Ae^{-E/kT}$, where E is the height of the energy barrier above the initial state, the transition probability in the presence of a field will be

$$\begin{aligned} \mathbf{k}(\theta \to \theta') &= A \exp\left[-(E_0 + \mu F(\cos\theta - \cos\theta_{\theta\theta'})/kT\right] \\ &= \mathbf{k}_1 \exp\left[\frac{\mu F}{kT}(\cos\theta_{\theta\theta'} - \cos\theta)\right] \\ &\cong \mathbf{k}_1\left[1 + \frac{\mu F}{kT}(\cos\theta_{\theta\theta'} - \cos\theta)\right] \end{aligned} \qquad (16)$$

since $\mu F/kT \ll 1$, $\mathbf{k}_1$ being the jump rate in the absence of the field. Substituting in Eq. (6) we find

$$dP/dt = B'_1 + B'_2 + B'_3 - A'_1 - A'_2 - A'_3 \qquad (17a)$$

where

$$B'_1 = \mu\mathbf{k}_1 \int \cos\theta d\Omega \int N(\theta')d\Omega' = 0$$

$$B'_2 = \frac{\mu^2\mathbf{k}_1 F}{kT} \int\int \cos\theta_{\theta'\theta} \cos\theta N(\theta')d\Omega d\Omega'$$

$$B'_3 = -\frac{\mu^2\mathbf{k}_1 F}{kT} \int \cos\theta d\Omega \int N(\theta') \cos\theta' d\Omega' = 0$$

$$A'_1 = \mu\mathbf{k}_1 \int \cos\theta N(\theta)d\Omega \int d\Omega' = 4\pi\mathbf{k}_1 P$$

$$A'_2 = \frac{\mu^2\mathbf{k}_1 F}{kT} \int\int \cos\theta_{\theta\theta'} \cos\theta N(\theta)d\Omega d\Omega'$$

$$A'_3 = \frac{\mu^2\mathbf{k}_1 F}{kT} \int \cos^2\theta N(\theta)d\Omega \int d\Omega'.$$

Since μF, the orienting energy, is in practice almost always very much smaller than the thermal energy kT, the distribution function $N(\theta)$ will usually be very nearly uniform. That is,

$$N(\theta) \cong N(\theta') \cong N_0/4\pi + \text{terms in } F,$$

where N_0 is, as defined before, the number of dipoles per unit of volume. The terms in F here can be neglected in the integrals of B'_2, A'_2, and A'_3, giving

$$B'_2 = \frac{N_0\mu^2\mathbf{k}_1F}{4\pi kT}\int\int \cos\theta_{\theta'\theta}\cos\theta d\Omega d\Omega'$$

$$A'_2 = \frac{N_0\mu^2\mathbf{k}_1F}{4\pi kT}\int\int \cos\theta_{\theta\theta'}\cos\theta d\Omega d\Omega'$$

$$A'_3 = \frac{N_0\mu^2\mathbf{k}_1F}{4\pi kT}\int\int \cos^2\theta d\Omega\int d\Omega' = 4\pi\mathbf{k}_1\frac{N_0\mu^2}{3kT}.$$

Now it must always be true that the position of the top of the energy barrier (i.e., the nature of the activated state) for any transition must be the same as that for the corresponding reverse transition; were this not so, thermodynamic equilibria would not in general be possible. Therefore,

$$\theta_{\theta'\theta} = \theta_{\theta\theta'}$$

and

$$B'_2 = A'_2.$$

Collecting all terms, we arrive at the expression

$$dP/dt = -4\pi k_1\left(P - \frac{N_0\mu^2}{3kT}F\right)$$
$$= -k_0(P - N_0\alpha_\mu F). \quad (17b)$$

We see that at equilibrium, when $dP/dt = 0$, this gives the correct relationship between field and polarization, since $\alpha_\mu = \mu^2/3kT$ is the contribution to the polarizability due to a dipole.

The same treatment may be carried out for the case of a discrete set of orientations to give

$$\frac{dP}{dt} = -\mathbf{k}_0\left(P - \frac{N_0\mu^2}{kT}\frac{\sum\cos^2\theta_i}{n}F\right). \quad (18)$$

Here n is the total number of orientations available to a dipole. Since the dipolar contribution to the polarizability is easily shown to be

$$\alpha_\mu = \frac{\mu^2}{kT}\frac{\sum\cos^2\theta_i}{n}, \quad (19)$$

we have as before $dP/dt = -\mathbf{k}_0(P - N_0\alpha_\mu F)$.

c. Assumption that individual jumps involve only a very small change in direction.—Equation (6) can also be thrown into simple form if in each jump the dipole changes its direction by a relatively small amount. This treatment is very similar to that given by Debye, and with certain further assumptions leads to his well-known relation for the relaxation rate in terms of the viscosity.

Assume, as in the first paragraph of Section *a*, that in the absence of a field the probability that a dipole will jump from one position (θ, φ) to another (θ', φ') depends only on ϑ, the angle between the two directions. Then, including the effect of the field as before,

$$k(\theta, \varphi \to \theta', \varphi') = \mathbf{k}_0(\vartheta)$$
$$\times\left[1 + \frac{\mu F}{kT}(\cos\theta_{\theta'\theta} - \cos\theta)\right] \quad (20)$$

Assume further that $k_0(\vartheta)$ decreases very rapidly with increasing ϑ, so that both $N(\theta', \varphi', t)$ and $\cos\theta'$ may be expanded about (θ, φ). (Having chosen the field direction as $\theta = 0$ we can safely assume that N depends on θ and not on φ.) Then

$$N(\theta', \varphi', t) = N(\theta') = N(\theta) + (\theta' - \theta)\frac{\partial N}{\partial\theta}$$
$$+ \tfrac{1}{2}(\theta' - \theta)^2\frac{\partial^2 N}{\partial\theta^2} + \cdots \quad (21)$$

$$\cos\theta' = \cos\theta - (\theta' - \theta)\sin\theta$$
$$- \tfrac{1}{2}(\theta' - \theta)^2\cos\theta + \cdots \quad (22)$$

Remembering that the derivatives of N are all proportional to the field F at the small fields we are concerned with, so that they may be neglected in integrals B'_2, B'_3, A'_2 and A'_3, we may substitute Eqs. (20), (21), and (22) into Eq. (6) and again obtain Eq. (17a), where

$$A'_1 = \mu\int\int \mathbf{k}_0(\vartheta)N(\theta)\cos\theta d\Omega d\Omega'$$

$$A'_2 = \frac{\mu^2F}{kT}\int\int \cos\theta_{\theta\theta'}\cos\theta\mathbf{k}_0(\vartheta)N(\theta)d\Omega d\Omega'$$

$$A'_3 = -\frac{\mu^2F}{kT}\int\int \mathbf{k}_0(\vartheta)N(\theta)\cos^2\theta d\Omega d\Omega'$$

$$B'_1=A'_1+\mu\int\int \mathbf{k}_0(\vartheta)N(\theta)(\theta'-\theta)\frac{\partial N}{\partial\theta}\cos\theta d\Omega d\Omega'$$

$$+\frac{\mu}{2}\int\int \mathbf{k}_0(\vartheta)(\theta'-\theta)^2\frac{\partial^2 N}{\partial\theta^2}\cos\theta d\Omega d\Omega'$$

$B'_2=A'_2$ (since $\theta_{\theta'\theta}=\theta_{\theta\theta'}$ as before)

$$B'_3=A'_3+\frac{\mu^2F}{kT}\int\int \mathbf{k}_0(\vartheta)(\theta'-\theta)\cos\theta \times\sin\theta N(\theta)d\Omega d\Omega'$$

$$+\frac{\mu^2F}{2kT}\int\int k_0(\vartheta)(\theta'-\theta)^2 \times\cos^2\theta N(\theta)d\Omega d\Omega'. \quad (23)$$

These integrals are evaluated by transforming θ' to a new polar coordinate system, ϑ and ϕ, whose pole is along (θ, φ), the new polar angle ϑ being the same as the argument in $\mathbf{k}_0(\vartheta)$, while the new azimuthal angle ϕ is measured from the plane made by the $\theta=0$ and $\theta=\theta$, $\varphi=\varphi$ directions. Then it can be shown that[13]

$$\theta'-\theta=-\vartheta\cos\phi+\tfrac{1}{2}\vartheta^2\frac{\cos\theta}{\sin\theta}\sin^2\phi+\cdots \quad (24)$$

The net result of the integration is that

$$dP/dt=-\tfrac{1}{2}\langle\mathbf{k}\vartheta^2\rangle_{\mathrm{Av}}\left(P-\frac{N_0\mu^2}{3kT}F\right)$$

$$=-\tfrac{1}{2}\langle\mathbf{k}\vartheta^2\rangle_{\mathrm{Av}}(P-N_0\alpha_\mu F), \quad (25)$$

where $\langle\mathbf{k}\vartheta^2\rangle_{\mathrm{Av}}dt$ is the mean square angle moved in an interval of time dt, and is defined by

$$\langle\mathbf{k}\vartheta^2\rangle_{\mathrm{Av}}=\int\vartheta^2\mathbf{k}_0(\vartheta)d\Omega. \quad (26)$$

It is interesting to note that whereas with the previous assumption all of the change in the polarization comes from A'_1 and A'_3, here the contributions from these terms are cancelled out by similar terms in B'_1 and B'_3 and 'the total change comes from the remaining terms in B'_1 and B'_3. This signifies that for the present type of behavior the change in polarization with time comes predominantly from motions in which dipoles return to their original orientations several times before finally wandering out on the road toward complete equilibrium. The indecisive continuity of this motion is in direct contrast to the prolonged hesitancy and sudden, unrestrained decision which may be said to characterize the motion of a dipole obeying the kinetics previously considered.

Equation (6) can be thrown into a form which will give Debye's theory of the molecular process determining the relaxation rate if we alter the interpretation which we have made of the transition probability $\mathbf{k}$. We have up to now regarded $\mathbf{k}(\theta, \varphi\rightarrow\theta', \varphi')dt$ as the probability of a single jump in a time interval dt. Instead, we may regard it as the probability that, in an interval dt sufficient for a relatively large number of jumps to have taken place, a dipole originally in one specified direction will be found in another specified direction. (The minimum number of jumps considered here must be at least such that by the time of the last jump, all memory of the direction of the first jump is gone.) Under these circumstances, Einstein[14] showed that

$$\int\vartheta^2\mathbf{k}_0(\vartheta)d\Omega=\langle\mathbf{k}\vartheta^2\rangle_{\mathrm{Av}}=4kT/\zeta, \quad (27)$$

where $\langle\mathbf{k}\vartheta^2\rangle_{\mathrm{Av}}$ is the mean square deviation of angle per unit time and ζ is the average coefficient of frictional resistance opposing the angular rotation, such that the torque required to maintain a given average angular velocity $d\theta/dt$ is

$$\mathcal{T}=\zeta d\theta/dt. \quad (28a)$$

If we assume that the rotatory motion of a dipole in a liquid may be adequately described as that of a sphere of radius a immersed in a homogeneous medium of viscosity η, hydrodynamics (Stokes' law) tells us that

$$\zeta=8\pi\eta a^3. \quad (28b)$$

Substituting in Eq. (25) one finds that,

$$dP/dt=-\frac{1}{\tau}(P-N_0\alpha_\mu F), \quad (29)$$

where $\tau=4\pi\eta a^3/kT$, which is Debye's familiar result.

It should be clearly realized that for Eq. (29) to be true, it must be possible to choose an angular displacement which is large enough that several jumps are on the average required in order to

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[13] See reference 2, p. 80.

[14] A. Einstein, Ann. d. Physik **17**, 549 (1905); **19**, 371 (1906); *Theory of the Brownian Movement* (ed. by R. Fürth) (Methuen, 1926), p. 32.

cover the interval; at the same time it must be small enough for only a small fraction of a rotation to have taken place. Even if the individual jumps cover angles large enough to make the use of the expansions of Eqs. (21), (22), and (23) questionable, the treatment leading to Eq. (25) may still be fairly accurate, whereas that leading to Eq. (29) will be invalid. It is far from certain that this condition will be met in general even for Eq. (25) in dielectrics in which the rotating molecules are of about the same size as those in which they are embedded.

d. Before going on to a review of the solutions of Eqs. (17), (25), and (29) in terms of more usual electrical quantities, it is well to mention three significant facts. First, the same differential equation may be obtained with the present "chemical kinetic" point of view for dipole relaxation as is obtained with the older "rotatory Brownian motion" point of view. Therefore, no judgment between them is possible on the basis of the phenomenology of dielectric behavior. Second, only rather special kinds of kinetics will lead to the simple form of Eqs. (17), (25), and (29). In general, we can go no further than Eqs. (6) and (10). It is possible that this accounts for some of the discrepancies which exist between the results of the following section and experiments on the frequency dependence of dielectric loss and dielectric constant. Third, the discussion has been carried out with reference to the rotation of individual dipoles; actually there is no point in the presentation which requires us to restrict ourselves to relaxation processes involving only single molecules; the treatment will be just as valid if we wish to speak in terms of the net dipole moment of a larger region which may actually be involved in the unit molecular process of relaxation in many cases.[15]

B. Solution of the Relaxation Equation for Static and Oscillating Fields

The relaxation equation in the form in which we have it in Eqs. (17), (25), and (29) can be very readily manipulated to give the relaxation and dispersion properties of real dielectrics, and in this way we may gain a clearer physical insight into these properties than is possible with the more usual methods of derivation.

First suppose that for $t<0$ there is a constant external field E acting on a specimen of the dielectric, and that at $t=0$ this field is removed. Then for $t>0$ we have the differential equation

$$dP_\mu/dt = -\mathbf{k}_0(P_\mu - N_0\alpha_\mu F), \tag{30}$$

where we now write P_μ to signify that we mean only that part of the polarization which is contributed by the dipoles. If we assume the Lorentz field, $F=E+4\pi P_T/3$, to be acting, since $E=0$ and $P_T=P_\mu+P_{el}$ (where P_{el} is the portion of the polarization contributed by the distortion of the electronic orbits by the field, given by $P_{el}=N_0\alpha_{el}F$, and P_T is the total dielectric polarization), we find

$$\begin{aligned} F &= \frac{4\pi}{3}(P_\mu + N_0\alpha_{el}F) \\ &= \frac{4\pi}{3}P_\mu/(1-4\pi N_0\alpha_{el}/3). \end{aligned} \tag{31}$$

Now $4\pi N_0\alpha_{el}/3 = (\epsilon_0-1)/(\epsilon_0+2)$, where ϵ_0 is the dielectric constant measured at frequencies much greater than the relaxation rate, while $(4\pi N_0/3)(\alpha_{el}+\alpha_\mu) = (\epsilon_s-1)/(\epsilon_s+2)$, where ϵ_s is the statically measured dielectric constant to which the dipoles contribute their full share.[16] Thus we find that

$$F = \frac{4\pi}{3}\left(\frac{\epsilon_0+2}{3}\right)P_\mu, \tag{32}$$

and

$$\begin{aligned} dP_\mu/dt &= -\mathbf{k}_0\left[1 - \frac{4\pi N_0}{3}\alpha_\mu\frac{\epsilon_0+2}{3}\right]P_\mu \\ &= -\mathbf{k}_0\left(\frac{\epsilon_0+2}{\epsilon_s+2}\right)P_\mu = -\mathbf{k}_0'P_\mu, \end{aligned} \tag{33}$$

so that the rate of relaxation of the *dielectric* should be *decreased* by the factor $(\epsilon_0+2)/(\epsilon_s+2)$ under the jump rate for the *dipoles* in the absence of all fields, simply because of the tendency of the polarization already present to maintain itself. This is the same sort of behavior which leads to the prediction of a Curie point and ferro-electric behavior for strongly polar liquids when the Lorentz field is assumed. The latter prediction

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[15] Cf. Kirkwood's discussion of the dielectric constant of polar liquids and the role of association between molecules in determining the effective dipole moment, J. Chem. Phys. **7**, 911 (1939).

