ELECTRIC MOMENT, MOLECULAR ORIENTATION AND STRUCTURE IN ALIPHATIC COMPOUNDS

CHARLES P. SMYTH

Department of Chemistry, Princeton University, Princeton, New Jersey

MATHEMATICAL THEORY OF DIELECTRICS AND EXPERIMENTAL CONFIRMATION

The dielectric constant is generally familiar as a constant in the expression for Coulomb's law and as a quantity to which the capacity of a condenser is proportional, and it is as the latter that it is commonly determined experimentally. It may, however, be conveniently defined from a slightly different point of view. If a difference of potential is set up between two like conducting plates and no medium exists between them, the strength of the electric field at some point between them may be represented by E_0. If now some medium be allowed to fill the space between the plates, the new field strength E_1 at this point will be proportional to E_0 and equal to E_0/ϵ where ϵ is the dielectric constant of the medium, that is, $\epsilon = \dfrac{E_0}{E_1}$. It was supposed by Mossotti (34) and by Clausius (4) that the molecules of the medium acted as perfectly conducting spheres on which charges were induced by the charges on the plates (see figure 1(a)). A negative charge would be induced on the side of the molecule toward the positive plate and an equal positive charge on the side toward the negative plate. The field present before the introduction of the medium is thus opposed and reduced and each molecule becomes temporarily an electric doublet or dipole, the moment of which is the product of one of the induced equal charges by the distance between the two. The simple mathematical development of this assumption, when the medium is a pure substance, leads to the equation:

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4 \pi N}{3} \gamma,$$

in which M = the molecular weight, d = the density, N = the number of molecules in a gram-molecule = 6.061×10^{23}, and γ = the molecular polarizability, that is, the moment induced on a molecule by a field of unit strength. γ is a constant characteristic of the substance. This expression, called the molar polarization, is, in many cases, found approximately equal to the Lorenz (24)-Lorentz (23) expression for molar refraction, $\dfrac{n^2 - 1}{n^2 + 2} \cdot \dfrac{M}{d}$, as would
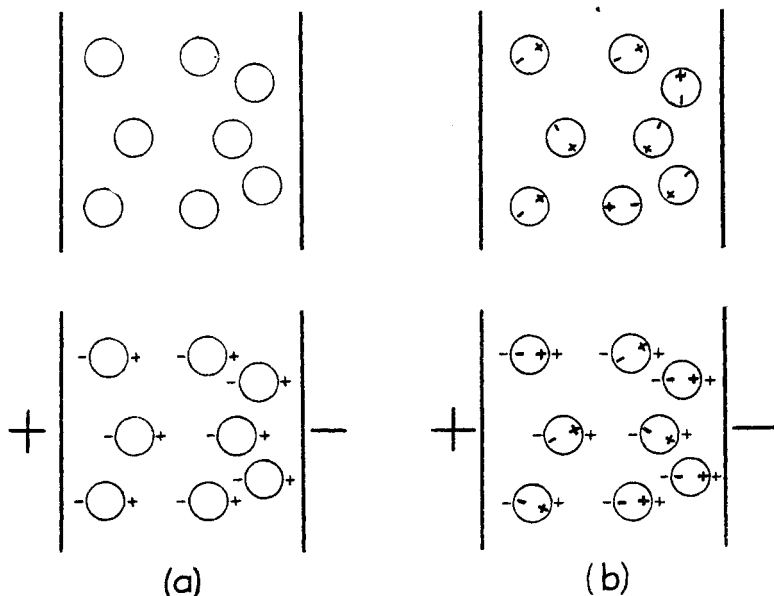

(a)   (b)

FIG. 1. MOLECULAR THEORY OF DIELECTRICS ACCORDING TO (a) MOSSOTTI AND CLAUSIUS AND (b) DEBYE

be expected from the well-known Maxwellian (31) relation $\epsilon = n^2$. For many substances, however, when n, the index of refraction measured for light in the visible region, is extrapolated to the region of long electric waves in which the dielectric constant is measured, ϵ is found to be much larger than n^2. For these same substances, the molar polarization, which will be represented by P, is found to depart from the constancy required by the Clausius-Mossotti equation and vary considerably with temperature.

Debye (6) (7) has applied to dielectrics a treatment analogous to that used by Langevin (20) in discussing paramagnetism, assuming that a molecule may contain a permanent doublet of moment, μ, which causes the molecule to become oriented in an electric field (see figure 1(b)). If all the molecules were oriented in the applied field so that the axes of their doublets lay in the direction of the field, the permanent moment μ would be added to the induced moment γ in the Clausius-Mossotti expression for the polarization, but orientation of the molecules containing the doublets is opposed by the thermal agitation of the molecules, which, of course, varies with the temperature, so that the polarization becomes a function of the temperature. Debye has expressed this relation as

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} = \frac{4\pi N}{3} \gamma + \frac{4\pi N}{3} \frac{\mu^2}{3\,kT},$$

in which k = the molecular gas constant = 1.372×10^{-16}, and T = the absolute temperature. $\frac{\mu^2}{3kT}$ is the mean component of the moment per molecule in the direction of an internal field of unit strength and it is this, instead of μ, which is added to γ. As T is the only variable on the right-hand side of the equation, it is evident that, when the molecule contains no permanent doublet ($\mu = 0$), the second term on the right drops out and the equation becomes equivalent to the Clausius-Mossotti expression, which takes account only of doublets induced in the molecules. However, when the molecule is unsymmetrical electrically, containing a permanent doublet, the polarization is a linear function of $\frac{1}{T}$ and the second term on the right may be much larger than the first.

The equation may be written in the form:

$$P = a + b/T,$$

in which $a = \frac{4\pi N}{3} \gamma$ and $b = \frac{4\pi N \mu^2}{9k}$. When ϵ and d are measured over a range of temperature, the values of the constants a and b

may be calculated and the value of μ obtained from that of b. a may also be calculated approximately as the molar refraction for infinite wave length obtained by extrapolation of the refraction in the visible region. b/T is then given as the difference between a and P at one temperature. This method of obtaining the moment is somewhat less accurate and is misleading when any molecular association occurs.

In the derivation of this equation on the basis of the classical mechanics, it is necessary to suppose that, in the absence of an external field, the molecules are oriented at random. The first applications of the principle of quantized orientation to the problem led to an equation of the same general form but with a different coefficient for the second term (35) (36). However, applications of the new quantum mechanics to simple poly-atomic molecules have given equations from which results practically identical with those of the Debye equation may be obtained (18) (32) (30) and Van Vleck (63) has recently given a general proof of the equation on the basis of the new mechanics.

Obviously, when the molecules are not entirely free to orient in an applied field, the equation cannot be expected to apply. For gases, the dielectric constants of which are very close to 1, simplification may be effected by setting $\epsilon + 2$ equal to 3. The validity of this simplified equation has been established experimentally by Jona (15), Zahn (75) (76) (77), Sänger (39), Stuart (59) (60), and others (65) (54a). In liquids, the molecules are so close together that large doublets attract one another strongly, forming complex molecules or restricting one another's freedom of motion. When the doublets are sufficiently separated from one another by the molecules of a non-polar solvent, they should behave much as if in the gaseous condition.

The polarization $P_{1,2}$ of a mixture of two substances 1 and 2 is expressed by Debye as:

$$P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{c_1 M_1 + c_2 M_2}{d} = c_1 P_1 + c_2 P_2,$$

in which c_1 and c_2 = the mole fractions, M_1 and M_2 = the molecular weights, and P_1 and P_2 = the polarizations of substances 1

and 2 respectively.   Written in the form: $P_2 = \dfrac{P_{1,2} - P_1}{c_2} + P_1$,

the expression may be used to calculate P_2 when P_1 is known.   If substance 1 is non-polar, its value of b is 0 and P_1 is equal to the constant a, which is the molar refraction for light of infinite wave-length.   Since measurements of refraction shortly to be published (51) show that the molar refractions of a variety of substances in mixtures are independent of their concentrations,
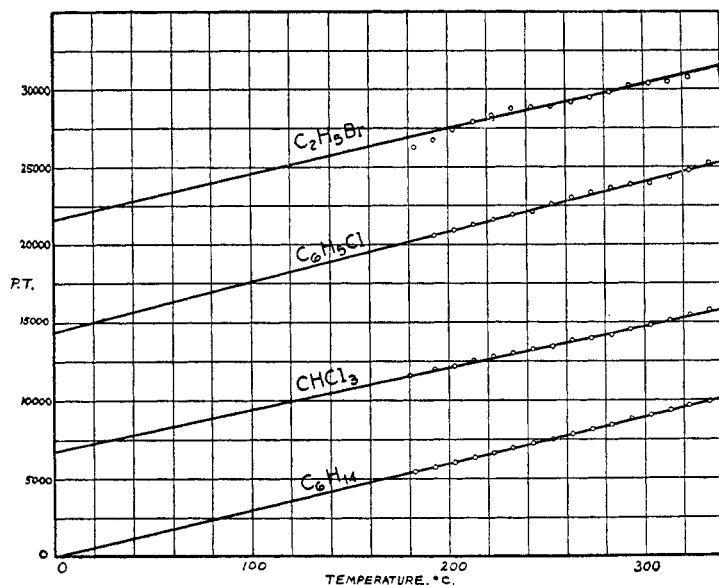

FIG. 2. VARIATION OF PT WITH T

the value of P_1 may be regarded as constant and used to calculate P_2.   If P_2 is obtained for several values of c_2 and the results extrapolated to $c_2 = 0$, that is, to infinite dilution, the mutual effects of the doublets in neighboring molecules should be eliminated and the polarization should be the same as in the gaseous condition at the same temperature.   Lange (19) and Williams (67a) and his collaborators have obtained the same results for the extrapolated values of P_2 in different solvents.   Figure 2, in which the extrapolated values of P multiplied by T are plotted

against T, shows the excellent conformity of some diluted polar liquids to the Debye relation and a similar linearity has been obtained in the results for several other liquids as yet unpublished. Table 1 shows very satisfactory agreement between the values of the moment in the liquid condition and those in the vapor calculated by means of the Debye equation.