[16] These relations are derived in Debye, *Polar Molecules*, Chap. 1, and in many elementary texts.

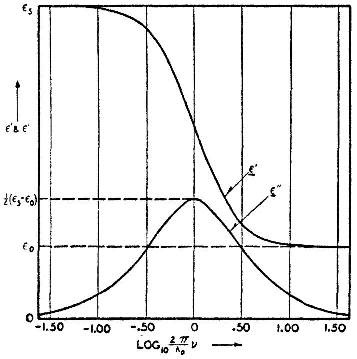

FIG. 2. Frequency dependence of the dielectric constant and loss factor according to Eqs. (37).

is, of course, not found to be verified because of the inadequacy of the Lorentz field for pure polar liquids;[17] nevertheless, such an effect of the internal field on the dielectric relaxation should always be present to some degree.

For the case in which the external field E is not zero it is easily seen that (again assuming the Lorentz field)

$$dP_\mu/dt = -\mathbf{k}_0'\left[P_\mu - N_0\alpha_\mu\left(\frac{\epsilon_s+2}{3}\right)E\right]. \tag{34}$$

When E is periodic with a frequency ν, $E = R[E_0 e^{2\pi i\nu t}]$, where $R[\ ]$ means that we are to take the real part of the expression in the brackets; when the transients in the dielectric have died out, we can assume that P_μ is periodic with the same frequency as E, $P_\mu = R[P_{0\mu}e^{2\pi i\nu t}]$. Substituting in Eq. (34), it is found that

$$P_{0\mu} = \frac{N_0\alpha_\mu}{1+2\pi i\nu/\mathbf{k}_0'}\left(\frac{\epsilon_s+2}{3}\right)E_0. \tag{35}$$

If we regard $[(\epsilon_s+2)/3]E_0$ as the total field acting inside the dielectric, then $\alpha_\mu/(1+2\pi i\nu/\mathbf{k}_0')$ performs the function of the contribution to the polarizability due to dipole orientation, in agreement with the well-known rule of Debye. To obtain the total polarization in terms of E_0 we must add $P_{0el} = N_0\alpha_{el}F_0$ to (35).

$$P_{0T} = P_{0\mu} + P_{0el} = \frac{N_0\alpha_\mu}{1+2\pi i\nu/\mathbf{k}_0'}\left(\frac{\epsilon_s+2}{3}\right) \times E_0 + \alpha_{el}\left(E_0 + \frac{4\pi}{3}P_{0T}\right). \tag{36}$$

It is a simple matter to solve this for P_{0T} in terms of E_0. And since we know that $4\pi P_{0T} = (\epsilon-1)E_0$, we have a relation for the dielectric constant ϵ in terms of the frequency. ϵ is evidently complex, showing that P and E are out of phase. If we write $\epsilon = \epsilon' - i\epsilon''$, we find very easily that

$$\epsilon' = \frac{\epsilon_s - \epsilon_0}{1+x^2} + \epsilon_0 \tag{37a}$$

and

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_0)x}{1+x^2}, \tag{37b}$$

where

$$x = 2\pi\nu/\mathbf{k}_0' = 2\pi\frac{\nu}{\mathbf{k}_0}\left(\frac{\epsilon_0+2}{\epsilon_s+2}\right), \tag{37c}$$

which are the familiar dispersion equations, whose form is given in Fig. 2, and which are well known to give a fairly close (but rarely precise) description of dispersion effects in dielectrics.

The relationship of ϵ' and ϵ'' to the quantities usually used in describing dielectric behavior is as follows: ϵ' is the *dielectric constant* as it is usually measured. ϵ'' is usually called the *loss factor*. The ratio ϵ''/ϵ' is frequently called the *dissipation factor*. The angle δ defined by $\tan\delta = \epsilon''/\epsilon'$ is known as the *loss angle*, while its complement, $\theta = 90° - \delta$, is the *phase angle*. The quantity $\sin\delta = \cos\theta$ is the *power factor*. For small values of ϵ''/ϵ', the power factor, loss angle and dissipation factor are for all practical purposes equal.

C. Physical Nature of Energy Losses in Dielectrics

For convenience, suppose that $F = E$ and

$$dP/dt = -\mathbf{k}_0(P - N_0\alpha E). \tag{38}$$

Now the rate of dissipation of energy per unit volume is given by Ei, where i is the current density in the medium. It is easily seen that when the polarization of a dielectric is changing there is flowing an effective current $i = dP/dt$. Thus the polarization current flowing in a dielectric at any time is given by the relaxation rate multiplied by the difference between the actual polarization and the equilibrium value corresponding to the applied field at the moment; this makes possible a very simple formulation of the physical nature of the losses at high frequencies.

Suppose that E is a very high frequency field

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[17] J. H. Van Vleck, J. Chem. Phys. 5, 556 (1937).

with $\nu \gg \mathbf{k}_0$, so that at no time does the polarization have a chance to build up appreciably. Then $P \cong 0$ and $dP/dt \cong \mathbf{k}_0 N_0 \alpha E$ and the average power loss is at the rate of $\mathbf{k}_0 N_0 \alpha \langle E^2 \rangle_{\text{Av}}$ per unit time or $\mathbf{k}_0 N_0 \alpha \langle E^2 \rangle_{\text{Av}}/\nu$ per cycle. This behavior is identical with that of a conductor having a specific conductivity of $\mathbf{k}_0 N_0 \alpha$ reciprocal ohms. Physically it arises from the fact that if a dipole be regarded as a positive and a negative ion separated by a fixed distance, we cannot detect the fact that the ions are bound to one another unless we use fields which oscillate so slowly that the ions can move a distance greater than that separating them during a single oscillation (i.e., fields with periods greater than the time required on the average for one complete rotation). It is as if in an ionic solution we were to connect each pair of oppositely charged ions with a long thread; the solution would act as an ohmic conductor only as long as the field was reversed before the ions could move roughly the distance corresponding to the lengths of one of the threads.

At low frequencies ($\nu \ll \mathbf{k}_0$) the physical nature of the loss is less obvious. Here P lags slightly behind E. If P is broken up into two parts, one part in phase with E, and the other out of phase by $\pi/2$, it is readily found that the in-phase part of P is given by $N_0 \alpha E(1 - 4\pi^2\nu^2/\mathbf{k}_0^2)$. (The out-of-phase part of P in Eq. (38) will, of course, contribute nothing to the polarization current which will result in the dissipation of energy as heat.) Substituting this in Eq. (38) to obtain the energy dissipating "current," we find that

$$dP/dt \cong 4\pi^2 \alpha \nu^2 E/\mathbf{k}_0$$

and the average energy dissipated per unit time is $(4\pi^2 N_0 \alpha \nu^2/\mathbf{k}_0)\langle E^2 \rangle_{\text{Av}}$, while the energy lost as heat per cycle is $(4\pi^2 N_0 \alpha \nu/\mathbf{k}_0)\langle E^2 \rangle_{\text{Av}}$.

Thus we see that if we plot the energy loss per cycle against the frequency, we get a direct proportionality at low frequencies and a hyperbolic relationship at high frequencies, with a maximum in between. Since the energy loss per cycle is also given by $\epsilon \langle E^2 \rangle_{\text{Av}}$, the form of this energy loss curve should be similar to the ϵ'' curve given in Fig. 3; by the above arguments, therefore, we see the physical reason for the familiar symmetrical ϵ'' *vs.* log ν plot of Fig. 2.

The actual conversion of electrical energy into heat in a dielectric may be regarded in the Debye Brownian motion treatment as the result of the viscous resistance offered by the medium to dipole rotation. In the chemical kinetic theory the conversion results from the transformation of the potential energy of the misaligned dipole into kinetic energy when the dipole jumps toward the field direction. This last is the same in principle as the conversion of chemical energy into heat during an ordinary chemical reaction. Since viscous flow in condensed phases is probably most readily interpreted in terms of reaction rate theory, the ultimate dissipation mechanism in the two theories is really essentially the same.

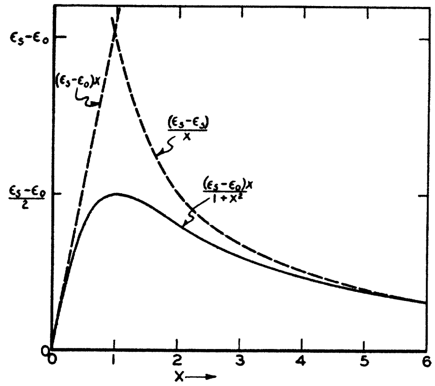

FIG. 3. Linear and inverse dependence of the loss factor on the frequency.

A class of dielectrics exists in which the energy losses per cycle are independent of the frequency over wide ranges of frequency. These clearly have the important property that the energy dissipated per unit time increases with the frequency, so that they may be expected to tend to lose their usefulness at high frequencies. Glass, hard rubber, polystyrene, and non-polar materials in general act in this manner, though these losses are apparently to be found as a background in polar materials as well.

Such behavior is clearly very different from that deduced above although it might be explained if a uniform logarithmic distribution of relaxation rates—see Section IIA below—were assumed to exist. Bäz[18] found that for polystyrene ("trolitul") the power factor changes only from about 5×10^{-4} to about 7×10^{-4} when the frequency is changed by a factor of 10^4, and hard rubber, porcelain, and phenol-formaldehyde-paper pulp ("pertinax") showed about the same small relative change in power factor with a frequency change of 10^5. That a uniform logarithmic distribution of relaxation rates should exist over such a wide range seems hardly plausible.

Such losses may well arise from dimensional changes of the dielectric due to electrostriction, with consequent rubbing over electrode surfaces, etc., with which the dielec-

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[18] G. Bäz, Physik. Zeits. **40**, 394 (1939).

tric is in contact while subject to an oscillating field. If the frictional force between the dielectric and the electrode were independent of the velocity (as is characteristic of solid-solid interfaces), the same amount of work would be expended in a single cycle of a given amplitude no matter what its frequency. Also, the electrostriction varies as the square of the field, as does the total energy stored, so the power factor (which is the ratio of losses per cycle to energy stored) would be independent of the amplitude, as is observed. A calculation on the basis of this picture shows, however, that power factors of only the order of magnitude of 10^{-8} are possible from this source acting alone. Inhomogeneities in the dielectric, such as microscopic cracks, might give rise to similar effects many times as great if there were enough of them. In any case the phenomenon of frequency-independent power factors probably arises from something more nearly like ordinary friction or certain types of plastic flow, where dissipative forces are essentially velocity independent, rather than from forces similar to those arising from fluid viscosity such as are the subject of this paper. In this connection, it seems likely that a comparison of the behavior of the damping capacity for mechanical vibrations with this frequency-independent dielectric loss factor in various substances would shed some light on the origin of both of these little understood phenomena.

D. Discussion of Debye's Molecular Model for Dielectric Losses

In Sections A3*b* and *c*, above, using three essentially different assumptions, we have reduced the relaxation equation, Eq. (6), to the simple form from which dispersion effects are obtained more or less in agreement with the actual observations. Previously the method of Debye has been used almost exclusively in interpreting the results of dispersion experiments, partly because it was for long the only one available, and partly because it gives such a clear and sometimes quantitatively satisfactory physical picture of what the relaxation process is. Because of this wide use, it has been thought desirable here to devote some space to a criticism of this treatment (and similar treatments) when applied to condensed phases in which the rotating dipolar molecules are of about the same size as the molecules of the surrounding medium. It is to be emphasized, however, that the use which is made of this theory in the investigation of the sizes and shapes of large, rigid molecules, such as cellulose derivatives and proteins, in low molecular weight solvents is not seriously affected by these arguments insofar as the molecules *are* large and rigid.

A. The most obvious objection to the development is in its use of Stokes' law for rotating spheres, Eqs. (28a) and (28b), in giving the torque resisting rotation. This relation is derived hydrodynamically assuming stream-line motion in the surrounding fluid and using as one boundary condition that the layer of liquid in contact with the surface of the sphere moves about with the same velocity as the sphere. For this latter condition to be met by a molecule surrounded by others of about the same size would mean that the effective radius of the "sphere" would have to be multiplied by three. If on the other hand we are willing to allow for a certain amount of slippage between the two, we must decide just how much slip to allow, and this is indeterminate without further information. There is certainly no reason to believe that the slip would be just sufficient to give the same effect as a sphere in a homogeneous fluid.

If this criticism is to be admitted, then the entire picture of stream-line flow here becomes questionable. Thus the most that can be said for this assumption is that it might (and apparently sometimes does) give the correct order of magnitude for the relaxation rate. Discrepancies between observed viscosities and those calculated from the known molecular radii and the observed relaxation rate by means of Eq. (29), or discrepancies equivalently stated, should not be taken too seriously, and the relationship between viscosity and the dielectric relaxation must be regarded as somewhat less direct, at least, than is implied in Eq. (29).

B. As we learn more about the structure of liquids, the picture of a dipolar molecule as a sphere or other solid body immersed in a homogeneous viscous fluid which shows stream-line motion becomes less and less pleasing, even as a crude approximation. Thus we know today that in the immediate neighborhood of a molecule in a liquid the molecular arrangement approaches that found in a crystal; this is especially true of polar liquids, but is also true of non-polar liquids.

Debye and Ramm[19] have used the picture of restricted molecular rotation in condensed phases in order to improve the agreement of Eq. (29) with the observed relaxation times for certain pure polar liquids. They assume that, because of

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[19] P. Debye and W. Ramm, Ann. d. Physik **28**, 28 (1937).

the quasi-crystalline structure, a molecule is subject to an angular energy dependence, given by $-E\sin\theta$, in addition to that arising from the external field, where θ is the angle between the dipole and a slowly changing direction of stability for the dipole which is determined by the structure of the surrounding medium, and $2E$ is the height of the energy barrier preventing rotation. E is known from other applications[20] of the theory to have values up to $10kT$ at around room temperature. If this is to be accepted as a valid description of the environment of a molecule, it becomes exceedingly difficult to understand why the macroscopically observed viscosity, let alone any viscosity whatsoever, can still be accepted as useful in describing the relaxation process. The attempt to improve the agreement with experiment in this way seems only to undermine further our faith in what is started out to support, and makes even more questionable the picture of stream-line flow in the description of the molecular process involved in dielectric relaxation.

C. In introducing the viscosity in the way that it does, this theory throws much of the burden of the task of formulating a molecular theory of dielectric relaxation upon those who seek to explain liquid viscosity on the basis of a molecular theory. A truly molecular theory has thus been only half achieved. Actually the problem of viscous flow is probably considerably more complex than that of the mere rotation of a molecule, particularly when the latter can be so readily pictured in terms of the much more thoroughly understood unimolecular reaction rates. We would, therefore, be much more justified in calling upon the dielectric relaxation to help us in formulating a molecular theory of viscosity than we are in attempting the reverse.

The most fruitful attitude in this connection would probably be to maintain that when there *is* a correlation between the viscosity and the relaxation, the molecular motions involved in each must be similar. When these motions are understood, we will understand both phenomena. And if the correlation between the viscosity and the relaxation is not so direct, as is sometimes the case, we may conclude that the molecular motions involved are not quite similar and proceed to investigate the reason why.

This criticism is even more justified when the dispersion of solids and polymers is interpreted in terms of the Stokes' law relation for the relaxation time. The concept of an "internal viscosity" must be invented if we are to proceed on the assumption that the same type of process is involved here as in liquids. The difficulty which one has in picturing the real physical nature of this internal viscosity makes it very questionable if anything useful has been accomplished in this way.

D. In the process of deriving the relaxation equation from the standpoint of ordinary Brownian motions it was pointed out that the treatment is valid only if after several jumps the dipole has moved through but a small angle (that the molecule must move by jumps being clearly indicated by the exponential dependence of the relaxation rate on the temperature, and whether this dependence comes in through the viscosity or otherwise being of no consequence here). It will become evident in Part II of this paper that in the majority of cases of dielectric relaxation which have been studied experimentally, there is reason for strongly suspecting the validity of such an assumption in general.

E. In Section IIC3*a*, below, it will be shown that the Debye relation for the relaxation time neglects certain effects analogous to those appearing in the Debye-Hückel theory of ionic conductance. In polar liquids these effects should be very considerable and are such as to make the agreement of the Debye relation for the relaxation rate with experiment even poorer than is usually found for such liquids.

E. Factors Determining the Transition Probabilities

In Eqs. (37) we have at least an approximate description of the dispersion phenomena of dielectrics in terms of molecular dynamics described by the transition probabilities $\mathbf{k}_0$. It has been suggested that we focus our attention on this quantity rather than on Debye's relaxation time, $\tau=4\pi\eta a^3/kT$, which we have seen is based on assumptions unsuited for use in studying ordinary dielectrics.

Little has been said of the factors which deter-

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[20] P. Debye, Chem. Rev. **19**, 171 (1936); Physik. Zeits. **36**, 100, 193 (1935).

mine the magnitudes of these $\mathbf{k}_0$'s, other than to say that their large temperature coefficients indicate that they almost certainly depend upon thermal activation similar to that required in many chemical reactions. This last fact led Eyring to point out that the relaxation rate may be regarded as equivalent to a chemical rate constant for a unimolecular reaction and as such that it should be amenable to the same sort of interpretation as are such reactions. In the next sections such an interpretation will be applied to available dielectric data, but in order to make this more intelligible to the reader who is not familiar with the mode of reasoning employed in interpreting chemical rate constants, it is probably well to present at this point a brief resumé of this field. More complete details, with applications to chemistry, will be found elsewhere.[21]

For chemical reactions taking place in gases the most obvious procedure to be used in calculating the reaction rate would start from the kinetic theory of gases. For bi-molecular reactions, i.e., reactions in which two molecules react with one another (as in $H_2+I_2\rightarrow 2HI$), the total number of collisions per second Z is easily calculated; the large temperature coefficients for the rates of such chemical reactions indicate that of these Z collisions only those involving more than a certain amount of energy E will result in reaction, this fraction being given roughly by $e^{-E/kT}$. Then $Ze^{-E/kT}$ should give the reaction rate at any temperature T. Actually rates are found to be somewhat smaller than those calculated in this way—usually by from 1/10 to 1/1000—a result which is ascribed to a further requirement that only for those collisions in which molecules are favorably oriented will there be a reaction. Unimolecular reactions in gases (i.e., reactions whose rate is independent of concentration of reactant) presumably result when the slow process in the reaction is not the occurrence of sufficiently energetic collisions, but the localization of the energy at the point in the molecule at which the reaction is supposed to take place.

This simple procedure loses its usefulness when it is applied to reactions in condensed phases in which the reaction involves the activation of groups of molecules—as is likely to be the case with dielectric relaxation. The difficulties of determining the effective collision frequency and of enumerating the relative numbers of ways, favorable to reaction, in which the activation energy can be distributed in the group here become very difficult. Fortunately, another approach to the problem is available in the absolute rate theory of Eyring,[22] which we shall now outline.

When a system, say one made up of two atoms of hydrogen and two of iodine, goes from one state of equilibrium (say H_2+I_2) to another (say $HI+HI$), there will be some point along the easiest and hence most usual path of reaction at which the system will have a maximum of potential energy—corresponding to the "activation energy." If we describe the configurations of the system in terms of suitable coordinates, it will be possible to choose one coordinate—the *reaction coordinate*—motion along which will correspond to motion along this easiest path of reaction. Plotting the potential energy against the value of this coordinate we will in general obtain a curve similar to that shown in Fig. 4. Now owing to our choice of coordinates, at any point along the reaction path the system is in a state of minimum potential energy with respect to all coordinates save the reaction coordinate. But analysis of our notion of what is ordinarily meant by the term *stable molecule* shows that we may define a stable molecule as a complex of atoms in a local potential energy minimum with respect to motions along the internal coordinates of the complex; applying this to our present example we see, therefore, that at any point along the reaction path we may regard our system as a molecule in all respects save its behavior along this single reaction coordinate. In particular, all configurations in the neighborhood of the energy maximum along the reaction path may in this sense be regarded as corresponding to a molecule, which is usually called an *activated complex*. Centering our attention on this "molecule," it is easy to see that the rate of formation of one stable system (say $HI+HI$) from another

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[21] C. Hinshelwood, *Kinetics of Chemical Change* (Oxford, 1940); R. Fowler and E. Guggenheim, *Statistical Thermodynamics* (Macmillan, 1939); S. Glasstone, K. Laidler, and H. Eyring, *Theory of Rate Processes* (McGraw-Hill, 1941).

[22] H. Eyring, J. Chem. Phys. 3, 107 (1935).

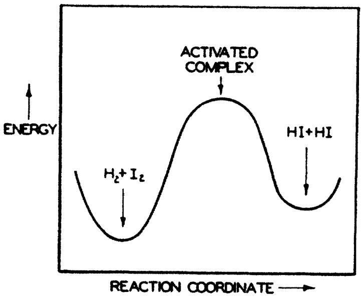

FIG. 4. Schematic diagram of the course of a chemical reaction.

(say H_2+I_2) is given by

$$\text{Number of molecules reacting in unit time} = \kappa N^* z, \qquad (39)$$

where N^* is the number of activated complexes present, z is the rate at which each decomposes in the proper direction (i.e., the inverse of the mean life of an activated complex), and κ is the fraction (usually very close to unity) of those complexes which, having started decomposing in the right direction, actually end up as two hydrogen iodide molecules rather than somehow getting turned around and going back to their initial state of H_2+I_2. The so-called ***absolute rate theory*** consists in formulating an expression for these various quantities in terms of the potential energy function of the system as a whole. Since the latter can in principle always be determined from the fundamental laws of motion of elementary particles, we have here a method for calculating rates of reaction from first principles —whence the adjective "absolute."[23]

The number N^* of activated complexes present in an actual ensemble is calculated by assuming that these are in thermodynamic equilibrium with the reactants. There will then be an equilibrium constant K whose value will be given by the ratio of the partition function F^* of the activated state of those, F_i, of the reacting molecules; the number of activated complexes can in turn be found from the numbers of reactant molecules multiplied into the constant K.

$$K = F^*/\pi_i F_i. \qquad (40)$$

It may be objected that this assumption of thermodynamic equilibrium is a very serious one; actually it probably is not. As long as molecules are activated and deactivated frequently compared with the rate at which they react once activated, this assumption will be satisfied. In unimolecular reactions, such as we are concerned with here, this condition breaks down only in gases at low pressures (that is, where energy interchanges between molecules are rare)—quite the opposite of what we shall be dealing with.[24]

The partition function F^* above contains in it a factor dependent upon motion along the reaction coordinate. If we regard this coordinate as a translational degree of freedom in the neighborhood of the activated complex, this factor will be given by $(2\pi m^* kT)^{\frac{1}{2}} l/h$, where m^* is the inertial mass corresponding to motion along this coordinate, l is the linear dimension along this coordinate of the region included by the activated complex, and k, T, and h are Boltzmann's constant, the absolute temperature, and Planck's constant. In addition, the mean velocity along this coordinate in one direction is

$$\bar{v} = (kT/2\pi m^*)^{\frac{1}{2}} \qquad (41)$$

and the mean rate of passage through the activated state is

$$z = \bar{v}/l = (kT/2\pi m^*)^{\frac{1}{2}}/l. \qquad (42)$$

If we restrict ourselves to unimolecular reactions, the equilibrium constant K can be written, as a simple ratio $F^*/F_0 = (2\pi m^* kT)^{\frac{1}{2}}(l/h) F\ddagger_0/F_0$, where $F\ddagger_0$ is a new partition function including only those motions of the activated complex which typify its molecule-like aspect (i.e., which omits the contribution due to the incongruous reaction coordinate). Collecting the factors and expressing the rate of reaction as the mean rate of reaction of a molecule [which is the unit in which **k** of Eq. (6) is expressed], we get for the

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[23] It should be noted, however, that the method is actually an approximate one in the sense that, from what we know of quantum mechanics, the above formulation is inconsistent: we have specified both a configuration and an internal velocity of the activated complex, and we know from the Heisenberg uncertainty principle that such a specification is limited. But it can be shown that for particles as heavy as ordinary molecules moving over potential energy surfaces of the sort that are likely to be encountered in most reactions, the error thus introduced is not serious, particularly when we are interested only in determining orders of magnitude, as will be the case in our present applications to dielectric relaxation. Indeed, it is not difficult to show that even in the very unfavorable case of reactions involving hydrogen atoms alone (e.g., reactions of the type $H_2+D_2 \rightarrow 2HD$), errors of something less than factors of two are introduced into the expression for the reaction rate by this assumption. We shall usually be interested in much larger molecular weights and not be worried by uncertainties as small as this.

[24] This point is lucidly discussed in Chapter 12 of Fowler and Guggenheim, *Statistical Thermodynamics*.

reaction rate

$$\mathbf{k}=\kappa K z=\kappa(kT/h)(F\ddagger_0/F_0). \tag{43}$$

Since $F\ddagger_0$ and F_0 can be calculated from the potential energy function of the system, and κ can usually be estimated sufficiently accurately (for our purposes, it can always be taken as unity), this is a satisfactory expression for the reaction rate. It is more convenient, however, to throw the factor $F\ddagger_0/F_0$ into another form. $F\ddagger_0/F_0$ is itself a sort of equilibrium constant, and thermodynamics tells us that equilibrium constants for reactions can be written in terms of the free energies or of the entropies and energies of the reaction as follows:

$$\begin{aligned} K=F\ddagger_0/F_0&=e^{-\Delta F\ddagger/RT}\\ &=e^{\Delta S\ddagger/R}e^{-\Delta E\ddagger/RT}, \end{aligned} \tag{44}$$

where $\Delta F\ddagger$, $\Delta S\ddagger$, and $\Delta E\ddagger$ are the molar free energy, entropy, and energy increases required to convert one mole of the normal state into one mole of the activated state, disregarding, however, the contributions to these quantities by the motions along the coordinate of reaction in the activated state. ($\Delta E\ddagger$ is thus essentially the activation energy of which we have been speaking previously in this paper.)

Then we can write the reaction rate as

$$\begin{aligned} \mathbf{k}&=\kappa\frac{kT}{h}e^{\Delta S\ddagger/R}e^{-\Delta E\ddagger/RT}\\ &=\kappa\frac{kT}{h}e^{-\Delta F\ddagger/RT}. \end{aligned} \tag{45}$$

The quantities $\Delta S\ddagger$ and $\Delta E\ddagger$ may be evaluated from experimental data by obvious methods (see below, Section IIB).

The value of this formulation of reaction rates is that if we know something of the thermodynamics of the normal state, we can, from it and from the observed reaction rate constants, learn something of the thermodynamics of the activated state. Since thermodynamics, through statistical mechanics, is related to the properties of molecules, this in turn tells us something of the molecular nature of the activated complex, which is equivalent to understanding the molecular dynamics of the rate process in question.

II. COMPARISON OF THE THEORY WITH EXPERIMENT

A. The Existence of Distributions of Relaxation Rates

1. *Evidence for Distributions of Relaxation Rates*

Equations (17), (31), (37a), and (37b) should suffice for a complete description of the dielectric behavior of a medium with respect to temperature, density, and frequency of applied fields, in terms of molecular properties, since α_{el} and α_μ can be calculated from the number of molecules per unit volume, the dipole moment, the temperature, and the average polarizability of a molecule, while $\mathbf{k}_0'$ can be found from the molecular relaxation rate $\mathbf{k}_0$. Actually, however, this is never found to be the case; dielectric properties are well known not to vary with frequency, density, and temperature as predicted here in anything like a satisfactory manner from a quantitative standpoint. Qualitatively, however, the agreement is definitely as predicted, showing that the general approach first used by Debye is correct, and that the discrepancies involve only matters of detail.

Much of the discrepancy in the static properties (i.e., for $dP/dt=0$) probably arises from the error of assuming that the Lorentz field is valid for condensed media. The relationship between $\mathbf{k}_0'$ and $\mathbf{k}_0$, the relaxation rates of the dielectric and of the individual uncoupled molecules, is also affected by this. That the general form of the frequency dependence of the loss factor, ϵ'', should not be changed much by this factor, however, is shown by the work of Cole;[25] the frequency of the maximum loss factor is shifted about for the different kinds of reasonable internal fields, but otherwise the shape of the dispersion curve remains nearly the same. Yet it is in just this latter respect that the loss factors often deviate most markedly from predictions: according to Eq. (37a) and more obviously from Fig. 2, the dielectric constant should have dropped effectively to its high frequency value ϵ_0, when the frequency has changed from that at the maximum of absorption by a factor of about 10. The frequency change actually required is usually several times as great as this, a typical example being given in Fig. 5, for

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[25] R. Cole, J. Chem. Phys. 6, 385 (1938).

vulcanized rubber, where the factor is about 300. For polyvinyl chloride polymers[26] it can under some conditions become so great that only about half of the entire change between ϵ_s and ϵ_0 can be measured on an ordinary bridge going from 60 cycles to 10,000 cycles, showing that the frequency must be changed by a factor of something like 5,000,000 in order to bring about an amount of change equivalent to that which would be predicted from Eq. (37a) to occur in the change by a factor of 10.

This discrepancy can be expressed in other ways. Thus, Cole and Cole[27] have pointed out that according to Eqs. (37a) and (37b), a plot of ϵ' *vs.* ϵ'' for different frequencies at a given temperature should give an arc of a circle, as shown in Fig. 5 for vulcanized rubber, with the center of the circle falling on the ϵ' axis. They have shown that while circular arcs are usually obtained with real dielectrics, the centers actually fall considerably below the ϵ' axis, a measure of the extent of the discrepancy being given by them as the angle $\alpha\pi/2$ in the figure. They have also shown that simple equivalent forms of Eqs. (37) can be written introducing α as a parameter. This result of the Coles is very probably a consequence of the same factor which causes the other discrepancy noted above.

A third and equivalent way of expressing the magnitude of this discrepancy is to compare the magnitude of the maximum loss factor, $\epsilon''_{\max}$, with that predicted by Eq. (37b). Since the maximum occurs at such a frequency that $x=1$, we have

$$\epsilon''_{\max}=\tfrac{1}{2}(\epsilon_s-\epsilon_0) \qquad (46)$$

for the value of the predicted maximum. Observed loss factors rarely ever become this great; the ratio R of the observed maximum to that calculated from Eq. (4b) will then be a very convenient measure of the deviation of the behavior of a dielectric from that given by the simple theory. Values of R may vary from 20 percent or less to nearly 100 percent. For vulcanized rubber in Fig. 5, $R=45.6$ percent.