In the majority of the determinations of electric moment in the liquid condition, the dielectric constant and density are measured at one temperature only, so that it is impossible to calculate the induced polarization from these measurements alone.

TABLE 1

Electric moments ($\times$ 10^{18}) *in the liquid and vapor states*

	LIQUID	VAPOR
H_2O	1.8 (67)	1.8 (60)
CH_3OH	1.64 (58)	1.67 (33)
C_2H_5OH	1.74 (58)	1.69 (33)
C_4H_9OH	1.74 (57)	1.66 (33)
$(C_2H_5)_2O$	1.22 (67a)	1.14 (60)
$(CH_3)_2CO$	2.71 (17) (73)	2.84 (60)
$CHCl_3$	1.05 (53)	1.05 (43a)
C_2H_5Br	1.86 (53)	1.78 (29)
C_2H_5I	1.66 (57)	1.62 (29)

As has been stated, the induced polarization, $\dfrac{4\pi N}{3}\gamma = a$, commonly differs little from the molar refraction, $\dfrac{n^2 - 1}{n^2 + 2} \cdot \dfrac{M}{d}$. Consequently, when the latter is subtracted from the total polarization P, a value is obtained for b/T, which, in most cases, is not seriously inaccurate and may be used to calculate the moment. However, the molar refraction for light in the visible region arises mainly from the action of the electrons in the rapidly alternating field of the light wave and, when extrapolated to infinite wave-length, which is practically equivalent to the wave-length used in determining the dielectric polarization, does not contain the contribution of the shifts of atoms or groups of atoms which may be induced by the relatively slow alternating electric field used in the

dielectric constant measurement. This contribution, which may be termed the atomic polarization P_A, is usually small and may at times be practically negligible in comparison with the electronic contribution or extrapolated refraction for infinite wave-length, P_E. The sum, $P_E + P_A = a$, may be determined not only from the temperature variation of the total polarization, but also as the polarization in the solid state where the dipole contribution is eliminated by the fixing of the molecules. The atomic polarization has been considered by the writer (49). The conclusion has been reached that it is generally not an additive property, but tends to be greater, the greater the number of atomic nuclei or groups in the molecule, the greater the number of electric doublets, and the more unsymmetrical the arrangement of these doublets in the molecule and that, in the calculation of the electric moment, it may be disregarded without risk of introducing appreciable error only when the moment is large and the molecule small.

Some years ago, when few values were available for the study of the relation between electric moment and molecular structure, the writer (46) (47) used a modified form of an equation developed by Gans (13) to calculate the moments of a large number of molecules. As the equation attempted to take into account, in approximate fashion, the mutual effects of neighboring molecules, which cannot be treated accurately, and as certain of its assumptions are open to criticism (7), the values of the moments obtained with it might be expected to be only very approximate. However, as many of these values are now in use in the literature, it seems desirable to compare them with the values obtained with the Debye equation from more recent measurements upon gases or dilute solutions and obtain an estimate of their accuracy. In the calculation by the modified Gans equation, the quantities used in the Debye equation are required at one temperature only and in addition the molecular diameter is used in an attempt to evaluate the effect of the molecular field. The values thus obtained for typical substances in the liquid condition are shown in table 2 in the column headed "Calculated," while the column headed "Observed" gives values which should be correct to within 0.1×10^{-18}, being better than this in many cases.

The expression for the induced polarization in the Gans equation is identical with that in the Debye equation so that the part played by the atomic polarization is the same in both. Disregard of P_A, the values of which were unknown when these calculations were made, introduced errors into the moments of substances for which small values were found. The moments calculated for benzene and carbon tetrachloride are probably due to this cause and it has been pointed out by the writer in the

TABLE 2

Electric moments ($\times 10^{18}$) *calculated by modified Gans equation and observed by other methods*

	CALCULATED (46)	OBSERVED
Hexane	0	0 (53)
Benzene	0.2	0 (38)
Toluene	0.4	0.4 (67a)
Methyl alcohol	1.78	1.67 (33)
Butyl alcohol	2.06	1.66 (33)
Ethyl ether	1.37	1.14 (60)
Hydrogen sulphide	1.02	1.10 (2)
Acetone	2.08	2.84 (60)
Methyl ethyl ketone	2.29	2.79 (73)
Aniline	1.35	1.51 (14)
Ethyl acetate	1.62	1.74 (17)
Hydrogen chloride	1.07	1.03 (75)
Hydrogen bromide	0.92	0.79 (75)
Hydrogen iodide	0.64	0.36 (75)
Ethyl bromide	1.56	1.86 (53)
Chlorobenzene	1.42	1.52 (53)
Bromobenzene	1.39	1.5 (69)
Chloroform	1.25	1.05 (53)
Carbon tetrachloride	0.48	0 (39)

paper (49) just referred to that neglect of P_A may give rise to even larger apparent values for molecules possessing no moment. Actually, some of the experimental data for benzene indicated that the moment was zero and it was recognized that the value calculated was not of sufficient accuracy to be distinguishable from zero.

The good agreement between the calculated value for liquid methyl alcohol and the accurate value obtained for the vapor is

due not to the excellence of the method of calculation but to some compensation between the complicated effects of orientation in the liquid.   The reasonable accuracy of the values obtained by some investigators who measured alcohols in solutions without using considerable dilution or variation in temperature may also be attributed to this compensation.   The fact that the calculation gave different values for the moment at different temperatures in supposedly associated liquids showed that the Gans equation did not take care of the effect of molecular association.   The increase in the calculated values of the moment with increasing length of the carbon chain in the alcohols, ketones, and some other series must now be attributed mainly to change in the effect of molecular association.   Among the halides the calculated values show fairly satisfactory agreement with the accurately observed values, and, in general, the less strongly associated substances show not unsatisfactory agreement.   It is evident then that this method of calculation commonly gives fairly accurate values of the moments of molecules which are not strongly associated, although conclusions cannot safely be drawn from small differences between these values; but in strongly associated liquids the equation cannot be relied upon to give results of any significance, although it often gives the order of magnitude of the moment.

DISTRIBUTION OF ELECTRICITY AND ELECTRIC MOMENT OF THE MOLECULE

The mutual effects of the doublets in neighboring molecules may be better understood if the relation of the doublets to molecular structure is considered.   In view of the uncertainty and the rapidity of change in the hypotheses of atomic structure and our ignorance of the fundamental nature of the chemical bond, it is impossible to assign definite electronic arrangements to the atoms in a molecule.   It is generally believed, however, that a single chemical bond involves a pair of electrons and the electrostatic effect of the charge in the molecule is represented by picturing certain locations in the structure as occupied by the electrons. The consideration of these locations makes possible the discussion of the distribution of the electricity in the molecule.

The argon atom is believed to consist of a positive nucleus with 18 electrons distributed about it, the total charge of the atom being zero. The symmetry of the distribution is such that the mean position of the center of gravity of the electrons is coincident with that of the positive nucleus, the atom thus having no permanent moment. When the atom is placed in an electric field the electrons shift so that their center of gravity is no longer coincident with the positive nucleus, the system thus temporarily forming an electric doublet as do the molecules in figure 1(a). Since the molecule contains no permanent doublet, the second term in the Debye equation is zero and the polarization should, therefore, be constant. The chloride ion, Cl^-, is supposed to consist of a symmetrical arrangement of 18 electrons around a nucleus which has 17 positive charges. Since the center of gravity of the electrons coincides with the positive nucleus, the system of charges may, as an approximation, be resolved into a single negative charge located at the nucleus. If, now, a hydrogen nucleus could, without distortion of the system, be attached to form a neutral hydrogen chloride molecule, a permanent electric doublet should result. The moment of the doublet should be the product of the single electronic charge, 4.774×10^{-10} e.s.u., by the distance between the nuclei, which has been calculated from infra-red absorption spectra as 1.27×10^{-8} cm. The moment 6.06×10^{-18} calculated in this way is far larger than the value 1.03×10^{-18} obtained by application of the Debye equation to measurements of the dielectric constant of gaseous hydrogen chloride, because the positive hydrogen nucleus draws the electrons of the chloride ion toward it, distorting the system of charges and greatly diminishing the distance between their centers of gravity. The extent of the distortion has been calculated to be of approximately the right amount to cause the difference between the values of the moments calculated from the molecular structure and those obtained from experimental data (45). When placed between the plates of a condenser, the hydrogen chloride molecules orient in the externally applied field as far as permitted by the thermal agitation and the effect of the induced doublet is superimposed upon that of the permanent.