It will be well to emphasize at this point, however, the significant fact that in spite of frequently large discrepancies of these more or less equivalent types, a plot of the energy loss per cycle, or its equivalent ϵ'', against the logarithm of the frequency is almost always found to be very nearly symmetrical about a central value of $\log\nu$; the symmetrical bell-shape of the loss curve of Fig. 2 is thus usually maintained for real dielectrics even though its maximum value is reduced below the theoretical one.

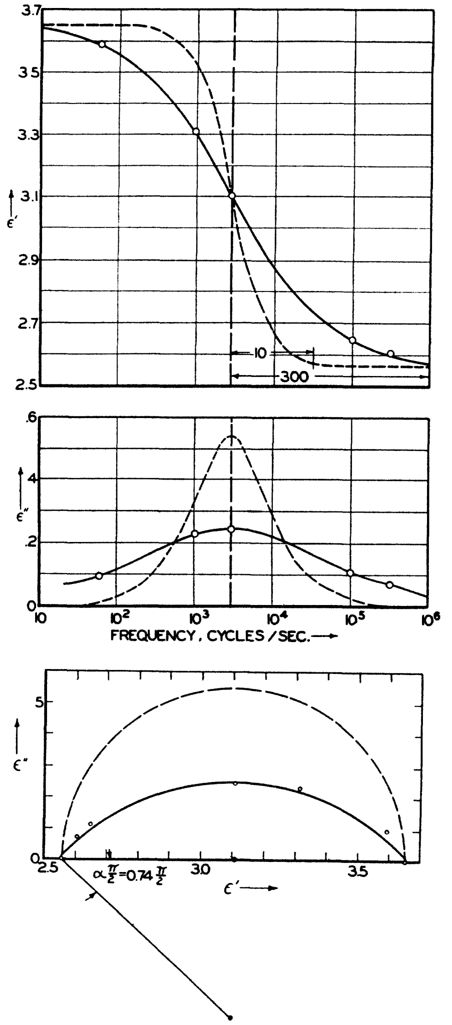

FIG. 5. Dielectric behavior at 0°C of rubber vulcanized with 8 percent sulphur. Dotted curves calculated from Eqs. (37) with $\epsilon_s=3.65$, $\epsilon_0=2.56$, $\log_{10} k_0'/2\pi=3.48$. (Data from reference 11, Table III.) Upper curve, dependence of dielectric constant on frequency. Middle curve, dependence of loss factor on frequency. Lower curve, plot of loss factor against dielectric constant as suggested by Cole and Cole.

2. *Probable Origin of the Distribution*

We must now inquire, what in the theoretical development might give rise to these observed

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[26] R. M. Fuoss, J. Am. Chem. Soc. 63, 378 (1941).

[27] R. Cole and K. Cole, J. Chem. Phys. 9, 341 (1941).

discrepancies. As already noted, Eqs. (17), (25), and (29) result only when certain simplifying assumptions are applied to the more general Eq. (6), so that Eqs. (37), which result from the former, may not always be correct. This may result in some change in the frequency dependence of the loss factors, but it does not seem likely that such drastic deviations as those found, for instance, in polyvinyl chloride, can be expected from this source.[28]

There seems to be no other way out of the difficulty than to accept the long recognized[29] possibility that in our relaxation equations, as they apply to many substances, at least, there is not one single relaxation rate constant $\mathbf{k}_0$, but a distribution of these constants about a mean value. This distribution tends to spread out the frequency range over which the dispersion effects take place; the range of the distribution is roughly of the same order of magnitude as the observed frequency range ratio in which the dispersion takes place is to the calculated range ratio of about 10, as shown above. Thus, in the case of the polyvinyl chloride cited above, the relaxation rates vary by a factor of roughly 5,000,000/10, or about 500,000, on either side of the observed maximum. This is an unusually large value for such a factor, but values of ten to one hundred are very common in other substances. For vulcanized rubber in Fig. 5, a value of about thirty is found (=300/10).

Such frequently very large factors lead us to ask what, after all, can be the significance of the rate "constant" $\mathbf{k}_0$ if it is subject to so large a variation. A little closer examination of the problem, however, shows not only that such factors are very easily understandable, but that it is also possible to explain the symmetry of the dispersion effects in the logarithm of the frequency on the basis of the concepts already outlined: if we were able to get a close look at the molecules in a liquid or a solid which shows dielectric dispersion, we would find that due to thermal fluctuations the conditions in the neighborhood of all molecules at any given moment are not at all identical. In particular, the energy of activation or, even more generally, the free energy of activation required for rotating the molecules into new positions of equilibrium would very probably be found to vary about a certain mean value in going from one molecule to another at any given time. In other words, there should be a distribution of free energies of activation $\Delta F\ddagger$ in Eq. (45). From the nature of thermal fluctuations, it is reasonable to suppose that this distribution will be more or less symmetrical about the mean value. This means that the distribution of the relaxation rates themselves will be symmetrical only when expressed in terms of the logarithms of the relaxation rates, since the rates depend exponentially on the free energy. This in turn means that the loss factor ϵ'' will be symmetrical in the logarithm of the frequency, which is just what is so frequently observed to be true.

If we were to use the Debye treatment to explain this result, we would conclude that the uncertainty in the relaxation rate must come from an uncertainty in the viscosity of the medium surrounding the rotating dipole, the viscosity in turn being variable due to a similar variability in the exponential energy factor which is now well known[30] to play a dominant role in the viscosity of liquids.

That large changes in the relaxation rate can result from reasonably small values of the uncertainty in the activation energy is easily shown: thus an uncertainty of only double kT, the mean thermal energy, will result in a variation of the relaxation rate by a factor of more than seven. Considerably larger variations of the free energy of activation than this are easily imaginable.

If this interpretation is correct, we may ask why the same effect is not observed in the kinetics of ordinary chemical reactions, for instance, because similar causes for distributions of activation energies must often operate there, especially in condensed phases. And since the factors involved are usually so large, they should surely have the effect of making it impossible for ordinary chemical rate expressions to account for the observed course in time of chemical reactions, at least in condensed phases. If, for instance, the rate of a unimolecular reaction in

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[28] In Section II C4 a more quantitative attempt will be made to assign to this source a part of the discrepancy found for the particular cases of the methyl chlorobenzenes.

[29] E. von Schweidler, Ann. d. Physik **24**, 711 (1907).

[30] J. Frenkel, Zeits. f. Physik **35**, 652 (1926); Trans. Faraday Soc. **33**, 58 (1937); E. Andrade, Phil. Mag. **17**, 497, 698 (1934); H. Eyring, reference 8.

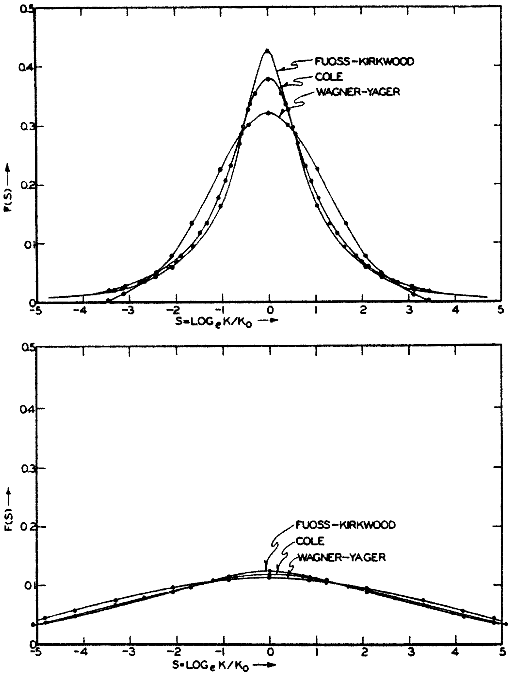

Fig. 6. Distributions of relaxation rates given by various empirical functions. a. (lower) Corresponding to $R=\epsilon''_{\max\,\mathrm{obs}}/\frac{1}{2}(\epsilon_s-\epsilon_0)=0.333$. b. (upper) Corresponding to $R=0.667$.

solution is indefinite by a factor of ten (and such factors of distribution are commonplace in dielectric relaxation), the final stages of the reaction should appear to have a rate constant ten times smaller than that found for the beginning of the reaction. Such effects are not, however, known to occur.

The resolution of this problem involves the relative magnitudes of the rates at which the molecules respectively rotate or react and the rates of migration from one molecule to another of the thermal fluctuations leading to the variations in the activation energy. If the rates of migration are of the same order as or smaller than the rotation or reaction rates, as we can easily expect them to be for dielectric relaxation,[31] the medium could as well be considered as more or less frozen into whatever configuration it might have at any given time as far as the effect on the kinetics of relaxation is concerned, and there will be a distribution of relaxation rates. On the other hand, if the process we are measuring goes on over a period of seconds or minutes, as with nearly all measurable chemical reactions in condensed phases, while the fluctuations leading to the distribution change many times a second, the *time average* of the activation energy alone will govern the reaction rate, and there will be only one rate constant.

This fact leads to the rather interesting and significant conclusion that *by means of a study of dielectric properties in alternating fields we may gain information concerning some kinetic aspects of the structure of matter which few other properties are capable of uncovering in so direct a form.* The ordinary chemical kinetic properties, while they should show such a distribution effect in the very first stages of reaction, cannot be measured rapidly enough, while the viscosity or d.c.-conductance, which undoubtedly involve movements of molecules rapid enough to show such an effect, can by their nature furnish only average rates and not distributions.

The derivation of the dielectric properties by assuming the distribution of relaxation times has been carried out by Kirkwood and Fuoss,[32] who have also shown how to obtain the distribution function from observed data. The reader is referred to this paper for the details.

3. *The Form of the Distribution Function*

So far in the literature four different distribution functions for relaxation rates have been utilized. These can be and usually are given in terms of the logarithm of the relaxation rate, in which three of them are symmetrical about a certain maximum value.

Wagner[33] and Yager[34] have shown that some data, at any rate, can be duplicated if we assume a Gauss-error distribution:

$$f(s)=\frac{b}{\sqrt{\pi}}\exp(-b^2s^2), \tag{47}$$

where $s=\ln \mathbf{k}/\mathbf{k}_0$, $\mathbf{k}_0$ is the most probable relaxation rate, and b is a constant which determines the breadth of the distribution. $f(s)ds$, of course, is the probability of finding a relaxation rate $\mathbf{k}$, the logarithm of whose ratio to $\mathbf{k}_0$ lies between s and $s+ds$.

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[31] This is true because the two phenomena very probably involve similar types of molecular movements. This point will be discussed in a forthcoming paper.

[32] R. Fuoss and J. Kirkwood, J. Am. Chem. Soc. **63**, 385 (1941).

[33] K. W. Wagner, Ann. d. Physik **40**, 817 (1913); Archiv f. Elektrotechnik **3**, 83 (1914).

[34] W. A. Yager, Physics **7**, 434 (1936).

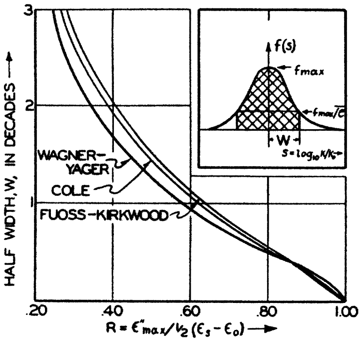

FIG. 7. Equivalent breadths of various distribution functions.

Fuoss and Kirkwood (reference 32), applying their method of determining the distribution from the observed dispersion to an empirical relation for the loss curve which they find holds for certain polymers, obtain as the logarithmic distribution function

$$f(s)=\frac{\alpha}{\pi}\frac{\cos\frac{1}{2}\alpha\pi\cosh\alpha s}{\cos^2\frac{1}{2}\alpha\pi+\sinh^2\alpha s}. \tag{48}$$

The Coles' arc function (i.e., the circular arc illustrated in Fig. 5) arises when we have the distribution

$$f(s)=\frac{1}{2\pi}\frac{\sin\beta\pi}{\cosh\beta s+\cos\beta\pi}. \tag{49}$$

Kirkwood and Fuoss[35] have obtained theoretically for an isolated long chain molecule executing free rotations about the bonds within itself

$$f(s)=e^{-s}/(e^{-s}+1)^2. \tag{50}$$

This is not quite symmetrical about $s=0$, but gives a loss curve which is so nearly symmetrical as to be effectively so within ordinary experimental limits.

When the parameters in the three empirical distributions, Eqs. (47), (48), and (49), are adjusted so as to give the best possible fit for any particular set of data, it is found that the resulting distributions are rather closely similar. This is evident from Fig. 6, where the distributions which result in ratios R of observed to calculated loss maxima, $\epsilon''_{\max\ \mathrm{obs}}/\frac{1}{2}(\epsilon_s-\epsilon_0)$, of $66\frac{2}{3}$ percent and $33\frac{1}{3}$ percent are plotted. It is also evident from Fig. 7, where the half-widths of the distribution functions at the points at which they have fallen to $1/e$th of their maximum values have been plotted against the corresponding values of R.

B. Summary of Observed Data on Dielectric Relaxation Rates

In Tables I, II, and III are given the values of various quantities derived from observed relaxation rates, these quantities having significance in terms of the development of the previous sections. The procedure used in analyzing the observed data was as follows.

The *dielectric* relaxation rate $\mathbf{k}_0'$ was taken as 2π times the frequency giving the maximum loss factor at each temperature. For ice and the monohydroxy alcohols, the Lorentz field correction, $(\epsilon_0+2)/(\epsilon_s+2)$, was applied to this value of $\mathbf{k}_0'$ to obtain the *molecular* relaxation rate $\mathbf{k}_0$; this undoubtedly overcompensates for the internal field effect. In all other cases it was assumed that $\mathbf{k}_0'=\mathbf{k}_0$, which will be sufficiently accurate for our purposes.

Some assumption must be made concerning the change in direction which results on the average from a single jump in order to evaluate the jump rate from the relaxation rate. Here it has been assumed throughout that the molecular relaxation rate is equal to the molecular jump rate, which means that the point of view of Sections IA3*a* and *b* has been utilized—i.e., that jumps into all new directions are equally probable, regardless of the size of the jump. This has the effect of making the tabulated entropies of activation minimum possible values.[36] These minimum values are already usually significantly large; since the more important conclusions of this part of the paper are based upon the largeness of these values, this assumption is not serious. Indeed, we shall see that the very fact that the entropies are large offers strong support for this assumption.

The activation energies $\Delta E\ddagger$ were found by plotting the Briggsian logarithm of the observed molecular jump rate against the inverse of the absolute temperature. If σ be the slope of this curve (usually a straight line), the activation

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[35] J. Kirkwood and R. Fuoss, J. Chem. Phys. 9, 329 (1941).

[36] Thus, comparing Eqs. (25) and (17), we see that if each jump results in a root mean square change of direction of 1°, the jump rate would be of the order of $2\times180^2/\pi^2$, or about 6600 times greater than the relaxation rate of the dielectric, and $\Delta S\ddagger$ would be about 17 entropy units *larger* than that given.

energy is given by

$$\Delta E\ddagger = 2.303R\sigma - RT; \quad (51)$$

the variation with the temperature of the factor kT/h in Eq. (45) has thus been neglected, but this is insignificant in practically all cases. (The extra term of RT in Eq. (57) arises from the absence of one degree of freedom in $F\ddagger_0$ of Eq. (43).)

The entropy of activation is found from the activation energy and the jump rate $\mathbf{k}_{0T}$ at any given temperature T by

$$\Delta S\ddagger = 2.303R\left(\log_{10}\mathbf{k}_{0T} - \log_{10}\frac{kT}{h} + \sigma/T\right) - R. \quad (52)$$

A method of evaluating the activation energy different from that used here has been utilized by Fuoss[37] and by Davies, Miller, and Busse.[38] These authors have supposed that [as is suggested by the form of Eq. (37b)] the value of x in the expression $\epsilon'' = 2\epsilon''_{\max}x/(1+x^2)$ is at any given frequency and at different temperatures proportional to the relaxation time. Thus from the values of ϵ'' as a function of the temperature at constant frequency the temperature variation of the relaxation rate can be determined and the activation energy obtained. A comparison of the results of this method with the results of the method used here, however, shows that the two are not in agreement. Thus for pure polyvinyl chloride we find an activation energy of 116,000 cal. per mole from the temperature effect on the maximum loss frequency, while Davies, Miller, and Busse get 40,000 cal. per mole—obviously a very serious difference. Also, it is found that the calculated activation energy depends on the frequency which is used in obtaining the ϵ'' *vs.* temperature curve. The explanation of this difference is to be found in the distribution of relaxation rates; owing to the distribution, which is very broad for pure polyvinyl chloride (and which in addition changes considerably with the temperature, see Fig. 8), ϵ'' changes much more slowly as frequencies diverge from that corresponding to the relaxation rate of the dielectric than would be supposed from the dispersion equation for a single relaxation rate. Therefore, the activation energy appears to be much smaller than it actually is, and it is likely that more reliable values can be obtained from the frequency maxima. Frank[9] has also given various methods of obtaining activation energies from loss data, but the method used in this paper is, as he agrees, probably the most reliable.

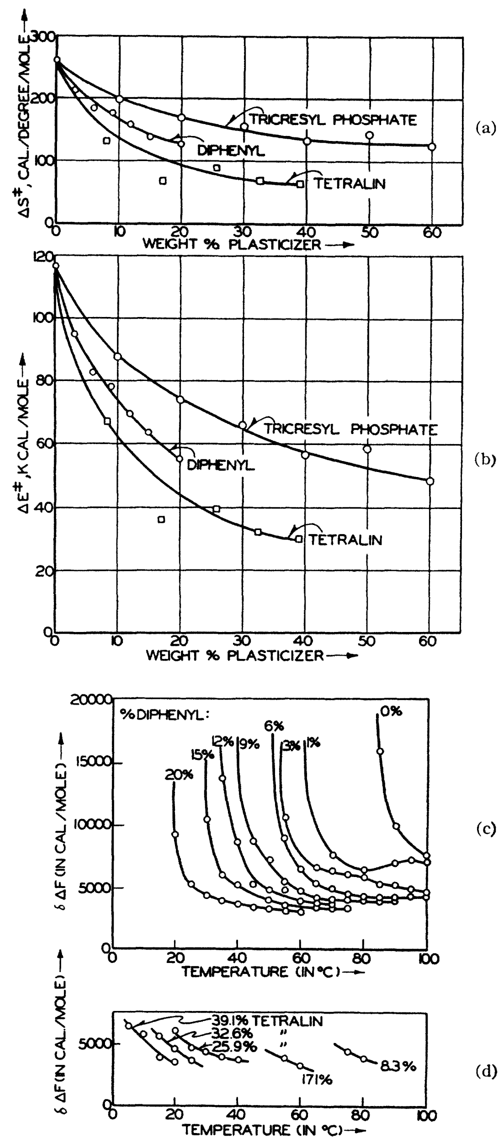

FIG. 8. Dielectric properties of polyvinyl chloride and their dependence on plasticizer concentration. a. (top) Activation entropies of polyvinyl chloride with various plasticizers. (Data from references 6, 7, and 8 of Table III.) b. (upper center) Activation energies of polyvinyl chloride with various plasticizers. (Data from references 6, 7, and 8 of Table III.) c. (lower center) Effect of temperature and concentration of diphenyl on the breadth of the distribution of free energies of activation for polyvinyl chloride. (Data from reference 32.) d. (bottom) Same for tetraline on polyvinyl chloride. (Data from reference 6 of Table III.)

An additional quantity which should be of interest in investigating the mechanism of dielectric relaxation is $\delta\Delta F\ddagger$, the range of distribution of the free energies of activation for relaxation on either side of the average free energy of activation. In attempting to estimate the magnitude of this range, some decision must be made as to the nature of the distribution function which is to be used in describing the

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[37] See reference 4, Table III.

[38] See reference 8, Table III.

rate distribution. Fortunately, as we have seen, any of the three empirical distribution functions mentioned previously, when so adjusted as to yield a given ratio R of observed to calculated maximum loss factors, furnishes very similar distributions.

In the actual calculation of the values of $\delta\Delta F\ddagger$ for Tables I, II, and III, the Wagner-Yager function, Eq. (47), was assumed. The theoretical value of the maximum loss factor at a given temperature was calculated from the relation $\epsilon''_{\max}=\frac{1}{2}(\epsilon_s-\epsilon_0)$, using observed or extrapolated values of ϵ_s and ϵ_0 at each particular temperature. In Fig. 7 is a plot of the ratios of observed to theoretical loss maxima against the half-width W of the corresponding Wagner-Yager distribution function when this function has fallen to $1/e$th of its maxima value, or equivalently stated, the half-width within which 84.3 percent of the relaxation rates are to be found, assuming this distribution. These half-widths being given in the figure as Briggsian

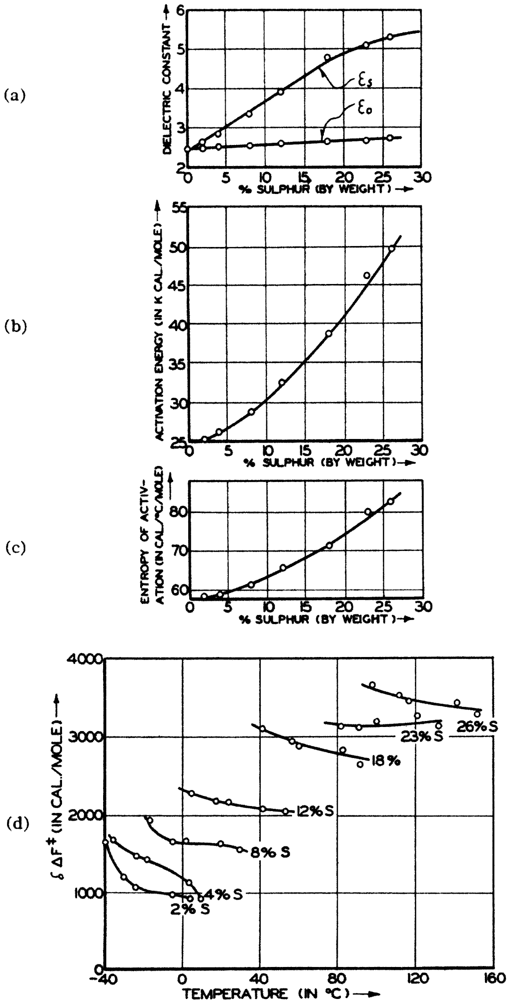

FIG. 9. Dielectric properties of vulcanized rubber as a function of sulphur concentration. (Data from reference 11 of Table III.) a. (upper) Static dielectric constant at 50°C. b. Energies of activation for relaxation. c. (center) Entropies of activation for relaxation. d. (lower) Distribution of free energies of activation.

TABLE I. Quantities governing the dielectric relaxation of solids.

Solid	Ref.	$\Delta E\ddagger$ kcal./mole	$\Delta S\ddagger$ cal./°C/mole	$\delta\Delta F\ddagger$ cal./mole
Ice	1	9.3	0	—
	2	14.6	17	100–600
	3	12.2	13	<100
Chlor pentamethyl benzene	4	7.7	0	500–710
1,2-dichlortetramethyl benzene	4	7.8	2	750
1,2,4-trichlortrimethyl benzene	4	8.9	3	600
1,2,3-trichlortrimethyl benzene	4	9.1	5	470–800
1,2-dimethyltetrachlor benzene	4	9.1	0	500
1,3-dimethyltetrachlor benzene	4	8.3	−2	500
Methyl pentachlor benzene	4	11.1	3	600
Equimol. solid solution of methylpentachlor benzene and 1,2-dichlortetramethyl benzene	4	9.1	2	800
$C_6H_5-CO-C_6H_5$	5	45.0	103	—
Alpha-terpineol	6	42.3	160	1450
d,1-camphor	7	10.0	14	1550
Cyclopentanol	8	8.5	2	400
d,1-bornyl bromide	8	11.4	26	2000
3,*x*-dichlor-*d*,1-camphor	8	34.7	123	800–1000
3-nitro-*d*,1-camphor	8	27.4	91	900
Halowax (solid solution of di-, tri-, and tetrachlor naphthalenes)	9	16.0	38	(1100–2400?)
Dry paper	10	9.6	7	—
Solid solutions in paraffin wax:				
Paraffin heated to 100°C for 10 days	11	30.2	61	—
Cetyl palmitate in paraffin	11	28.6	68	(400)
Amyl stearate in parafin	12	16.6	31	—
Butyl stearate in paraffin				
spec. I	13	17.6	40	
spec. II	13	15.5	35	—
spec. III	13	15.0	22	
Cetyl palmitate in paraffin	13	16.0	23	—
Octyl palmitate in paraffin	13	16.7	30	—
Ethyl stearate in paraffin	13	15.2	32	—

[1] H. Wintsch, Helv. Phys. Acta **5**, 126 (1932).
[2] E. J. Murphy, Trans. Am. Electrochem. Soc. **65**, 133 (1934).
[3] C. P. Smyth and C. S. Hitchcock, J. Am. Chem. Soc. **54**, 4631 (1932).
[4] A. H. White, B. S. Biggs, and S. O. Morgan, J. Am. Chem. Soc. **62**, 16 (1940).
[5] C. E. Sun and J. Williams, Trans. Am. Electrochem. Soc. **65**, 129 (1934).
[6] S. O. Morgan, Ind. Eng. Chem. **30**, 277 (1938).
[7] W. Yager and S. O. Morgan, J. Am. Chem. Soc. **57**, 2075 (1935).
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[9] W. Yager, Conf. on Elect. Insul., Nat. Res. Council (1937), p. 12.
[10] G. T. Kohman, Ind. Eng. Chem. **31**, 807 (1939).
[11] W. Jackson, Proc. Roy. Soc. **150**, 197 (1935).
[12] D. R. Pelmore and E. L. Simons, Proc. Roy. Soc. **175**, 253 (1940).
[13] R. W. Sillars, Proc. Roy. Soc. **169**, 66 (1938).

TABLE II. Quantities governing the dielectric relaxation of liquids.

Liquid	Ref.	$\Delta E\ddagger$ kcal./mole	$\Delta S\ddagger$ cal./°C/ mole	$\delta\Delta F\ddagger$ cal./mole
Nitrobenzene in Shell oil BL3	1	5.8	9	—
Transformer oil	2	16.8	26	nearly 0
Ethyl alcohol	3	4.7	6	—
Propyl alcohol	4	5.0	5	<300?
Propyl alcohol	5	4.0	1	—
Propyl alcohol	6	8.0	15	—
Propyl alcohol	3	9.4	20	—
Propyl alcohol (supercooled)	7	14.6	63	—
n-Butyl alcohol	6	6.1	7	—
n-Butyl alcohol	3	7.5	13	—
Isobutyl alcohol (supercooled)	7	18.2	75	—
n-Amyl alcohol	5	5.7	5	—
n-Amyl alcohol	6	6.1	7	—
Isobutyl bromide (supercooled)	8	22.7	156	300
Isoamyl bromide (supercooled)	8	15.8	84	150–300
Isobutyl chloride (supercooled)	8a	19.0	139	350
1,2-dichloro-isobutane (supercooled)	8a	23.2	136	500
Glycerol (supercooled)	4,9	32.5 23.0 21.2 15.6 12.4	106 at −60° 60 at −50° 53 at −20° 31½ at 0° 20 at 10°	~600
Propylene glycol (supercooled)	10	20.0	66	1500
Trimethylene glycol (supercooled)	10	13.0	32	1150
2-methyl pentandiol 2,4	10	24.0	71	1200
83% methyl pentandiol in dioxane	10	24.0	72	1200
Glucose (supercooled)	11	78.0	192	—
Chlorinated diphenyl (4 Cl's per mole)	12	53.8	150	500–1000
Chlorinated diphenyl				
No. 1-mobile oil	13	47.3	136	700
No. 2-viscous oil		49.4	123	800
No. 3-sticky resin		55.4	128	850
No. 4-brittle resin		63.0	133	1200
Abietic acid	9	50.4	103	2500
Ethyl abietate	9	37.7	109	1500–2000
Phenolphthalein (supercooled)	7	137.0	310	(~1500)

logarithms, they must be multiplied by $2.303RT$ to give the $\delta\Delta F\ddagger$ of Tables I, II, and III, which is thus the range of variation of the free energies of activation on either side of the average free energy of activation, within which the free energies of activation of a major part (about 84.3 percent) of all the relaxing molecules are to be found.

In Figs. 8 and 9 are given the variations of $\Delta E\ddagger$, $\Delta S\ddagger$, and $\delta\Delta F\ddagger$ with composition for polyvinyl chloride with various plasticizers and for rubber vulcanized with different amounts of sulphur.

C. Interpretation of the Observed Data on Relaxation Rates in Terms of Molecular Processes

1. *Relationship between Viscosity, Direct Current Conductance, and Relaxation*

In Fig. 10 are plotted logarithmically the relaxation rates at different temperatures against the viscosities at the same temperatures for a number of pure substances for which such data are available. It is apparent from the nearly unit slopes usually obtained that there is a fairly close relationship between the two. This signifies that the molecular motions involved in the two phenomena are, for the substances shown in the figure (with the possible exception of supercooled glucose), closely similar.

According to the Debye relation, $1/\mathbf{k}_0' \cong \tau = 4\pi a^3\eta/kT$, the intercepts of these lines at, say, $\log \eta = 0$ should show some dependence on the volume of the rotating dipole (the temperature T having nearly the same value for all substances under the conditions of measurement used here).

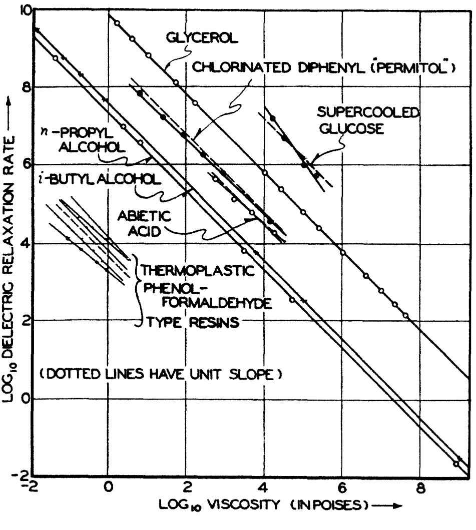

FIG. 10. Relationship between viscosity and dielectric relaxation. [Data on glycerol, *i*-butyl alcohol, and *n*-propyl alcohol from P. Kobeko, E. Kuvshinski, and N. Shishkin, Tech. Phys. U.S.S.R. **6**, 413 (1938). Viscosity of glucose from G. S. Parks, L. E. Barton, M. E. Spaght, and J. W. Richardson, Physics **5**, 198 (1934). Viscosity of abietic acid from G. S. Parks, M. E. Spaght, and L. E. Barton, Ind. Eng. Chem. Anal. Ed. **7**, 115 (1935). Other data, see Tables II and III.]