The treatment of the system of positive and negative charges in the molecule as giving rise to a single doublet is a rough approximation even in the simpler molecules. In more complex molecules, the structure should act as a single doublet only at a considerable distance. The oxide ion, O^{--}, may be regarded as a symmetrical structure, just as was the chloride ion. If two hydrogen nuclei are attached to form a water molecule, two electric doublets should be formed, the positive end of each being a hydrogen nucleus. If the two portions were on opposite sides of the molecule and equidistant from the oxygen nucleus which lay on the straight line joining them, the two doublets would cancel one another and the moment of the molecule as a whole would be zero. The considerable moment, 1.8×10^{-18}, found for the molecule may be very satisfactorily explained by supposing that the two doublets make an angle with one another and, consequently, give a considerable resultant moment. It was calculated by the writer (46) that, if the structure of the methyl group could be regarded as that of a regular tetrahedron, it should be possible to substitute it for that of a hydrogen atom without directly altering the moment of the molecule, provided that the hydrogen nuclei in the methyl group were at the same distance from their binding electron pairs as was the replaced hydrogen nucleus from its bonding pair, and provided further that there were no alteration in the hypothetical position of the electron pair to which the original hydrogen, now replaced by methyl, was attached. This is contrary to the idea of a varying electronegativity among hydrogen and the alkyl radicals, which will be discussed later, and cannot be expected to be true in all cases. Thus, in hydrogen chloride, bromide, and iodide, the proton is thought to penetrate the halogen structure somewhat (1), thereby shortening the distance between the positive and negative centers of gravity. Such penetration cannot occur when the hydrogen is replaced by methyl, so that the distance between the electrical centers of gravity is greater and the moments observed for methyl chloride, bromide, and iodide are considerably higher than those of the corresponding hydrogen halides. However, when one of the hydrogens in the water

molecule is replaced by a methyl group to form methyl alcohol, little change in moment occurs and a hydrogen of the methyl may be replaced by another methyl to form ethyl alcohol and, indeed, the hydrocarbon chain may be lengthened to give octyl alcohol without causing an appreciable change in moment (see table 3). On the other hand, if the hydroxyl hydrogen in methyl alcohol is replaced by methyl, there is a repulsion between the two methyl groups because of their bulk which widens the angle between the two doublets, thereby decreasing the resultant moment of the molecule. Further increase in the size of these groups to ethyl increases the repulsion between them and further widens the angle between the doublets, so that the moment observed for ethyl ether is slightly lower than that for methyl, although the difference is much less than that between methyl ether and methyl

TABLE 3

Electric moments ($\times 10^{18}$) of water, alcohols, and ethers

HOH.................... 1.8 (60, 67)		
CH_3OH.................. 1.67 (33)	CH_3OCH_3.................. 1.29 (60)	
C_2H_5OH................. 1.69 (33)	$C_2H_5OC_2H_5$................. 1.14 (60)	
$n\text{-}C_3H_7OH$.............. 1.75 (58)	$CH_2\diagdown$	
$n\text{-}C_4H_9OH$.............. 1.66 (33)	$\quad\big|\quad$ O.................... 1.88 (60)	
$n\text{-}C_8H_{17}OH$.............. 1.70 (57)	$CH_2\diagup$	

alcohol. In ethylene oxide, the same doublets should exist as in methyl ether and methyl alcohol; but the positive ends of the doublets are drawn together because of the bond between the carbons and the angle between the doublet axes is thus made less than in the alcohol, so that the resultant moment is larger as shown in table 3.

EFFECT OF THE SIZE AND LOCATION OF THE ELECTRIC DOUBLETS
IN THE MOLECULE UPON MOLECULAR ORIENTATION

In the water molecule, the positive ends of two large doublets lie near the surface causing a very strong field of force around the molecule, so that the molecules affect one another greatly, strong association occurs, and the liquid is highly abnormal. In methyl alcohol the doublets may be supposed to have the same

location with reference to the oxygen that they have in the water molecule, but one of them is screened by the methyl group which cuts down its field outside of the molecule, thereby reducing the effect of the molecule upon its neighbors and rendering methyl alcohol less abnormal than water. The screening effect is slightly increased when methyl is changed to ethyl and, as the hydrocarbon chain lengthens in going up the series of the alcohols, the doublets in adjacent molecules approach one another less frequently and the abnormality of the liquids diminishes. However, the strong field of force around the OH doublet still remains and n-octyl alcohol shows a great variation of P_2 with the concentration of its solution in benzene and in heptane (57), When the hydroxyl hydrogen of ethyl alcohol is replaced by an ethyl group to form ether, the unscreened doublet is shielded and the field of force around the molecule is so reduced that the liquid is quite normal and, in solution in benzene, the polarization of ether is independent of concentration (7), although the moment is still $\frac{2}{3}$ that of the alcohol.

Ethyl bromide (table 2), in spite of the moment, 1.86×10^{-18}, possessed by its molecule, is ordinarily termed a normal liquid. Its doublet should lie in the region of attachment of the ethyl group to the bromine atom and should thus be screened not only by the ethyl group but also by the large bromine atom, which should greatly reduce the molecular field as compared to that of the ethyl alcohol molecule. In ethyl iodide, the screening effect of the large iodine atom should be greater than that of the bromine atom, and this, taken in conjunction with the slightly smaller moment of the molecule, 1.66×10^{-18}, should give a smaller molecular field. Measurements of the partial vapor pressures of binary mixtures (50) show the abnormalities resulting from the very strong forces exerted by the alcohol molecules, while the effect of the forces is much less in the case of ethyl bromide and, for ethyl iodide, slightly less than for ethyl bromide.

It is difficult to construct a completely satisfactory picture of the interaction of the molecular force fields. The effect of the molecules upon one another must depend not only on the size of their doublets, but also upon the location of the doublet or dou-

blets in the molecule, and upon the mere geometrical shape of
the molecule. It is not difficult to picture the molecules of a
liquid possessing no electric moment as roughly oriented merely
because of their shapes, such an orientation as that found by
Stewart (55) for the isomeric heptanes. There are two possible
simple orientations which two doublets in adjacent molecules might
be expected to adopt relative to one another (figure 3). The nega-
tive end of one doublet might attract the positive end of the other
so that the axes of the two doublets would fall in line and the two
would support one another (figure 3, I). The attraction between
the ends would lengthen each separate doublet giving a moment
for the two together greater than 2μ, μ being the moment of each
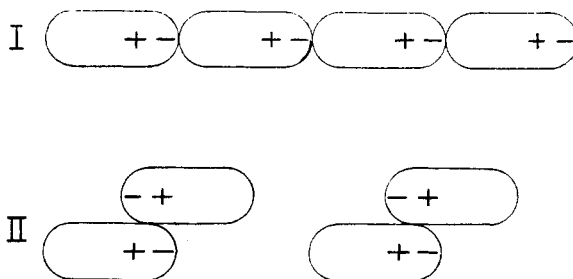doublet alone. If the force of attraction were so great that the

FIG. 3. TYPES OF ORIENTATION OF DIPOLE MOLECULES

two molecules actually associated to form a double molecule, the
number of molecules in the liquid would be cut in half, but, since
in the Debye equation the moment of the molecule is squared,
we should have in the expression for the polarization a quantity
somewhat greater than $4\mu^2$ instead of μ^2 and the polarization
would, therefore, be increased in spite of the reduction in the
number of molecules. Even if the two molecules were not defi-
nitely associated to act as one, they would attract one another
and tend to orient more or less with respect to one another so
that when a field was applied externally to measure the dielectric
constant, the orientation would be greater than that calculated.
The shape of the molecules would commonly prevent an exact
lining up of the doublets and their axes would, consequently,

make an angle of somewhat less than 180° with one another. As this angle decreases, the polarization diminishes and the common effect of orientation is to decrease the polarization instead of increasing it. When the angle between the axes becomes zero, that is, when the doublets are parallel and pointing in opposite directions, (figure 3, II), the moments cancel one another and the doublet contribution, the second term of the Debye equation, becomes zero. This position of the doublets, which represents the other extreme of the two possible simple orientations, would result in a polarization for a polar substance differing little from its molar refraction. More than two molecules would tend to line up if the first type of orientation prevailed and one might imagine a polarization built up almost indefinitely in this way. Also, more than two molecules may possibly orient in some complex arrangements which either increase or decrease the polarization. The stability of the orientation of one molecule relative to another must depend to some extent upon the forces exerted upon it by the other neighboring molecules. It appears probable, therefore, that, when there is not much difference between the energies of two different orientations, one orientation may change to the other as the mean distance between the dipole molecules changes. Thus, when a polar liquid is dissolved in a non-polar, the orientation of the polar molecules relative to one another may change from one type to another with change in concentration. Of course, when the polar molecules are in very dilute solution and, on the average, far away from one another, they should assume a random orientation unless they actually associate to form a definite complex molecule which is not much dissociated even in the dilute solution, as appears to be the case with acetic acid in benzene solution (37) (53a). Change in temperature also might affect the type of orientation. It must be borne in mind that the supposed orientation which has been discussed is not complete and, indeed, may be little more than a condition in which a tendency toward a certain arrangement of the molecules exists. As orientation is opposed by thermal agitation, rising temperature reduces the abnormalities of liquids and conformation to the Debye equation becomes closer.