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[1] F. H. Müller, Ann. d. Physik **24**, 99 (1935).
[2] H. H. Race, Phys. Rev. **37**, 430 (1931).
[3] W. Hackel, Physik. Zeits. **38**, 195 (1937).
[4] S. Mizushima, Physik. Zeits. **28**, 418 (1927).
[5] W. Ziegler, Physik. Zeits. **35**, 476 (1934).
[6] E. Keutner, Ann. d. Physik **27**, 29 (1936).
[7] E. Kuvshinsky and P. Kobeko, Tech. Phys. U.S.S.R. **5**, 401 (1938).
[8] W. O. Baker and C. P. Smyth, J. Chem. Phys. **7**, 574 (1939); J. Am. Chem. Soc. **61**, 2063 (1939).
[8a] A. Turkevich and C. P. Smyth, J. Am. Chem. Soc. **64**, 737 (1942). These authors have found that at higher temperatures the observed loss factor maxima become considerably *larger* than $\frac{1}{2}(\epsilon_s - \epsilon_0)$—a very remarkable result, which deserves further investigation. An apparently similar result reported by Baker and Smyth, reference 8, seems, however, to be due to an arithmetical error.
[9] S. O. Morgan and W. Yager, Ind. Eng. Chem. **32**, 1523 (1940).
[10] A. H. White and S. O. Morgan, Physics **2**, 312 (1932).
[11] B. Thomas, J. Phys. Chem. **35**, 2103 (1931).
[12] W. Jackson, Proc. Roy. Soc. **153**, 158 (1935).
[13] A. H. White and S. O. Morgan, J. Frank. Inst. **216**, 635 (1933).

If the rotating unit is to be identified with the molecule (as is certainly reasonable), no such relationship is very evident from the figure. Although the large resin molecules as a group have the smallest intercepts (corresponding to the largest radii[39]), the relationships for other molecules bear no apparent relationship to expected molecular dimensions. Indeed, the apparent volume for normal propyl alcohol (molecular weight 60), the smallest molecule for which data are shown, is 16 times *greater* than that for abietic acid (molecular weight 302), 20 times *greater* than that for Jackson's chlorinated diphenyl (which has about 4 chlorine atoms per molecule, or a molecular weight of about 300), 300 times *greater* than that of glycerol (molecular weight 92), and nearly 10,000 times *greater* than that of supercooled glucose (molecular weight 180). It is once again difficult to avoid the conclusion that the Debye-Stokes' law theory of relaxation is unsuitable for the interpretation of data of this kind.

A similar plot is made in Fig. 11 for solutions of nitrobenzene in various hydrocarbons. The dotted lines give the relationships which would be expected for radii of 3.0A and 1.2A, the former being more nearly what one would expect for the nitrobenzene molecule, though it is in poorer agreement with the results. In order of magnitude, however, the agreement is about all one can expect for the low molecular weight solvents, though the theory obviously fails badly even in a qualitative sense for the solutions in the heavier "Shell oil BL3."

A comparison is made in Table IV between the activation energies for direct current (probably ionic) conductance and those for dielectric relaxation in several polymers measured by Fuoss. It is apparent that there must be a considerable difference between the molecular processes involved here, and that any concept of an "internal viscosity," such as it would be natural to apply here, must be a very vague one, with little real physical meaning. It should be mentioned, however, that Kobeko, Kuvshinski,

TABLE III. Quantities governing the dielectric relaxation of polymers.

Polymer	Ref.	$\Delta E^{\ddagger}$ kcal./mole	$\Delta S^{\ddagger}$ cal./°C/mole	$\delta\Delta F^{\ddagger}$ cal./mole
Phenol-formaldehyde	1	84.5	208	3800
m-cresol-formaldehyde		69.7	155	3500
m-5-cresol formaldehyde		73.8	164	3900
o-cresol formaldehyde		83.6	225	(2500)
p-cresol formaldehyde		69.7	173	3500
Benzyl alcohol formaldehyde		52.6	122	(1600)
Polytrimethylene succinate	2	26.3	64	—
Polytrimethylene malonate		22.1	52	—
Ethylene glycol phthalate	3	52.7	112	2000
80% polychlorstyrene 10% *o*-chlor diphenyl 10% *p*-chlor diphenyl	4	48.0	103	—
80% polystyrene, 20% *p*-chlor diphenyl	4	18.5	23	—
80% polyvinyl chloride of various molecular weights, 20% diphenyl	5	50.0	106 to 120	2300 to 3300
Polyvinyl chloride plus:				
8.3% tetralin	6	64.0	130	(4000)[a]
17.1% tetralin		36.0	70	(3500)
25.9% tetralin		39.8	90	(4000)
32.6% tetralin		32.0	68	(4500)
39.1% tetralin		30.0	64	(4500)
Polyvinyl chloride plus:				
0% diphenyl	7	120.0	300	7500–16000[b]
1% diphenyl		152.0	363	6500–7500
3% diphenyl		95.0	214	4700–10500
6% diphenyl		83.0	185	4400–9000
9% diphenyl		78.0	178	3800–14000
12% diphenyl		70.0	158	3700–14000
15% diphenyl		62.0	139	3300–11000
20% diphenyl		56.0	127	3000–9000
Polyvinyl chloride plus:				
0% tricresyl phosphate	8	116.0	263	3900
10% tricresyl phosphate		88.0	199	·
20% tricresyl phosphate		74.0	170	·
30% tricresyl phosphate		66.0	156	·
40% tricresyl phosphate		57.0	133	·
50% tricresyl phosphate		(59.0)	(154)	·
60% tricresyl phosphate		49.0	127	3200
Vinsol (mixtures of highly	9	59.0	115	4400
Petrex 5 polymerized		41.0	76	3000
Petrex abietic acid and terpenes)		43.0	101	1800
Rubber plus 10% sulfur	10	31.0	62	1800
Rubber plus:				
2% sulfur	11	25.2	58	900–1600[c]
4% sulfur		26.1	59	900–1600
8% sulfur		28.6	61	1600–1900
12% sulfur		32.3	66	2000–2300
18% sulfur		38.6	71	2600–3100
23% sulfur		46.0	80	3100–3200
26% sulfur		49.6	82	3200–3600
Polyvinyl acetate	12			
Gelva 60		57.3	122	1200
Gelva 15		[57.3][d]	123	1200
Polyvinyl chloracetate	12	57.3	122	1200

[a] See Fig. 8d.

[b] See Fig. 8c. These numbers are based upon the results of Fuoss and Kirkwood, ref. 32, Fig. 2, and may be somewhat in error owing to the uncertainty in the static dielectric constant, which was there evaluated by a rather long extrapolation of an empirical relation.

[c] See Fig. 9d.

[d] Assumed value.

[1] L. Hartshorn, N. Megson, and E. Rushton, J. Phys. Soc. London **52**, 796 (1940).

[2] D. R. Pelmore and E. L. Symons, Proc. Roy. Soc. **175**, 468 (1940).

[3] C. G. Garton, J. Inst. Elect. Eng. **85**, 625 (1939).

[4] R. M. Fuoss, J. Am. Chem. Soc. **63**, 377 (1941).

[5] R. M. Fuoss, J. Am. Chem. Soc. **63**, 2401 (1941).

[6] R. M. Fuoss, J. Am. Chem. Soc. **63**, 2410 (1941).

[7] R. M. Fuoss, J. Am. Chem. Soc. **63**, 378 (1941).

[8] J. M. Davies, R. F. Miller, and W. F. Busse, J. Am. Chem. Soc. **63**, 361 (1941).

[9] See reference 9, Table II.

[10] F. Müller, Kolloid Zeits. **77**, 260 (1936).

[11] A. H. Scott, A. T. McPherson, and H. L. Curtis, Bur. Stand. J. Research **11**, 173 (1933).

[12] D. Mead and R. M. Fuoss, J. Am. Chem. Soc. **63**, 2832 (1941).

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[39] In this connection it should be pointed out that the very small radii found by Hartshorn, Rushton, and Megson (see reference 1, Table III) for the phenol-formaldehyde thermoplastic resins are apparently the result of an error in calculation. They find values of around 1A for *a*, the dipole radius, and identify this with the radius of a hydroxyl group; values of around 100A seem to be more nearly in accord with their data, however.

TABLE IV. Activation energies for d.c. conductance and dielectric relaxation.

Substance	$\Delta E^{\ddagger}_{\text{relax}}$	$\Delta E^{\ddagger}_{\text{cond}}$
80% Polyvinyl chloride of various molecular weights with 20% diphenyl	50.0	40.0
Polyvinyl chloride with		
8.3% tetralin	63.5	24.8
17.7% tetralin	35.8	24.0
25.9% tetralin	39.8	24.2
32.6% tetralin	32.0	20.2
39.1% tetralin	30.0	18.1
Polyvinyl acetate		
Gelva 60	57.3	40.0
Gelva 15	[57.3]	31.0
Polyvinyl chloracetate	57.3	46.0

and Shushkin[40] found that log-log plots of viscosity against d.c. conductance give straight lines of unit slope for normal and isobutyl alcohols and glycerol.

Danforth[41] has found that the viscosity of glycerine increases with the pressure much more rapidly than does the relaxation rate.[42]

2. *Probable Significance of the Large Values of the Entropies of Activation*

In the tables given, one is struck by the frequent occurrence of very large positive entropies of activation. It may help in our formulation of a more physical feeling for just how large these values really are if it is pointed out that an increase in the entropy by 50 entropy units (which is an average value here) implies an increase in the number of configurations available to the molecule or molecules involved in an activated complex by a factor of $e^{50/2}=10^{11}$. Furthermore, most of the approximations which we have made in our treatment would tend to lead to an underestimation of this factor. Frank[9] and Baker and Smyth[11] have noticed similarly large entropy effects (or their equivalent) in the more limited number of compounds which they have examined; here we see that they are of wide occurrence indeed, so must be recognized as being one of the essential features determining the mechanism in general for the types of materials in Tables I–III.

It is obvious from the physical nature of entropy that some originally more or less rigid structure containing the dipole must become temporarily non-rigid in order that there can be a positive entropy of activation. Furthermore, when the values of this entropy are as large as they often are here, we know that the activation must involve more than merely a single molecule, or, in the case of the polymers, the few atoms making up the dipole and its immediate attachments.

Now from what we know of liquid and solid structure it is not difficult to see how this situation might come about. We know that even in a liquid the state of affairs in the immediate neighborhood of any single molecule is very probably almost the same as that in a crystal. This means that such requirements as the proper spatial packing of molecules, low energy mutual orientations of dipoles, and a maximum amount of intermolecular bonding (such as hydrogen bonds), when such bonds are possible, must be complied with in setting up any arrangement of a molecule among its neighbors which is expected to be stable. Keeping these prerequisites for a stable state in mind, suppose we attempt to go from one stable arrangement of a small region in a dielectric to another in the most rapid manner possible, utilizing only the thermal motions of molecules. It is clear that in general no new stable arrangement will result as far as the state of dielectric polarization is concerned if we attempt to reorient only a single molecule, since in that case no provision will have been made to adjust the molecule's surroundings to its new position. This will be particularly true of very irregularly shaped molecules and of molecules which make strong directional bonds with their neighbors. Therefore, the surroundings of a given molecule must move simultaneously with the molecule.

This might occur in two ways: (a) The various molecules involved may cooperate in their movements and rotate together in much the same manner as a set of interlocked gears is

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[40] P. Kobeko, E. Kuvshinski, and S. Shushkin, Tech. Phys. U.S.S.R. **6**, 413 (1938).

[41] W. Danforth, Phys. Rev. **38**, 1224 (1931).

[42] Attempts at correlating the relaxation rate with other mechanical properties have been made. Thus, Davies, Miller, and Busse (see reference 8, Table III) have obtained an "activation energy" by plotting the logarithm of Young's modulus for polyvinyl chloride—tricresyl phosphate against $1/T$. Now only the slope of a $1/T$ plot of the logarithm of something proportional to a rate can give an activation energy, just as only the slope of a $1/T$ plot of something proportional to an equilibrium constant can give a heat of reaction. The elastic modulus itself is not a rate, so that until a proportionality between it and some rate has at least been suggested, the significance of this type of plot must be questioned.

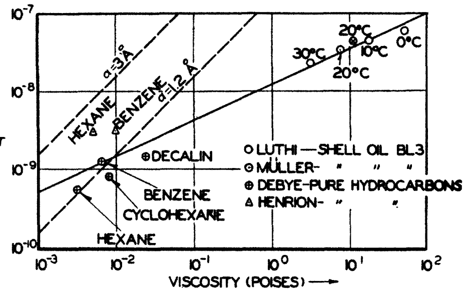

FIG. 11. Relaxation of nitrobenzene in various hydrocarbon solvents. [Data from H. Mueller, Erg. d. Exakten Naturwiss. **18**, 202 (1938). Dotted lines calculated from Eq. (29).]

caused to rotate when any one of the set is rotated; or (b) the molecules may momentarily completely disengage one another ("jump their gears") and reassume their stable configuration with their net dipole moment oriented in a new direction. Process (a) will presumably require relatively little energy, while (b) will require considerable energy. Since only a very special type of movement will be successful for the first mechanism, the entropy of the activated complex here will not be increased very much over that of the normal state, and might well be decreased. With mechanism (b), on the other hand, there will be a great increase of freedom in the activated complex, so giving a positive entropy of activation whose magnitude will be a measure of the extent of the momentary violation of the requirements for stability.

The data of Tables I–III rather clearly indicate that mechanism (b) is almost always the one which actually operates. This is found to be not too surprising when one attempts (using actual models) a more precise specification of the first mechanism for some real substances; it is soon realized that molecules will probably not behave in any way like gears, and that (b) is after all the most plausible mechanism available which can accord with observations.

3. *Interpretations and Calculations of the Actual Numerical Values of $\Delta E\ddagger$ and $\Delta S\ddagger$*

It is desirable to attempt some evaluation of the significance of the actual numerical values of $\Delta E\ddagger$ and $\Delta S\ddagger$ in terms of other quantities, in order that a somewhat more precise picture of the molecular movements in relaxation may be attained. This, of course, is not easy to accomplish, owing to the complexity of most of the substances listed in the tables; it is hoped, however, that the following considerations may suggest some rough lines of approach to this problem.

a. Possible role of electrostatic forces in determining relaxation rates for certain substances.—First let us assume that the only forces acting between molecules tending to orient them in definite directions relative to one another are simple electrostatic dipole-dipole forces. In this case, Onsager's description[43] of a polar liquid may be of considerable use. Onsager showed that if a molecule in a polar liquid be regarded as a dipole embedded in a simple solid body (say a sphere) which is immersed in a continuous dielectric having the dielectric constant of the liquid in question, then this molecule will polarize the surrounding medium in such a way as to give rise to what he calls a *reaction field* parallel to the dipole. Now when a dipole seeks a new orientation in space, it is necessary that its reaction field also reorient itself, or a stable arrangement will not result. Part of the reaction field is due to the electronic polarization of the surrounding molecules, and part is due to the orientation of neighboring dipoles. The readjustment of that part of the field due to the electronic polarization will present no difficulty since the dispersion frequencies for electronic polarization are much greater than the frequencies with which the molecules change their positions in a liquid. But the portion arising from dipole orientation obviously changes at about the same rate as the dipolar reorientation in question, so will introduce a definite factor in determining relaxation rates.