Dolezalek (8) (9) and many others (41) have explained the deviation of a physical property of a mixture from linear dependence upon the composition of the mixture by assuming a definite chemical equilibrium between single and complex molecules, the value of the property observed depending upon the proportions of the different complex and single molecules in the mixture. Although this is probably true in some cases, the method has been carried to such extremes as not infrequently to involve most improbable assumptions and, in most cases, merely to give equations which, because they contain a sufficient number of adjustable constants, provide adequate means of representing the experimental results.   The variation of the polarization of a polar substance with its concentration in solution in a non-polar substance may be represented quantitatively by assuming that a portion of the single molecules associates to form definite double molecules which possess a different moment from those of the single, the moment usually being assumed to be zero.   The assumptions involved are necessarily arbitrary, and the only indication that they correspond to the facts is given by the manner in which the equations with their adjustable constants are able to represent the experimental data.   Acetic acid in dilute solution in benzene is shown by molecular weight determinations to consist largely of double molecules which are shown by dielectric constant measurements, as yet unpublished, to possess little or no moment.   In a solvent in which these double molecules are largely dissociated in dilute solution, it may be possible to represent correctly the change of polarization with concentration in terms of the equilibrium between the single and the double molecules.

Debye (7) has developed an equation which represents neighboring doublets as orienting one another in such a way as to increase the polarization, and has found that it fits satisfactorily the variation of the polarization of ethyl alcohol with its concentration in dilute solution in benzene.   This equation can, however, represent orientation as effecting only an increase and never a decrease in polarization.   The writer, in unpublished work, has developed an equation from the approximate equation

of Gans (13), which satisfactorily reproduces the variation of the polarization of ethyl bromide in hexane not only with concentration but also with temperature. This equation can, however, represent orientation as bringing about only a decrease and never an increase in polarization. In view of the number of factors which determine the effects of the doublets upon one another, factors which cannot be quantitatively evaluated, it appears impossible to formulate any generally valid expression for the interaction of the molecular doublets, which will be much more than an empirical equation. It is possible, however, to show
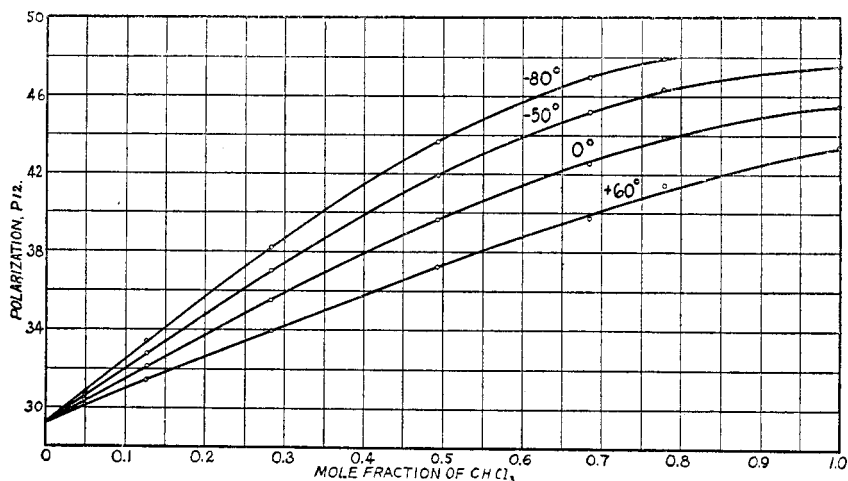

FIG. 4. MOLAR POLARIZATIONS OF HEXANE-CHLOROFORM MIXTURES

qualitatively how the different factors which have been discussed affect the polarizations of typical polar substances.

The $P_{1,2}$-composition curves may be advantageously considered. If there were no intermolecular action, each curve would be a straight line, the tangent to the observed curve at $c_2 = 0$. This is nearly the case for the hexane-chloroform mixtures (53) (figure 4) at 60°, where the $P_{1,2} - c_2$ curve shows almost no deviation from linearity, but, as the thermal agitation decreases with decreasing temperature, the mutual effects of the doublets in the chloroform molecules, the moments of which are only 1.05 $\times$

10^{-18}, increase and the curvature becomes more pronounced. The curvature is greater in the somewhat similar curves for the hexane-chlorobenzene mixtures (53) for the larger moment of the chlorobenzene molecules, 1.52×10^{-18}, makes them affect one another more strongly. In the hexane-ethyl bromide mixtures (53) (figure 5), the strong forces exerted by the large doublets ($\mu = 1.86 \times 10^{-18}$) in the ethyl bromide molecules actually cause the curves to pass through a maximum which becomes
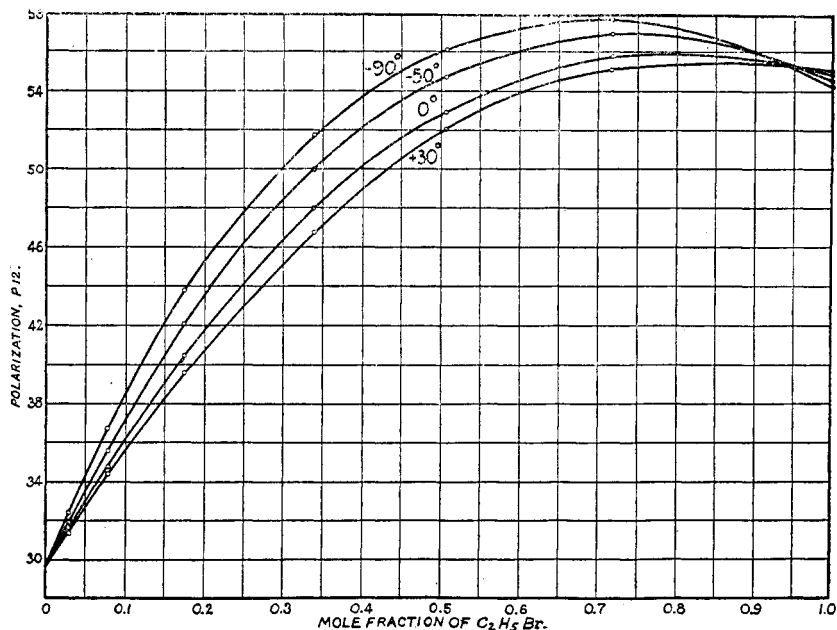

FIG. 5. MOLAR POLARIZATIONS OF HEXANE-ETHYL BROMIDE MIXTURES

flatter and flatter as the increased thermal agitation accompanying increasing temperature diminishes the orienting effects of the molecules upon one another. The intersection of the curves for different temperatures indicates a mixture containing 0.95 mole fraction of ethyl bromide as having a polarization independent of temperature. The polarization of pure ethyl bromide increases slightly with increasing temperature instead of decreasing as required by the Debye equation, but the dielectric constant
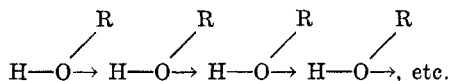
decreases. The behavior of ethyl iodide in heptane (57) is very similar to that of ethyl bromide in hexane. The slightly smaller moment, 1.66×10^{-18}, and the slightly greater screening of the doublet by the larger iodine atom reduces the molecular field somewhat, so that the curvature of the $P_{1,2} - c_2$ curves is a little less pronounced and the polarization of pure ethyl iodide decreases very slowly with rising temperature instead of increasing like that of ethyl bromide. As the hydrocarbon chain attached to the halogen lengthens, the number of doublets per unit volume diminishes and their effect upon one another therefore decreases, butyl bromide showing less deviation from linearity in the $P_{1,2} - c_2$ curves (37) and heptyl bromide much less.

The interaction of the dipoles in all these molecules decreases the polarization in the manner of the second type of orientation discussed, in which the doublets orient in such a way as to oppose and at least partly cancel one another. This is the effect observed in the great majority of the substances thus far studied, as might be expected from considerations of molecular structure. A doublet or small group of doublets which resolve themselves into one, usually lies at one end or side of the molecule with the bulk of the molecule behind it. An orientation of the first type necessitates a lining up of the molecules with the axes of the doublets more or less in line and the bulk of a molecule between each doublet and its neighbor in line as in figure 3, I. The screening effect of the bulk of the molecule should so reduce the forces between the doublets as to render the orientation unstable. The more probable orientation is the second type, in which the axes of the doublets tend to become more or less parallel to one another pointing in opposite directions as in figure 3, II.
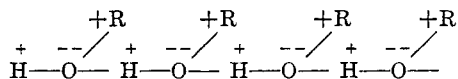
The behavior of the alcohols in solution in benzene (7) (57) may be explained by supposing that both types of orientation occur. In the very dilute solutions, the amount of orientation is slight and extrapolation of P_2 to infinite dilution gives values which conform approximately to the Debye equation. As the concentration of the alcohol increases, orientation increases and, apparently, orientation of the first type predominates since the polarization increases. However, as the concentration increases, the

second type of orientation appears to become more stable than the first and gradually to predominate, causing the polarization of the alcohol to reach a maximum and then decrease. Debye (7) has suggested a triangular arrangement of three molecules to account for the decrease in polarization in the concentrated solutions. It is not impossible that a more complex arrangement of the molecules may exist, but the supposition of the simple orientation of the second type is in accord with the conclusions of Stewart and Skinner (56) from x-ray studies, that in the pure normal alcohols the molecules are usually paired with the hydroxyl group in contact with one another.

The theory of a proton sharing a pair of electrons with each of two groups proposed by Latimer and Rodebush (22) has been applied by Sidgwick (43) to the association of the alcohols. Sidgwick states that "the great majority of associated substances contain a hydroxyl group," polymerization arising through the hydroxyl "hydrogen acting as acceptor and the oxygen as donor," that is, the hydrogen of one hydroxyl group becomes attached to the oxygen of the hydroxyl of another molecule and, as a result, shares electrons with both oxygens. Alcohol molecules would associate thus:

$$
\begin{array}{cccc}
R & R & R & R \\
\diagup & \diagup & \diagup & \diagup \\
\end{array}
$$
$$
H\!-\!O\!\rightarrow H\!-\!O\!\rightarrow H\!-\!O\!\rightarrow H\!-\!O\!\rightarrow, \text{ etc.}
$$

This actual sharing of electrons between molecules to form a complex has been criticised by the writer and his collaborators (51) on the ground that it would cause a small decrease in the molar refraction of the alcohol which is not observed experimentally. However, this arrangement of the molecules relative to one another would correspond to an orientation of the first type and would thus cause an increase of polarization as observed in the dilute solutions of the alcohols in benzene. A rough idea of this may be given by writing the + and − signs of the doublets in the formula:

$$
\begin{array}{cccc}
+R & +R & +R & +R \\
\diagup & \diagup & \diagup & \diagup \\
\end{array}
$$
$$
\begin{array}{cccc}
+ & --\ + & --\ + & --\ + & -- \\
H\!-\!O\!-- & H\!-\!O\!-- & H\!-\!O\!-- & H\!-\!O\!--
\end{array}
$$

There appears to be no reason why the mere attractive force of
the doublets for one another should not bring about an orientation
of the molecules roughly approximating this without any actual
sharing of electrons between them. This would account only
for the increase in polarization observed in the more dilute solu-
tions.   The decrease observed in the more concentrated solutions
could be explained by an orientation like the following:

$$\overset{--}{O}\text{---}\overset{+}{H} \quad +R$$
$$\underset{R}{\overset{+}{\diagup}}\ \underset{H\text{---}O}{\overset{+}{\diagup}\ \overset{--}{\diagup}}$$
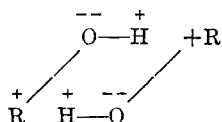
One might assume, according to Sidgwick's method, that each
hydrogen shares a pair of electrons with each of the two oxygens
or that only one hydrogen does so, but, in either case, the assump-
tion appears artificial. The mere attraction of the doublets
for one another should be able to cause the orientation to occur
to an extent sufficient to account for the observed behavior.   This
of course, cannot be regarded as evidence against Sidgwick's
theory, but, added to the evidence against it given by the con-
stancy of the molar refractions of the alcohols in solution, we
now have the fact that the complex molecule proposed by him is
able to account for the behavior of the polarization in dilute
solution only.   It is necessary to assume the formation of a
second type of complex molecule to account for the behavior in
concentrated solution.

   It appears much simpler to suppose that, in the dilute solutions
at higher temperatures, the molecules tend to arrange themselves
in an orientation of the first type.   The increased effect of the
moments gives an increased potential energy to this orientation as
the internal field of the liquid increases with increasing concentra-
tion of the alcohol.   The increased potential energy decreases
the stability of the orientation, which tends, therefore, to change
over into one of the second type in which the doublets more or
less cancel one another so that the potential energy of the system
diminishes.   This hypothesis does not explain entirely the be-
havior of the alcohols in solution in hexane and heptane, in which

TABLE 4

Dielectric constants, polarizations, and refractions of isomeric octyl alcohols at 25°C.

Structure	ϵ	P	MR_D	ϵ	P	MR_D	Structure
C-C-C-C-C-C-C-OH	9.8	118.3	40.68	3.58	75.5	41.43	C-C-C-C-C-C-C (C, OH branches)
C-C-C-C-C-C-C (OH)	7.7	110.1	40.64	7.16	106.9	40.28	C-C-C-C-C-C-C (C, OH branches)
C-C-C-C-C-C-C (OH)	6.8	104.9	40.41	3.46	72.8	40.93	C-C-C-C-C-C-C-C (OH, C branches)
C-C-C-C-C-C-C (OH)	5.0	91.0	40.61	5.4	100.1	41.65	C-C-C-C-C-C-C (C, OH branches)
C-C-C-C-C-C-C-OH (C branch)	9.8	118.6	40.72	6.00	99.6	39.99	C-C-C-C-C-C-C (C, OH branches)
C-C-C-C-C-C-C-OH (C branch)	7.1	106.9	41.01	5.15	95.1	41.28	C-C-C-C-C-C-C (C, OH branches)
C-C-C-C-C-C-OH (C branch)	4.37	85.4	41.30	3.76	75.4	40.35	C-C-C-C-C-C-C (OH, C branches)
C-C-C-C-C-C-OH (C branch)	2.85	63.1	42.21	3.44	71.0	40.51	C-C-C-C-C-C (OH, C branches)

Structure				Structure			
C C-C-C-C-C-C-OH	4.95	92.6	41.41	OH C-C-C-C-C-C C	2.92	61.8	40.50
OH C-C-C-C-C-C C	5.9	100.5	41.08	OH C C-C-C-C-C-C	7.18	104.8	39.61
C OH C-C-C-C-C-C			40.82	OH C C-C-C-C-C-C	3.36	70.6	40.64

the forces between the doublets are presumably a little greater than in benzene because of the somewhat smaller dielectric constant of the solvent. More extensive investigations must be carried out on these solutions before their behavior can be safely explained.

As the electric moments of all the alcohols thus far measured, including n-octyl (see table 3), differ little from 1.7×10^{-18}, it is reasonable to suppose that the various isomeric octyl alcohols have moments not far from this value. The dielectric constants of the nine isomeric heptanes differ from 1.93 by no more than 0.015 and their polarizations differ from 34.5 by no more than 0.26 (54). If no molecular orientation or association occurred, the polarizations and dielectric constants of the octyl alcohols should be approximately the same, being calculable by means of the Debye equation from the little differing molar refractions and densities and the moment 1.7×10^{-18}. The values thus obtained are 5.9 for the dielectric constant and 100 for the polarization at 25°. In table 4 are listed the dielectric constants, molar polarizations, and molar refractions of twenty-two isomeric octyl alcohols prepared by Mr. H. B. Glass and Mr. G. B. Malone working with Professor E. Emmet Reid. The dielectric constants were measured by Mr. W. N. Stoops and the polarizations and refractions were calculated from these values and from the densities and refractive indices determined by Messrs. Glass and Malone. The quantities of the materials available were, with two exceptions, insufficient to permit of study in solution and consequent determination of the electric moments. In the formulae given for the alcohols the hydrogens are omitted in order that the positions of the hydroxyl group and the branching of the carbon chain may be more readily apparent.

It is evident that the type of orientation predominating in the alcohol depends upon the location of the hydroxyl group in the molecule. When the doublets are at the end of a long carbon chain and remote from any branch in the chain, the first type of orientation predominates, although the bulk of the molecule is doubtless quite differently placed from that in figure 3, I; but, when the doublets are attached to a tertiary carbon, they appear

to be so screened that they cannot line up to any extent in the first orientation and the second predominates, making the dielectric constant and polarization abnormally low. Every intermediate condition may be represented. As the rigidity of the chain and hence the shape of the molecule depends upon the positions both of the hydroxyl group and of the branching of the chain, the relation of the orientation to the structural formula cannot be wholly explained as yet. It is hoped that investigation of these isomers in solution may throw more light upon the question.

It must be emphasized that the orientations discussed do not conform rigidly to one type or the other, that the extreme of one type may be so modified in some substances as to differ little from the other type, that both types may occur simultaneously, that very complex arrangements are not necessarily excluded, that the attraction of the dipoles may, in some cases, be so strong as to be virtually equivalent to secondary valence forces which cause the oriented molecules to be equivalent to polymers, and that, on the other hand, the interaction of the doublets may be so slight that the orientation is negligible. This flexible theory accounts for the abnormalities which are observed in many liquids and termed the result of molecular association, without the assumption of the formation of complex molecules to which chemical formulae are often assigned in a manner somewhat taxing to the imagination. Langmuir (21) in applying his theory of molecular surface energies to liquids has obtained satisfactory results on the assumption that a completely random orientation of the molecules exists. Smyth and Engel (50) have found, however, that while the effect of molecular orientation upon the vapor pressure of the liquid is negligible in many cases where the behavior of the polarization indicates the existence of orientation, the effect is appreciable in strongly polar liquids and so great in alcohols that the theory cannot apply in the simple form used by Langmuir. One must conclude that molecular orientation too slight to be apparent in its effect upon most physical properties of liquids may have a considerable effect upon the polarization.