If Debye's model for dipole relaxation were accurate, this effect would have to be taken into account. The problem is very similar to that solved by Debye and Hückel[44] in deriving the square root relation for the dependence of ionic conductance in solutions on concentration of electrolyte, since here (as there) a partially oriented (charged) "atmosphere" of dipoles (ions) surrounding any given dipole (ion) gives rise to a field whose motion lags behind that of the dipole (ion) and tends to slow it down. This is the so-called *atmospheric relaxation effect;* the analogue of the *electrophoretic effect* in electro-

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[43] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

[44] P. Debye and E. Hückel, Physik. Zeits. **24**, 305 (1923).

lytic conduction would also appear here owing to the entrainment of fluid with the rotating dipoles surrounding the given dipole—which entrainment would also tend to retard the rotation of the given dipole. Both of these effects thus tend to make the observed relaxation time of a dielectric greater than that calculated for the Brownian rotation of a sphere in a homogeneous fluid, and this in turn tends to result in an overestimation of the apparent radii of the rotating molecules when the relationship, $\tau = 4\pi\eta a^3/kT$, is utilized. Radii as determined from this relation for polar liquids are usually already too small, however, so these effects merely make matters worse for the Debye-Stokes' law theory.

It having been previously shown that the molecular aspects of Debye's theory of dielectric dispersion are probably not very well suited to the study of most dielectrics, it does not seem advisable to pursue the above modification any further, although it might be interesting for its own sake, and also would be important in determining the concentration dependence of the relaxation times of large molecules in low molecular weight solvents; this is, however, as yet an unimportant phenomenon. Instead, we shall now follow an alternative method of approach more in line with the ideas developed in Section B.

The most direct way in which the reaction field could be adjusted to a new dipole orientation would be to annihilate it, allow the dipole to point in a new direction, and then reestablish the field for the new direction. If the readjustment of the reaction field (or more accurately, that part of it arising from dipole orientation) is the main factor in determining the reorientation of dipoles, it will then be possible to estimate the energy and entropy of activation for dielectric relaxation as follows.

From thermodynamics and electrostatics it can be shown that the free energy stored up in any region V due to an electric field E is

$$\Delta F_{el} = \frac{1}{8\pi}(\epsilon - 1)\int_V EE_0 dV, \tag{53}$$

while the entropy due to the field is

$$\Delta S_{el} = \frac{1}{8\pi}\frac{d\epsilon}{dT}\int_V E^2 dV, \tag{54}$$

where E_0 is the field due to the same arrangement of charges in a vacuum as gives rise to E. Using Onsager's field, $E = 3E_0/(2\epsilon+1)$, and Wyman's[45] empirical relationship, that $(\epsilon - 1) = \text{const.}/T$, we find that

$$\Delta S_{el} = \frac{3}{2\epsilon+1}\frac{\Delta F_{el}}{T}. \tag{55}$$

For ethyl alcohol, assuming that all of the free energy of activation arises in this way, so that $\Delta F_{el} = \Delta F\ddagger \cong 4700 - 6T$ cal., and taking $\epsilon = 25$, $T = 300°\text{K}$, we see that $\Delta S_{el} = \Delta S\ddagger \cong 1$ entropy unit, which is of the order of that observed. This treatment is, of course, rather approximate, since no effort has been made to separate the energy stored up as electronic polarization from that contributed by dipole orientation.

Formulae (53) and (54) tell us that the portion of the entropy of activation arising from the present source generally should be rather small. We may invert this remark into the surmise that when entropies of activation for dielectric relaxation are small, it is possible that dipole-dipole forces are the only significant ones which cause molecules to assume definite relative orientations. Small entropies of activation seem to be characteristic of polar liquids of low molecular weight at room temperature, so this method of attack might prove fruitful in analyzing the flood of data on such substances which should in better days follow the recent rapid development of ultra-short radio waves.

An actual calculation of the electrostatic energy stored up in the medium around a dipole, based on Onsager's expressions[43] for the potential about a dipole in a liquid and Eq. (53), shows that for various simple polar liquids (e.g., water, alcohol, acetone) the energy thus stored is indeed of the same order of magnitude as the observed free energies of activation for these types of liquids. The value of such a calculation as being more than a check on orders of magnitude is impaired, however, by the fact that it can be shown that the field around many simple dipoles is large enough to cause saturation effects to become pronounced in just that portion of the dielectric which contains the major fraction of the stored-up energy. A better, but equivalent, method of evaluating this energy might be to compare the heats of vaporization of a given polar molecule with that of a non-polar molecule of a similar

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[45] J. Wyman, J. Am. Chem. Soc. 58, 1482 (1936).

shape and size (e.g., acetone and isobutane)—which should give directly something close to the true amount of electrostatic energy stored up in the dielectric around each dipole, and which should therefore be comparable with the activation energy for relaxation insofar as this is the only important contribution to that energy.

That this electrostatic field energy is not always the dominant factor, in the relaxation process, however, is proven by the large limiting activation energy for vulcanized rubber as the amount of sulphur present is reduced to zero (see Fig. 9). Since the rubber hydrocarbon is itself non-polar, the activation energy here must arise from the operation of steric factors which also, as is reasonable, involve larger entropy effects. The same conclusion must also be reached from the data (see Table I) on solid solutions of polar molecules in non-polar paraffin wax.

b. Evaluation of the entropy of activation in terms of a vaporization process.—Let us now consider the values of the entropies of activation from another point of view. We might characterize the mechanism proposed in Section 2, above, by the statement that a change in the position of a molecule in a dielectric requires that the crystalline structure surrounding the molecule be momentarily "melted"; actually, however, the temporary local change is probably even more severe than that which occurs in the melting of a crystal, since in melting there remains at least a part of the original crystal structure, merely the long-range order of which has been destroyed. It would probably be more accurate to interpret the process as a "vaporization," since the status of a group of activated molecules may be said to approach that of a gas as far as forces tending to cause intermolecular orientation are concerned. If this is accepted as approximately true, it is possible to arrive at a rough estimate of the number of molecules involved in each process of activation for relaxation: from Trouton's rule, the entropy of vaporization per molecule is about 20–25 E.U. for most liquids at the boiling point. This gives us the entropy for vaporization to a gas at 1 atmosphere, while we wish the entropy for a gas having the density of the liquid or solid in question, so that from the Trouton entropy we must subtract $R \ln R'T/V_0$ where V_0 is the molal volume in the solid and R' is expressed in cc atmospheres. At about room temperature for a substance with a molecular weight of 100, this correction amounts to 10 E.U., giving us a net entropy change of 10–15 E.U. per molecule for the "vaporization" in question. By dividing this into the observed entropies given in Tables I and II for solids and liquids, we see that anywhere from zero to ten or more molecules may be "vaporized" in each activation process, the simpler molecules in general rotating with the least trouble to their neighbors. The crudity of this approach to the problem of evaluating the quantitative significance of the observed entropies[46] makes it unprofitable to go further with such a calculation at the present time, but it is quite apparent that these results, rough as they are, do not lead to an unreasonable picture of the relaxation process.

If the implications of these numbers are accepted, it is clear that the assumption made in calculating the quantities in Tables I–III (that the transition probabilities **k** of Section IA are independent of the size of a jump) must be very close to the truth, since very little memory of any former orientation should remain with a dipole which, along with a considerable number of its neighbors, has been "vaporized" in the sense outlined above.

Beside the large positive entropy of activation, there are other evidences that more than the single rotating molecule is frequently involved in the activation process. Thus when a polar plasticizer is added to a polymer, as when tricresyl phosphate is added to polyvinyl chloride,[33] the dispersion does not seem to show any tendency to occur over two separate frequency ranges, but the single loss maximum observed in the pure polymer merely shifts its position. The same behavior was found by Aleksandrov and Dzhian[47] for the loss maxima of rubber which had absorbed varying amounts of bromobenzene; the original peak in the rubber specimen became higher and moved continuously toward higher frequencies as the amount of bromobenzene increased, rather than a new peak typical of the bromobenzene appearing while the old peak decreased. This can be taken as evidence that when one dipole seeks to reorient itself, all of its neighbors, including molecules of all types making up the mixture, are affected. Another way of stating this is to say that because of the coupling between dipoles arising from various causes,

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[46] Some improvement would result here if for V_0 we employed the "free volume"; that is, the volume not actually occupied by the molecules, these being considered as hard spheres. This would make the number of molecules vaporized somewhat larger, though still of the order of tens of molecules.

[47] A. Aleksandrov and J. Dzhian, Rubber Chem. Tech. **14**, 877 (1941); Tech. Phys. U.S.S.R. **5**, 836 (1938).

it is no longer strictly correct to speak of the relaxation of single dipoles, but that we must consider larger regions. This agrees with the approach used by Kirkwood,[15] who shows that in pure polar liquids the molecular dipole moment must be corrected by a factor depending upon the average mutual orientations of neighboring molecules. Indeed, accepting Kirkwood's considerations it is difficult to see how one can escape the conclusion that the relaxation process in strongly polar media must frequently involve something approximating what we have suggested here.

4. *Relaxation in Solids*

a. General remarks.—From the relaxation behavior of dielectrics as well as from other evidence we may thus conclude that in liquids and solids there is coupling between each dipole and its surroundings. That is, if the orientation of any one dipole is fixed, the orientations of its neighbors are also fixed to a greater or lesser extent in the normal state. If we say that the coupling is strong we mean that the orientations of many neighbors are relatively severely fixed. If the coupling is very strong, the fixing of the direction of any one dipole may determine the directions of the dipoles in an entire crystal. In this case the dipoles in the crystal may either be so lined up with respect to each other that the net dipole moment of the crystal is zero—in which case the dielectric constant of the crystal will be close to the square of the optical index of refraction—or they may be lined up in such a way that there is a net dipole moment—in which case the crystal will be ferro-electric, as is Rochelle salt at room temperature. The onset of crystal-wide coupling with decreasing temperature gives rise to the widely observed transitions in solids at which the dielectric constant changes considerably;[48] typical examples are given in Fig. 12. The transition temperature is usually described as the temperature above which molecular *rotation* in the solid sets in. Actually, of course, the molecules in the solid need not be free to *rotate* in order to contribute to the polarization, but need only be capable of changing their *orientations* more or less independently of one another.[49]

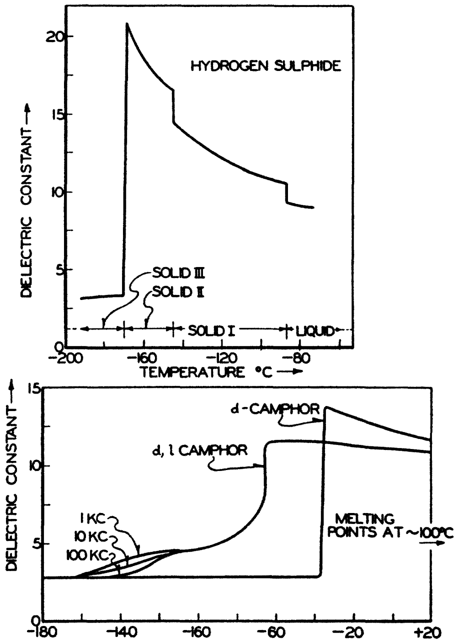

FIG. 12. Dielectric constants of some polar solids. [Data for hydrogen sulphide from C. P. Smyth and C. S. Hitchcock, J. Am. Chem. Soc. **56**, 1084 (1934); for the camphors, from reference 7, of Table I.]

Let us now see what we must expect in the light of these remarks when we attempt to change the state of polarization of a solid dielectric. For ferro-electric materials, which have very strong coupling, so that the dipoles of an entire crystal, or more probably of large regions of it (similar to ferromagnetic "domains"), have parallel components, the process of rotation of dipoles may depend on many factors, including such complex matters as internal stresses, and a change in the polarization may resemble the phenomena observed in the magnetization of ferromagnetic materials, where a similar state of affairs probably exists.[50] For these substances, therefore, the present method of attack requires supplementing, at least, by a consideration of these other factors which may be of importance.

When on the other hand the coupling is over a shorter range, the values of the entropies of activation probably give a very good idea of its relative extent for different solids. In Table I we see that this varies by a very considerable amount from one compound to another. Some compounds seem to show very little coupling—as the methyl chlorobenzenes and camphor; in general, it seems that these include the more highly symmetrical molecules. As side groups

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[48] C. P. Smyth, Chem. Rev. **19**, 329 (1936).

[49] A. H. White, J. Chem. Phys. **7**, 58 (1939). This is also evident from Eqs. (18) and (19).

[50] See, for example, H. Mueller, Ann. N. Y. Acad. Sci. **40**, 321 (1940), for hysteresis loops for Rochelle salt similar to those for magnetic materials.

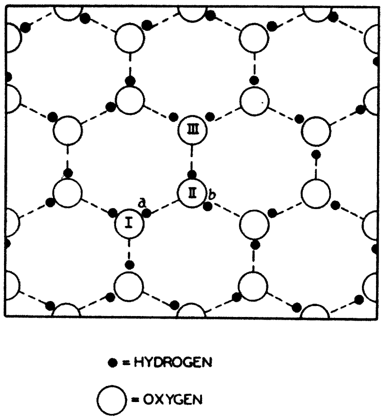

FIG. 13. Schematic diagram of the structure of ice.

become larger and shapes become more irregular, however, the neighborhood of a dipole appears to be much more extensively "vaporized" during a rotation, as one would expect.

It has been found by Yager and Morgan[51] and by White and Bishop[52] that the dielectric behavior of a pure solid optical isomer and that of the racemic compound with its mirror image are quite different for camphor (see Fig. 12) and for nitrocamphor. This indicates that mere questions of the sizes of groups and general molecular shapes must not be alone considered if we are to understand dielectric relaxation. The more complex question of how molecules pack together is also important.

For some polar solids there is a transition below which the dipoles' freedom of orientation is only gradually lost, so that the dielectric constant does not immediately drop to its optical value. This is apparently the case with racemic camphor, as is seen in Fig. 12. This substance also shows anomalous dispersion at low temperatures, the relaxation rates for which were analyzed for Table I. An interpretation of this type of behavior has been given by White.[49]

b. Dielectric relaxation of ice.—The mechanism of dipole orientation and relaxation in ice is very probably entirely different from that in other solids. It is possible that liquid water has essentially the same mechanism of relaxation, but more data are necessary before any decision can be made here.

It was pointed out by Huggins[53] that it is much more reasonable to expect that dipole orientation in ice occurs by means of movements of protons between two positions of equal minimum potential energy along a line between the two oxygen atoms with which each is coordinated rather than by the independent orientation of dipoles by simple molecular rotation. If we were to assume the latter, we would have great difficulty in accounting for the very open structure and low density which ice has, since molecules capable of independent rotation in this way would be expected to form a close-packed lattice.

This movement of protons is conditioned by the requirement that by far the greater fraction of the oxygen ions in the lattice must be directly bonded to but two protons at any one time. The method applied by Slater[54] to the calculation of the dielectric properties of KH_2PO_4 is well suited to the study of this problem, although the geometry of ice is slightly more complicated than that of KH_2PO_4; a rough application shows that Huggins' suggestion can indeed account for the order of magnitude of the observed dielectric constant of ice. Such being taken to be the case, the relaxation process in ice must be admitted to be quite different from that which occurs in other substances.