STRUCTURE OF DERIVATIVES OF METHANE

The symmetrical tetrahedral structure commonly ascribed to methane should have no electric moment, but some evidence has been adduced to show that the molecule may be a pyramid with the carbon at the apex and the four hydrogens at the corners of a quadrilateral base. The carbon tetrachloride molecule is regarded as tetrahedral and the advocates of the pyramidal structure suppose that a tetra-substituted methane may be either tetrahedral or pyramidal (66). The absence of electric moment in $C(NO_2)_4$, CCl_4, and $C(CH_2Cl)_4$ (10) (69) is regarded as evidence that these structures are tetrahedral, while the presence of considerable moments in the molecules of $C(OCH_3)_4$, $C(OC_2H_5)_4$, and $C(CH_2 \cdot O_2C \cdot CH_3)_4$ is supposed to show that they have the pyramidal structure (10) (66), which would almost certainly be electrically unsymmetrical and, therefore, possessed of a moment. However, in these latter compounds, as in the case of the ethers and alcohols, there are two doublets making an angle with one another at each oxygen. Since rotation is occurring around the bonds, as pointed out by Williams (69) and Höjendahl (14), the doublets would not at all times cancel one another and the average effect would result in a moment. A simple example of this effect of rotation is given by ethylene dichloride and ethylene glycol, which have large moments because of rotation about the $C-C$ bond (46) (70). Therefore, as far as the evidence given by electric moments is concerned, some of the tetra-substituted methane molecules may be pyramidal in structure but are not necessarily so, while for others the pyramidal structure is highly improbable. As the evidence favoring the pyramidal structure for methane itself is of very doubtful character, and as it is highly improbable that the pyramidal structure would have the zero moment found by Sänger for methane, we are fairly secure in adhering to the generally accepted regular tetrahedron for the methane molecule.

Reference has already been made to the moment of the methyl chloride molecule. It may be considered that the replacement of a methane hydrogen by chlorine forms a doublet, the axis of which lies in the straight line between the carbon and chlorine nuclei,

that is, the line drawn from the center through an apex of the tetrahedron. The replacement of a second hydrogen by chlorine gives another similar doublet, the axis of which should make an angle of 109° 28′ with that of the first doublet if there were no distortion of the tetrahedral structure. The resultant moment of these two doublets should then be $2\mu \cos 54° 44′$, where μ is the moment of the single doublet, that is, the moment of methylene

TABLE 5

Electric moments ($\times 10^{18}$) of certain halides and hydrocarbons

	X = Cl	Br	I
HX	1.03 (75)	0.79 (75)	0.38 (75)
CH_3X	1.59 (43a)		1.62 (29)
C_2H_5X	1.98 (43a)	1.86 (53)	1.66 (57)
C_4H_9X	1.89 (37)	1.87 (37)	
$C_7H_{15}X$		1.86 (37)	
C_6H_5X	1.52 (53)	1.5 (69)	
CH_2X_2	1.6 (39)		
CHX_3	1.05 (53)		
cis-CHX = CHX	1.85 (11)	1.22 (11)	0.75 (11)
trans-CHX = CHX	0 (11)	0 (11)	0 (11)
cis-CHCl = CHBr		1.54 (11)	
trans-CHCl = CHBr		0 (11)	
cis-CHCl = CHI			0.57 (12)
trans-CHCl = CHI			1.27 (12)
$CH_2 = CCl_2$	1.18 (11)		
$CH_2 = CH_2$		0 (54a)	
$CH_3CH_2CH = CH_2$		0.37 (54a)	
$CH \equiv CH$		0 (54a)	

chloride should be 1.155 times that of methyl chloride. The resultant of the three doublets in the chloroform molecule should be μ. Instead of being larger, the experimentally observed moment of methylene chloride is a little smaller than that of methyl chloride (table 5), because the mutual repulsion of the chlorine atoms pushes apart the negative ends of the two doublets, widening the angle between their axes and decreasing the resultant moment. In chloroform the repulsion of each of the chlorines by the other two is greater than that of the one chlorine by the other in methylene chloride, the spreading apart of the doublets is,

therefore, greater, and the resultant moment is so reduced as to be much smaller than that of methyl chloride.

The distortion of the molecule which shifts the positions of the electrical centers of gravity is shown by the moments of the hydrogen halides in table 5. As the infra-red absorption spectra show the distance of separation of the proton and the halogen nucleus to increase on passing from the chloride to the bromide to the iodide, one might expect the length and, therefore, the moment of the electric doublet to increase correspondingly. However, the reverse is true, for the binding forces on the electrons calculated from the refractions (48) decrease from chloride to bromide to iodide, thus making possible increased displacement of the electrons toward the hydrogen nuclei and shortening the distance between the positive and negative centers of gravity. In a similar fashion the moment of hydrogen sulphide is much lower than that of water (45) and the moment decreases on passing from ammonia to phosphine to arsine (64). The falling off in moment is much less pronounced in the alkyl halides, possibly because the attractive force upon the halogen electrons is less than that exerted by the proton which penetrates the halogen structure.

<center>UNSATURATED BONDS</center>

Electronic theories of valence have been applied very frequently to the double bond and, by many investigators, the double bond between two carbon atoms has been regarded as polar, one pair of electrons being shared between the two carbons and one of the carbons containing one more pair of electrons than the other. Smyth and Zahn (54a) have found the electric moment of the ethylene molecule to be zero, and have, therefore, concluded that no more than a small proportion of the ethylene molecules, if any, can be polar. Further, a molecule in which a single unpaired electron is held by each carbon might be expected to possess a moment and, if so, could not exist in any considerable quantity in ethylene. Support of this is given by the recent discovery of Vaidyanathan (62) that ethylene is diamagnetic instead of paramagnetic, as previously supposed, and should not, therefore, contain unpaired electrons. The zero moment found experi-

mentally for ethylene does not disprove the theory of Lowry (25) (26) and of Carothers (3) that a very small fraction of the molecules containing a double bond are polar at the bond and that it is this small fraction which is active. The small moment, 0.37×10^{-18}, found for α-butylene may be due to the difference in the electronegativities of the hydrogen on one side of the doubly-bonded carbons and the ethyl on the other side, as the electrons of the double bond are shown by the high refraction associated with them to be mobile and more easily displaceable than those in a single C—C bond.

If the double bond consisted essentially of a single electron pair held between the atoms and a second pair held by one atom or the other as supposed in most theories of a polar double bond, the difference in freedom of rotation between singly and doubly linked atoms would not be explained. This well recognized difficulty, which has been discussed by Sidgwick (42), is, of course, obvious in the problem of geometrical isomerism. The comparative rigidity of the double bond is brought out strikingly by the results of Errera for the moments of the acetylene dihalide molecules given in table 5, where the absence of moment in the *trans*-compound fits in admirably with the conventional representation of the double bond as formed by the sharing of an edge between two carbon tetrahedra. The doublets at the other imaginary tetrahedral apices thus brought into one plane would cancel one another in the *trans*-compounds so that the moments of the molecules would be 0. Any freedom of rotation about the bond would tend to produce electrical dissymmetry and a resultant moment, as found in ethylene chloride, bromide, and glycol (46) (70). One might wonder why the *cis*-compounds with the two halogen doublets reënforcing each other on the same side of the molecule do not have larger moments than the alkyl halides where there is only one halogen doublet. As was found in the chloromethanes and also in the dihalogenated benzenes, the two halogen atoms repel each other, widening the angle between the axes of their doublets and decreasing the resultant moment of the molecule as a whole. The repulsion and consequent widening of the angle should be greater, the larger the halogen atoms, and it is

evident that the moment is increasingly reduced on passing from chlorine to bromine to iodine. Purely geometrical considerations show that, when the two halogens are attached to the same tetrahedral carbon, the angle between their doublets is greater and the resultant moment less, as evidenced in the value for $CH_2=CCl_2$. Why the moment of $CH_2=CCl_2$ is lower than that of CH_2Cl_2 is not apparent. It may be due to some effect of the doublets upon the double bond. There is a similar difference between the approximate values calculated by Höjendahl (14) for $CH_2=CHBr$ and CH_3Br. One might expect the moments of *cis*- and *trans*-CHCl=CHI to bear somewhat the same relation to one another as those of *cis*- and *trans*-CHCl=CHBr, but the difference in electronegativity between the chlorine and iodine is apparently so great that the mobile electrons of the double bond are drawn much more strongly toward the chlorine and the electronic displacement in this direction is so great that the iodine becomes positive. Errera (12) supposes the positive end of the iodine doublet to lie toward the iodine while the negative end of the chlorine doublet is toward the chlorine. Thus, the doublets partly oppose each other and give a small moment in the *cis*-compound and partly support one another and give a larger moment in the *trans*-compound.

The rigidity of the double bond between carbon atoms is maintained in the structure proposed by Kharasch and Darkis (16) in which two pairs of electrons are shared between the two carbons, one pair being close to the carbon to which the less electronegative groups are attached and a definite polarity being postulated. This is neither proved nor disproved by the moments in table 5, but the zero moment found for ethylene shows the absence of any detectable polarity in this simple molecule, while the postulates of Kharasch and Darkis would lead us to expect a marked polarity. There appears to be no physical foundation for the postulate of Kharasch and Darkis that "the relative position of the second pair of valence electrons of the double bond depends upon the nature of radical attached to it in such a way that they are always on the carbon atom opposite to that carrying the most electronegative radicals." The more electronegative

radicals draw their binding electron pairs farther away from the carbon to which they are attached, thus increasing the effective nuclear charges of this carbon. The increased charge should tend to shift any other adjacent electrons toward this carbon and thus increase very slightly the effective nuclear charge of the carbon away from which they have shifted. A mechanism of this general character is commonly assumed to explain the transmission of an effect through a chain. The postulate of Kharasch and Darkis requires that the electrons be forced away from the carbon with the higher effective nuclear charge toward that with the lower charge. This would explain the somewhat doubtful differences observed between $CH_2{=}CCl_2$ and CH_2Cl_2 and between $CH_2{=}CHBr$ and CH_3Br, as, in the compounds containing the double bond, it would require a shift of electrons toward the carbons to which the halogens are not attached, which would decrease the moments. However effective such a postulate may be in explaining chemical behavior, it appears electrostatically unsound.