The most probable mechanism of changing the state of polarization of a piece of ice is one which is very similar to the chain reactions of chemistry; in Fig. 13 is given the projection of the arrangement of the atoms in a basal plane of an ice crystal (actually the plane is "puckered" and each oxygen atom is bonded through a hydrogen bond to a fourth oxygen atom alternately in the planes above and below that shown). A large number of arrangements of the hydrogen atoms between the oxygen atoms are possible, each arrangement giving a definite net dipole moment in any specified direction. Thus, in the presence of a field, certain arrangements are favored, and if the field is changed, there must be a change in these arrangements. One of the hydrogen ions will move from its one position of equilibrium to its other position of equilibrium (say hydrogen ion *a* moves from O I to O II). But this results in three hydrogen ions adjoining O II while only one is next to O I;

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[51] See reference 7, Table I.

[52] See reference 8, Table I.

[53] M. Huggins, J. Phys. Chem. **40**, 723 (1936).

[54] J. C. Slater, J. Chem. Phys. **9**, 16 (1941).

that is, there is a separation of charge, which requires energy and which energy appears as a part of the observed activation energy. (The rest of the activation energy is probably associated with the actual movement of the proton over the barrier between the two equilibrium positions.) Next, one of the other hydrogen ions about O II moves toward a third oxygen (say ion *b* moves to O III), relieving the unfavorable situation about O II only to set it up again at O III, while in the same manner the deficiency of ions about O I will be transferred to other oxygen ions in the lattice. This migration of charged centers will continue until other centers with one and three hydrogen ions are encountered by the respective moving centers, when the "reaction chains" will be broken. The analogy to the well-known chemical chain mechanisms such as that for the reaction of hydrogen and chlorine is obviously very close, the initial step in this case being the splitting of a stable chlorine molecule into two active atoms which then start two chains of reactions which are in turn ended when a chain-breaking reaction such as a recombination of atoms occurs.[55]

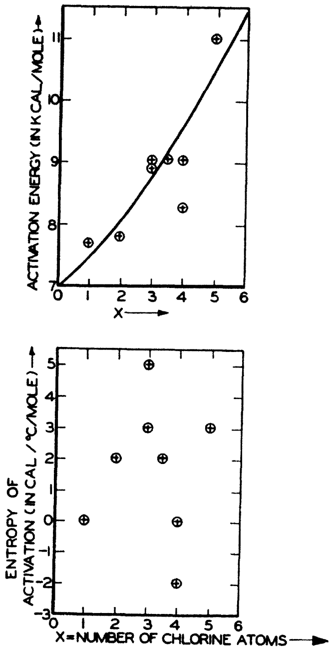

FIG. 14. Energies and entropies of activation for relaxation in the methyl chlorbenzenes,

$C_6(CH_3)_{6-x}Cl_x$.

c. Relaxation in the methyl chlorobenzenes.—It is well known from the crystal structure of solid hexamethyl benzene as determined by Brockway and Robertson[56] that the observed positions of the methyl groups in the crystal preclude the possibility that the molecules in hexamethyl benzene are freely rotating at room temperature. Yet the closely similar substituted polar methyl chlorobenzenes are all known from dielectric evidence[57] to behave as if they were rotating in the solid down to very low temperatures. There being little reason to expect any such great difference in behavior among these very similar compounds, it is obvious that this suggests that the molecules of the methyl chlorobenzenes are very probably not actually freely *rotating*, but are merely free to choose between (probably) six equilibrium positions. This can be taken as an indication that the treatment developed in Section IA2 for discrete orientations of dipoles should be applied here.

It is possible to apply this picture to the relaxation process starting with two different assumptions. First assume that in any jump there is a complete disconnection with the previous state of affairs and that the new position taken up may with equal probability be any of the six possible orientations. If **k** is the probability of a jump between two given orientations, we have seen that [Eq. (15)] the relaxation rate will be six times this jump rate. On the other hand, each jump may only result in a change of orientation from a given position to an immediately adjoining one. It is found on using this assumption in Eq. (10), and utilizing the hexagonal

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[55] It may be of some interest to point out in connection with the dielectric properties of ice that there is good reason to believe that ice should show ferro-electric properties at sufficiently low temperatures. Ice has a hexagonal structure, and it seems clear that of all the possible arrangements of the hydrogen ions in the lattice some few should be slightly more stable than others. A consideration of the details of the structure shows that the most symmetrical arrangements of hydrogen ions in ice result in very large dipole moments along the hexagonal axis. Since the most symmetrical arrangements are also usually energetically the most stable, we should expect that at low enough temperatures the ice crystal should become ferro-electric, probably along its optic axis. Unfortunately, the relaxation time of ice becomes very long at low temperatures, so that it might not be feasible to wait long enough to observe the ferro-electricity at the very low temperatures required. Murphy (see reference 2, Table I) made a measurement of the dielectric constant of ice at −139°C and found a value of the dielectric constant of the same order of magnitude as that at room temperature with a relaxation time of about one hour, and third law treatments show that during the periods of time utilized in specific heat measurements, disorder remains in the crystal down to very low temperatures.

[56] L. O. Brockway and J. M. Robertson, J. Chem. Soc. London 1324 (1939).

[57] See reference 4, Table I.

symmetry of the probable equilibrium positions, that here the relaxation rate is equal to the jump rate between two positions, **k** itself. Thus, if the state of affairs in the crystal were such that sometimes the jumps are random and sometimes they are restricted, there would be a distribution of relaxation rates varying by a factor of six. But $\ln 6 = 1.8 = 2\delta\Delta F/RT$; for $T = 200°\mathrm{K}$ (which is roughly the temperature at which the measurements were made for these substances), $\delta\Delta F = 400$ cal., which is only slightly smaller than the observed values; this may therefore be a significant contributing factor to the distribution of relaxation rates found here. This conclusion may be taken as evidence that in some cases, at any rate, the observed "distribution of relaxation rates" may be a result of the non-reducibility of Eq. (6) to the simple form of the differential equation leading to an exponential decay of the polarization with time.

From Fig. 14 it is evident that there is some tendency for the compounds with the most chlorine atoms to have the largest energy of activation for relaxation, as is perhaps to be expected. There is no similar tendency for the entropies of activation, however. The generally low values of these entropies are an indication that here the relaxation involves only the rotation of single molecules, while the dependence of the activation energy on the number of chlorine atoms present is evidence that the barrier is determined by the sizes of the groups passing one another, chlorine atoms each apparently requiring on the average about (11,000–7,000)/6, or 700 calories more energy to get past one another than do methyl groups.

5. *Relaxation in Polymers*

The striking features of the data on the relaxation of polymers are the very much greater energies and entropies of activation which are found for these substances than for most others. This is probably due to the greater size of the region involved in the unit relaxation process, which is in turn due to the fact that we are no longer dealing with dipoles located in independent molecules, but with dipoles linked to one another by chemical bonds. Where these bonds between dipoles are relatively long and flexible and the concentration of dipoles is relatively low, as for the polymers of malonic and succinic acids with propandiol and for rubber containing small amounts of sulphur, the entropies and energies of activation are smaller, but where dipoles almost directly adjoin one another and the concentration of polar groups is high (as in the polyvinyl polymers), or where they are connected through more rigid links (as in the phenol formaldehyde resins), they are much larger. The increase in the energy and entropy of activation for rubber as the amount of sulphur present is increased (Fig. 9) is also probably a result of the shorter distance between links which comes about with the change in the sulphur content and increased bridging between chains.

Recently, Kirkwood and Fuoss[35] have presented a theory of the relaxation of flexible, long-chain polymers in *dilute solution* in low molecular weight solvents. Relaxation under such conditions is regarded by them as a result of readjustments of the molecule to the applied field brought about by the internal squirming motions of the long, flexible chain. Their mathematical formulation of the theory is based on the assumptions inherent in the Brownian motion and Stokes' law, hydrodynamical types of development against which some question has been raised previously. Nevertheless, it is believed that, insofar as application to truly dilute solutions alone is made, the more important and general conclusions of the theory may not be affected even if an exact agreement with experiment cannot be expected—such exact agreement having been made impossible anyway by the nature of the assumptions necessarily introduced in order to allow the solution of this very difficult problem. The most important conclusion of the theory is that the frequency of maximum dielectric absorption should be proportional to the molecular weight of the polymer in question, since this suggests a new method of determining the molecular weights of long-chain polymers. The distribution of relaxation rates given in Eq. (50) also results from this theory.

The theory has been applied by Fuoss[58] to polyvinyl chloride plasticized with 20 percent of

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[58] See reference 5, Table III.

diphenyl, and by Mead and Fuoss[59] to pure polyvinyl acetate. It should not, however, apply to such concentrated polymers since no account is taken in the theory of the important, probably dominant modifying effects of the interference of the chains with one another's motions at such high concentrations. Curiously, however, the predicted linear relationship between the frequency of maximum absorption at a given temperature and the molecular weight as determined from the relative viscosity of polymer solutions by the Staudinger method actually seems to be borne out. This is apparently taken as support for the validity of the application of the theory in concentrated solutions and even in the pure polymer.

A little consideration will show that if there is a linear relationship between the molecular weight and the relaxation time for concentrated polymers, it must arise from some other source than that contained in the original Kirkwood-Fuoss theory. Physically, the reason why, according to this theory, the most probable relaxation time, and hence the frequency of maximum absorption, should depend on the molecular weight arises from the fact that as chains get longer the number of different types of internal motions involving the chain as a whole increases and at the same time the motions become more complex and take longer to come about. The effect of the interference of the chains with one another's motions, particularly in concentrated polymer solutions, would seem to be to quench these motions of the chain as a whole and increase the relative importance of motions in which shorter lengths of the chain readjust themselves to the field without the rest of the molecule's having much effect on their motion. Perhaps an equivalent way of stating this is to say that the resistance to the movement of the links of the polymer chain which is offered by collisions with other chains is so completely different from that offered by a simple liquid that there is no reason whatsoever to expect that a theory valid for the latter will be even approximately true for the former.

Studies of the viscosities of pure polymers ("melt viscosities") point very strongly to the interpretation that the molecular motions invoked in the flow process here involve only small portions of the whole molecule, these portions being of about the same size for all molecular weights of a polymer in the macromolecular range. The evidence for this is to be found in the relatively small values observed for the activation energy for viscous flow compared with the value which would be expected if the entire molecule were to move as a unit. Also, Flory[60] has found that for linear polyesters of widely different molecular weights, the activation energy for viscous flow is strictly constant. This has led to the description of viscous flow in terms of *segments* of the polymer chain.[61] Estimates of the size of the segments for a number of different types of long-chain molecules give average values for the lengths of these segments of anywhere from 20 to 40 atoms.

It has also been suggested that the melt viscosity of a polymer should not depend merely on the motions of the individual segments of the polymer, but that it should also depend very much on the correlations and sequences of the motions of different segments, since only very few types of successions of segment motions can be expected to lead to an observable deformation of the polymer. The amount of this correlation should depend very drastically on the chain length. On the other hand, it was pointed out[61] that if, as seems very reasonable, dielectric relaxation also results from segment motions, not much cooperation of this type between the motions of different segments should be required here. Therefore, melt viscosities should be very sensitive to chain length while relaxation rates should not. This is now seen to be actually the case: Flory has found an exponential dependence of the melt viscosity on the square root of the molecular weight—a result verified by Baker, Fuller, and Heiss[62]—while Fuoss and Mead have found the much more mild linear dependence of relaxation rate on the molecular weight. For the polyvinyl chloride employed by Fuoss,[30] samples with molecular weights varying by a factor of 5.2 were studied, resulting in a variation of

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[59] See reference 12, Table III.

[60] P. J. Flory, J. Am. Chem. Soc. 62, 1057 (1940).

[61] W. Kauzmann and H. Eyring, J. Am. Chem. Soc. 62, 3113 (1940).

[62] W. O. Baker, C. S. Fuller, and J. H. Heiss, J. Am. Chem. Soc. 63, 2142 (1941).

relaxation times by a factor of 3.4. If we assume an average chain length of 1000 atoms for the lowest polymer, and if we assume the melt viscosity for polyvinyl chloride as a function of the chain length to be given by a formula similar to that given by Flory, then the melt viscosity should vary by something like 30,000 for the same molecular weight range. The prediction made previously by Eyring and the author therefor seems to have been fulfilled in its essentials, although a relatively small but apparently real effect does remain to be explained and it is not immediately evident how this can be done. (Effects of ends of chains would be the obvious first suggestion here, but it does not seem possible that these could give rise to such large changes as are observed.)

6. *Factors Determining the Distribution of Relaxation Rates*

The extent of the distribution of the free energy of activation $\delta\Delta F\delta$ for liquids and solids is seen from Tables I and II to be generally such as might be expected to arise from fluctuations due to the thermal energy of the specimen. Additional factors, similar to those which have already been given as possibly leading to some uncertainty in the rate for the methyl chlorobenzenes may also be acting in some instances, so that it is not at all difficult to understand how the observed distributions might arise.

The polymers (Table III), on the other hand, show much broader distributions in their free energies of activation. This undoubtedly arises largely from the indefiniteness in the size of the segments which are acting as the kinetic units in the relaxation process. Certain portions of the chain may be so arranged that they can reorient themselves by movements over a length of, say, 30 atoms of the polymer chain at any one time, while other portions may require a greater or smaller length in order to change their orientations.

In rubber (Fig. 9d) there is a marked effect of increased amounts of sulphur in broadening the distribution of relaxation rates; this is probably due to the random distribution of inter-chain sulphur bridges in the rubber such that the distances between bridges fluctuate rather widely. Thus, at higher sulphur concentrations there is a marked diversity in the amounts of interference offered by the presence of one sulphur link to the reorientation of another sulphur link.

The sharp increase in $\delta\Delta F$ for plasticized polyvinyl chloride below certain temperatures (Fig. 8c)—ascribed by Fuoss to the onset of a phase change in the polymer—will be discussed elsewhere in connection with the question of so-called "phase transitions" in polymers, glasses, and amorphous phases in general.

It seems to be generally true that for polymers (and possibly also for lower molecular weight substances), the Wagner-Yager distribution function, Eq. (47), decays too rapidly at large departures from the most probable relaxation rate to be able to account for the entire range of frequency dependence of the observed dispersion.[32] The Cole and Fuoss-Kirkwood functions, however, are apparently more satisfactory in this respect. Since the Wagner-Yager function decays exponentially in the *square* of the deviation, while the more successful functions decay exponentially in the deviation itself (for large deviations), and since fluctuations in the free energy are likely to occur in accordance with the latter type of decay (from the nature of the Boltzmann type of factor $e^{-E/kT}$), this behavior is not surprising.

The validity of the Coles' arc method of plotting dielectric dispersion effects on ϵ' and ϵ'' (Section IIA1) clearly rests on the accuracy of Eq. (49) as a description of the actual distribution of relaxation rates. Aside from the fact that its general form is reasonable—a characteristic equally true of the Fuoss-Kirkwood distribution and of many other similar possible expressions—there is no evident reason for the particular validity of this expression. Therefore, it would be well to keep in mind that in spite of its attractive simplicity, there is no *a priori* reason why the Coles' arc method should be regarded as anything more than convenient empirical approximation. It is easily possible that it will be found to break down in some instances—particularly when very broad distributions are encountered.

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