The triple bond in acetylene has been found to be electrically symmetrical (54a), the molecule having zero moment.

ELECTRICAL SYMMETRY OF THE PARAFFINS AND THE POLARITY OF SINGLE BONDS

The absence of electric moment found for the members of the paraffin series thus far studied must be considered in connection with the possible polarity of a single C—C bond and with the supposed difference in the electronegativities of alkyl radicals. The theory of alternating polarities has received much adverse criticism on chemical grounds, and the supposed physical evidence of alternation, given by melting points, heats of combustion, etc. has been shown to afford no proof of any intramolecular alternation of polarity (3) (16). The theory as proposed by Cuy (5) requires that, even in the paraffins, the carbons of the chain should be alternately positive and negative. The difference in polarity between the two carbons in ethane should give rise to an electric doublet, but no moment is found for the ethane molecule (54a). Although, because of the alternation and consequent cancelling

of the polarities, there should be no building up of large moments in the higher members of the series, there should certainly be moments in the molecules of many and differences should exist between adjacent members. n-Hexane and n-heptane have been shown to be without moment, as have also the other isomers of heptane and one octane (54). If any alternation in polarity occurred, it would be impossible that all of these molecules should be electrically symmetrical. Further evidence against an alternation in polarity is given by the absence of any difference in moment among the higher members of other homologous series to be considered presently.

The differences between the polarizations of the isomers of heptane were shown by Smyth and Stoops to be so small that the largest difference would, if due to but one pair of electrons, correspond to a displacement of the effective position of the charges of less than 3×10^{-11} cm. from a symmetrical location, that is, approximately .002 of the distance between the carbon nuclei in the chain. This distance was calculated as an upper limit for the displacement. Actually, such differences in polarization as were observed might easily occur without any lack of electric symmetry in the molecules. Hydrocarbon molecules may be resolved into various alkyl radicals to which it is customary to assign varying degrees of electronegativity. Thus, Lucas, Simpson and Carter (28) state that, in propane, due to the fact that hydrogen exerts a stronger pull on electrons than methyl does, the electron pairs joining the central carbon to hydrogens are presumably not so firmly held by the carbon, so that the polarities of all the carbon-hydrogen unions in propane are not the same, hydrogen joined to the secondary carbon being more negative than hydrogen joined to a primary carbon. If the carbon linkages are tetrahedrally arranged, this difference in the polarities would make the molecule electrically unsymmetrical. A greater effect should be produced at the central carbon of n-heptane, as the two propyl groups attached to it are supposed to be less electronegative than the methyl groups on the central carbon of propane, but n-heptane is found to possess no detectable moment. It is unnecessary to make any assumption of tetrahe-

dral linkages in order to conclude that the differently distributed groups in the isomers of heptane would give rise to electrical dissymmetry if their supposedly different electronegativities actually involved appreciably different displacements of their bonding electron pairs. The previously given calculation shows how small these displacements must be, if they exist at all. The electrical behavior of the paraffins thus gives no support to the hypothesis that the alkyl groups possess electronegativities which vary with the distance of the binding electron pair from the α-carbon.

TRANSMISSION OF INDUCED ELECTRONIC SHIFTS THROUGH A CARBON CHAIN

It would appear that the attachment of very strongly electro-negative groups to the alkyl radicals should cause greater electron displacements and accentuate the differences between the radicals. When the hydroxyl is attached to an alkyl radical to form an alcohol, a strong electric moment results. In considering the dielectric constants of methyl, ethyl, and propyl alcohols, Thomson (61) has pointed out that the intense electric field due to the principal moment of the molecule might be expected to give rise by induction on the rest of the molecule to moments of the same sign as the original moment, thus increasing the moment of the molecule as a whole. The increase in the moment of the molecule due to these small moments resulting from electronic displacement would be greater, the greater the length of the carbon chain. What appeared to be evidence of such a small increase with increasing length of the carbon chain was obtained in calculating the moments of several alcohols and in other series as well (46), but, as previously pointed out, it seems probable that the apparent small increase in moment with increasing size of the molecule was due mainly to error caused by molecular association. The strong molecular association of the alcohols and water makes their moments difficult to determine with accuracy in the liquid state, but the most recent values (table 3) lie within 0.15×10^{-18} of 1.7×10^{-18} and show no regular variation with increase in the length of the chain. This, taken in conjunction with the very

small differences observed between the accurately determined values for the vapors of water, methyl alcohol, and ethyl alcohol, shows that there is no transmission of a measurable electronic shift through the carbon chain of the alcohol molecule and no electrostatic evidence of a difference in the electronegativities of the alkyl groups in the different alcohols.

Wolf and Lederle (73) have found that the electric moments of a number of ketones, including methyl hexyl ketone and methyl nonyl ketone, differ from the value for acetone by no more than the experimental error. Their results give no evidence of any change in moment with increasing length of the hydrocarbon chain. There is thus no measurable electrostatic effect transmitted beyond the first carbons attached to the carbonyl group and no sign of any alternating polarity in the chains, the evidence agreeing with that given by the alcohols.

In the molecules of the alkyl halides, the negative end of the electric doublet is toward the halogen. Consequently, the more electronegative the group attached to the halogen, that is, the more strongly it draws the binding electron pair toward itself, the shorter is the distance between the centers of gravity of the positive and negative electricity and the smaller the moment. This works out quite satisfactorily for hydrogen, methyl, and ethyl chlorides in which the moment increases as the supposed electronegativity decreases. The difference between ethyl chloride and butyl chloride is no greater than the combined probable errors in the values. An accurate value for methyl bromide is lacking, but approximate values calculated by Höjendahl (14) indicate that the moment of methyl bromide is about 0.25×10^{-18} lower than that of ethyl bromide. The supposed differences in electronegativity of the bromides and iodides, as in the case of the chlorides, accord well with the increase in moment from hydrogen to ethyl. Beyond this, however, no difference is apparent in the chlorides and bromides, data for the iodides being lacking. The moments of chlorobenzene and bromobenzene are much higher than those of the corresponding hydrogen halides, although the phenyl group is supposed to be more electronegative than hydrogen. The supposedly different electronegativities are thus

only partially successful in explaining the differences in moment. It would appear that some effect is transmitted through the first two carbons of the chain in the halides, although the effect upon the second is small and, beyond the second, no effect is evident in the electric moment.

It is of interest to contrast this small or undetectable transmission of an electrical effect through a chain with the effect of the chain upon the ionization constants of unsubstituted and halogenated fatty acids (27). The constants for the unsubstituted acids show that, as in the case of the electric moments of the halides, lengthening of the hydrocarbon chain beyond two has little effect. The values for the halogenated acids are somewhat conflicting but, after a great drop in the effect upon the ionization when the halogen is moved from the first to the second carbon, the effect continues to diminish as the distance of the halogen from the carboxyl increases and is still noticeable in the δ-halogenated acid, where it has to be transmitted through five carbons and an oxygen. Yet, in the alkyl halides, no electronic shifts produced by halogen more than two carbons away can be detected by means of electric moments, and in the alcohols and ketones no induced shifts whatever are detected.

Our consideration of electric moments has shown that alkyl groups do not differ sufficiently in electronegativity to cause any detectable electrical dissymmetry in saturated hydrocarbons. When a halogen atom is attached to a carbon chain, only the first two carbons are apparently affected electrostatically, the β-carbon but slightly. It may be supposed that the shifts of electron pairs induced by the strongly electronegative halogen, or, putting it in other terms, by the large doublet at the end of the chain, are too small, in the carbons beyond the first two, to have any measurable electrostatic effect. Indeed, in view of the absence of any measurable induced electronic shifts in the chains of the alcohols and ketones, one may be skeptical of the differences in the halides as evidence of a general phenomenon. On the other hand, the ionization constants of the halogenated fatty acids show that the effect of a halogen is transmitted through five carbons and an oxygen. Moreover, the assumption of polarities

arising from the different electronegativities of radicals appears to be useful in explaining and predicting chemical behavior. It is difficult to believe that polarities as small as they must be, if they exist at all, in the chains of the alkyl groups or in a symmetrically located double bond can have powerful directive influence or greatly affect chemical activity or degree of ionization. The moments of any doublets existing must be so small that they would exert considerable forces only at very short distances and, at these distances, the interatomic forces which vary inversely as a high power of the distance should be so large that one might expect the effect of the forces due to the possible minute polarities to be negligible in comparison. In a molecule there is a possibility of a great variety of energy levels, many of which may differ from one another too little to give rise to measurable differences in polarity between molecules in which these levels are differently occupied. Too little is known of these levels in simple atoms to permit any certainty of reasoning in regard to complex compounds, but one cannot but wonder if the effects transmitted through long chains and the varied chemical behavior attributed to variation in polarity are not due to changes and differences in the energy levels occupied by the valence electrons.

CONCLUSIONS

The theory of Debye applies to gases and to dilute solutions in non-polar solvents and can be used to obtain the electric moments of molecules in the vapor state or in dilute solution. The effects of neighboring polar molecules upon one another cause deviations from the relations required by the Debye theory and these deviations may be used to study the orientation or possible association of the molecules. The deviation of various properties of liquids from normal behavior, which many investigators have attributed to the formation of molecular complexes of definite chemical formulae, may be explained in terms of mere orientation of the molecules relative to one another and of the electric forces acting between them. In extreme cases the orientation may become so pronounced and the forces so strong that definite complex molecules are formed. The tendency to orient

depends upon the shape of the molecule, upon the presence or absence of electric doublets in the molecule, upon the sizes and locations of the doublets and the directions of their axes, and, possibly, upon the nature of the molecular surfaces.   The molecular arrangements are probably simple and very incomplete and more than one type of orientation may occur in the same liquid.   The extent of the orientation, and even, in some cases, the type, varies with the temperature and the distance apart of the molecules.

The electric moment is shown to be the result of the electrically unsymmetrical distribution of electrons and nuclei in the molecule and, as such, to provide a means of studying molecular structure. The alcohols, ethers, and chloromethanes show how the moment of the molecule as a whole is the resultant of the moments of the doublets in the molecule, and how the directions of the axes of these doublets are altered by the steric effects of the atomic groups involved in the doublets.   The moments of the acetylene dihalides give evidence of the absence of rotation about the double bond and show that, in these molecules, the atoms all lie in the same plane.   The absence of electric moment in ethylene and acetylene shows the double and triple bonds to be essentially non-polar, although the small moment found for α-butylene indicates that the ease of displacement of the electrons in the double bond may give rise to some polarity when the bond is unsymmetrically located in the molecule.

The absence of moment in the paraffins gives no evidence of alternating polarities in the carbon chain or of any inherent dissymmetry in the electron linkages of alkyl radicals.   The constancy of the moments in the series of the alcohols, ketones, and higher alkyl halides leads to the same conclusion and shows no transmission of a measurable polarity through the carbon chain except in the alkyl halides, where a difference in moment between the methyl and ethyl halides indicates a small effect in the second carbon, beyond which no effect is detected in the longer chains.   The results suggest that the directive influences and effects upon chemical activity commonly attributed to differences in polarity may be due to differences in the energy levels occupied

by the valence electrons, which may or may not give rise to measurable polarity, and that polarity may occur as an accompanying result rather than as a determining factor in chemical behavior. Although pronounced polarity is doubtless a factor in chemical behavior, a large portion of the polarities assigned by the various electronic theories of valence must be regarded not as physical fact but merely as a pragmatic representation of chemical behavior.

REFERENCES

(1) BELL: Phil. Mag. **47**, 549 (1924).
(2) BRAUNMÜHL: Physik. Z. **28**, 141 (1927).
(3) CAROTHERS: J. Am. Chem. Soc. **46**, 2226 (1924).
(4) CLAUSIUS: Mech. Wärmetheorie **2**, 94 (1879).
(5) CUY: J. Am. Chem. Soc. **42**, 503 (1920).
(6) DEBYE: Physik. Z. **13**, 97 (1912).
(7) DEBYE: Handbuch der Radiologie (Marx) **6**, 597–667, Leipzig (1925).
(8) DOLEZALEK: Z. physik. Chem. **64**, 727 (1908); ibid. **93**, 585 (1918).
(9) DOLEZALEK AND SCHULZE: Z. physik. Chem. **83**, 45 (1913).
(10) EBERT AND VON HARTEL: Naturwissenschaften **15**, 668 (1927).
(11) ERRERA: Physik. Z. **27**, 764 (1926).
(12) ERRERA: Physik. Z. **29**, 689 (1928).
(13) GANS: Ann. Physik **64**, 481 (1921).
(14) HÖJENDAHL: Thesis, Copenhagen (1928).
(15) JONA: Physik. Z. **20**, 14 (1919).
(16) KHARASCH AND DARKIS: Chem. Rev. **5**, 571 (1928).
(17) KRCHMA AND WILLIAMS: J. Am. Chem. Soc. **49**, 2408 (1927).
(18) KRONIG: Proc. Nat. Acad. Sci. **12**, 488 (1926).
(19) LANGE: Z. Physik **33**, 169 (1925).
(20) LANGEVIN: J. Phys. (4) **4**, 678 (1905); Ann. chim. phys. (8) **5**, 70 (1905).
(21) LANGMUIR, Third Colloid Symposium Monograph, p. 3 (1925). The Chemical Catalog Company, New York.
(22) LATIMER AND RODEBUSH: J. Am. Chem. Soc. **42**, 1419 (1920).
(23) LORENTZ: Ann. Physik **9**, 641 (1880).
(24) LORENZ: Ann. Physik **11**, 70 (1880).
(25) LOWRY: Trans. Faraday Soc. **19**, 488 (1923).
(26) LOWRY: Trans. Chem. Soc. **123**, 822 (1923).
(27) LOWRY: Trans. Faraday Soc. **46**, 2226 (1924).
(28) LUCAS, SIMPSON AND CARTER: J. Am. Chem. Soc. **47**, 1462 (1925).
(29) MAHANTI AND SEN GUPTA: Indian J. Phys. **12**, 191 (1928).
(30) MANNEBACK: Physik. Z. **27**, 563 (1926).
(31) MAXWELL: Treatise on Electricity, Vol. II, Oxford (1881).
(32) MENSING AND PAULI: Physik. Z. **27**, 509 (1926).
(33) MILES: Unpublished measurements by Dr. J. B. Miles.
(34) MOSSOTTI: Mem. della Soc. ital. Sci. Modena **14**, 49 (1850).
(35) PAULI, W., JR.: Z. Physik. **6**, 319 (1921).

(36) PAULING: Proc. Nat. Acad. Sci. **12**, 32 (1926); Phys. Rev. **27**, 568 (1926).
(37) ROGERS: Unpublished measurements by Mr. H. E. Rogers.
(38) SÄNGER: Physik. Z. **27**, 165 (1926).
(39) SÄNGER: Physik. Z. **27**, 556 (1926).
(40) SÄNGER: Physik. Z. **28**, 455 (1927).
(41) SCHULZE AND HOCK: Z. physik. Chem. **86**, 445 (1914).
(42) SIDGWICK: Trans. Faraday Soc. **19**, 469 (1923).
(43) SIDGWICK: The Electronic Theory of Valency, p. 134, Oxford University Press, Oxford (1927).
(43a) SIRCAR: Indian J. Phys. **12**, 197 (1928).
(44) SMYTH: Phil. Mag. **45**, 849 (1923).
(45) SMYTH: Phil. Mag. **47**, 530 (1924).
(46) SMYTH: J. Am. Chem. Soc. **46**, 2151 (1924).
(47) SMYTH: J. Am. Chem. Soc. **47**, 1894 (1925).
(48) SMYTH: Phil. Mag. **50**, 361 (1925).
(49) SMYTH: J. Am. Chem. Soc. **51**, 2051 (1929).
(50) SMYTH AND ENGEL: J. Am. Chem. Soc. **51**, 2646, 2660 (1929).
(51) SMYTH, ENGEL AND WILSON: J. Am. Chem. Soc. **51**, 1736 (1929).
(52) SMYTH, MORGAN AND BOYCE: J. Am. Chem. Soc. **50**, 1536 (1928).
(53) SMYTH AND MORGAN: J. Am. Chem. Soc. **50**, 1547 (1928).
(53a) SMYTH AND MORGAN: Unpublished measurements.
(54) SMYTH AND STOOPS: J. Am. Chem. Soc. **50**, 1883 (1928).
(54a) SMYTH AND ZAHN: J. Am. Chem. Soc. **47**, 2501 (1925).
(55) STEWART: Phys. Rev. **32**, 153 (1928).
(56) STEWART AND SKINNER: Phys. Rev. **31**, 1 (1928).
(57) STOOPS: Unpublished measurements by Dr. W. N. Stoops.
(58) STRANATHAN: Phys. Rev. **31**, 653 (1928).
(59) STUART: Z. Physik **47**, 457 (1928).
(60) STUART: Z. Physik **51**, 490 (1928).
(61) THOMSON: Phil. Mag. **46**, 497 (1923).
(62) VAIDYANATHAN: Indian J. Phys. **12**, 165 (1928).
(63) VAN VLECK: Nature **118**, 226 (1926); Phys. Rev. **29**, 727 (1927); ibid. **30**, 31 (1927).
(64) WATSON: Proc. Roy. Soc. (London) **117A**, 61 (1927).
(65) WEIGT, H.: Physik. Z. **22**, 643 (1921).
(66) WEISSENBERG: Naturwissenschaften **15**, 662 (1927); Physik. Z. **28**, 829 (1927).
(67) WILLIAMS: Private communication by Prof. J. W. Williams.
(67a) WILLIAMS: Physik. Z. **29**, 174 (1928).
(68) WILLIAMS: Physik. Z. **29**, 204 (1928).
(69) WILLIAMS: Physik. Z. **29**, 683 (1928).
(70) WILLIAMS: Z. physik. Chem. **138A**, 75 (1928).
(71) WILLIAMS AND KRCHMA: J. Am. Chem. Soc. **49**, 1676 (1927).
(72) WILLIAMS AND OGG: J. Am. Chem. Soc. **50**, 94 (1928).
(73) WOLF AND LEDERLE: Physik. Z. **29**, 948 (1928).
(74) WOLFKE: Physik. Z. **29**, 713 (1928).
(75) ZAHN: Phys. Rev. **24**, 400 (1924).
(76) ZAHN: Phys. Rev. **27**, 329 (1926).
(77) ZAHN: Phys. Rev. **27**, 455 (1926).