The Dielectric Properties of Insulating Materials

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This paper gives a qualitative account of the way in which dielectric constant and absorption data have been interpreted in terms of the physical and chemical structure of materials. The dielectric behavior of materials is determined by the nature of the polarizations which an impressed field induces in them. The various types of polarization which have been demonstrated to exist are listed, together with an outline of their characteristics.

I. OUTLINE OF THE PHYSICO-CHEMICAL INTERPRETATION OF THE DIELECTRIC CONSTANT

THE development of dielectric theory in recent years has been along such specialized lines that there is need of some correlation between the newer and the older theories of dielectric behavior to keep clear what is common to both, though sometimes expressed in different terms. The purpose of the present paper is to outline in qualitative terms the way in which the dielectric constant varies with frequency and temperature and to indicate the type of information regarding the structure of materials which can be obtained from the study of the dielectric constant.

The important dielectric properties include dielectric constant (or specific inductive capacity), dielectric loss, loss factor, power factor, a.c. conductivity, d.c. conductivity, electrical breakdown strength and other equivalent or similar properties. The term *dielectric behavior* usually refers to the variation of these properties with frequency, temperature, voltage, and composition.

In discussing the dielectric properties and behavior of insulating materials it will be necessary to use some kind of model to represent the dielectric. The success of wave-mechanics in explaining why some materials are conductors and others dielectrics suggests that it might be desirable to use a quantum-mechanical model even in a general outline of the characteristics of dielectrics, but for the aspects of the theory of dielectric behavior with which we are immediately concerned here the behavior predicted is essentially the same as that derived on the basis of classical mechanics. However, in the course of the description of the frequency-dependence of dielectric constant we shall have occasion to make a comparison between the dispersion

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and absorption curves for light and those for electromagnetic disturbances in the electrical (i.e., radio and power) range of frequencies. The difficulty is then met that the quantum-mechanical model is the customary medium of description of the absorption of light. But, since the references to optical properties will be only incidental and for comparative purposes, there is little to be lost, even in this domain in which quantum-mechanical concepts are the familiar medium of description, in using the pre-quantum theory concepts of dispersion and absorption processes.   Thus a model operating on the basis of classical mechanics and the older conceptions of atomic structure will be sufficient for our present purposes.

On the wave-mechanical theory of the structure of matter a dielectric is a material which is so constructed that the lower bands of allowed energy levels are completely full at the absolute zero of temperature (on the Exclusion Principle) and at the same time isolated from higher unoccupied bands by a large zone of forbidden energy levels.[1] Thus conduction in the lower, fully occupied bands is impossible because there are no unoccupied energy levels to take care of the additional energy which would be acquired by the electrons from the applied field, while the zone of forbidden energy levels is so wide that there is only a negligible probability that an electron in the lower band of allowed levels will acquire enough energy to make the transition to the unoccupied upper band where it could take part in conduction. The bound electrons in a completely filled and isolated band of allowed levels can, however, interact with the applied electric field by means of the slight modifications which the applied field makes in the potential structure of the material and hence in the allowed levels.

On the other hand in the older theory of the structure of matter the essential condition which makes a material a dielectric is that the electrons and other charged particles of which it is composed are held in equilibrium positions by constitutive forces characteristic of the structure of the material. When an electric field is applied these charges are displaced, but revert to their original equilibrium positions when the field is removed.   In this account of the behavior of dielectrics this model will be sufficient, but no essential change in the relationships which will be discussed here would result if a translation were made to a model based upon quantum-mechanics.

When an electric field is impressed upon a dielectric the positive and negative charges in its atoms and molecules are displaced in opposite directions.   The dielectric is then said to be in a polarized

[1] Cf., for example, Gurney, "Elementary Quantum Mechanics," Cambridge (1934); Herzfeld, "The Present Theory of Electrical Conduction," *Electrical Engineering*, April 1934.

condition, and since the motion of charges of opposite sign in opposite directions constitutes an electric current there is what is called a *polarization current* or *charging current* flowing while the polarized condition is being formed.

For the case of a static impressed field a charging current flows in the dielectric only for a certain time after application of the field, the time required for the dielectric to reach a fully polarized condition. If the material is not an ideal dielectric, but contains some free ions, the current due to a static impressed field does not fall to zero but to a constant value determined by the conductivity due to free ions. More important than the static is the alternating current case, where the potential is continually varying and where, consequently, there must be a continuously varying current.

The dielectric behavior of different materials under different conditions is reflected in the characteristics of the charging or polarization currents, but since polarization currents depend upon the applied voltage and the dimensions of condensers it is inconvenient to use them directly for the specification of the properties of materials. Eliminating the dependence upon voltage by dividing the charge by the voltage, we have the capacity $(C = Q/V)$; and the dependence upon dimensions may be eliminated by using the dielectric constant, defined as $\epsilon = C/C_0$, where C is the capacity of the condenser when the dielectric material is between its plates and C_0 is the capacity of the same arrangement of plates in a vacuum. The dielectric constant is then a property of the dielectric material itself.

The term "dielectric polarization" is used to refer to the polarized condition created in a dielectric by an applied field of either constant or varying intensity. The *polarizability* is one of the quantitative measures of the dielectric polarization; it is defined as the electric moment per unit volume induced by an applied field of unit effective intensity. Another quantitative measure of the dielectric polarization is the *molar polarization;* this is a quantity which is a measure of the polarizability of the individual molecule, whatever the state of aggregation of the material.

The concept of polarizability is as fundamental to, and plays about the same role in, the theory of dielectric behavior as does the concept of free ions in the theory of electrolytic conduction. Just as the conductivity of a material is a measure of the product of the number of ions per unit cube and their average *velocity* in the direction of a unit applied field, so the polarizability is a measure of the number of bound charged particles per unit cube and their average *displacement* in the direction of the applied field.

In the early investigations of dielectrics two distinct types of charging current were recognized, the one in which the charging or discharging of a condenser occurred practically instantaneously and the other in which a definite and easily observable time was required. A charge accumulating in a condenser in an unmeasurably short time was variously referred to as the instantaneous charge or geometric charge or the elastic displacement. The current by which this charge is formed was called the instantaneous or geometric charging current, and similarly the terms *instantaneous dielectric constant* or *geometric dielectric constant* were used to describe the property of the medium giving rise to the effect between the condenser plates. An even wider variety of names has been used for the part of the charge which formed or disappeared more slowly. Among these are residual charge, reversible absorption, inelastic displacement, viscous displacement and anomalous displacement. The modern theory still recognizes these two distinct types of condenser charges and charging currents but the simple descriptive designations *rapidly-forming or instantaneous polarizations* and *slowly-forming or absorptive polarizations* will be adopted here, as they seem sufficient and to be preferred to terms which have more specialized connotations as to the mechanism upon which the behavior depends. The properties of these two types of charging currents and the dielectric polarizations corresponding to them appear prominently in the theories of dielectric behavior.

The total polarizability of the dielectric is the sum of contributions due to all of the different types of displacement of charge produced in the material by the applied field. Constitutive forces characteristic of the material determine both the magnitude of the polarizability and the time required for it to form or disappear. The quantitative measure of the time required for a polarization to form or disappear is called the *relaxation-time*. In the following a description will be given of the physical processes involved in the formation of dielectric polarizations, indicating the effect of chemical and physical structure upon the two quantities, magnitude and relaxation-time, which determine many of the properties of dielectric polarizations of the slowly-forming or absorptive type.

The magnitude of the polarizability k of a dielectric can be expressed in terms of a directly measurable quantity, the dielectric constant ϵ, by the relation

$$k = \frac{3}{4\pi} \frac{(\epsilon - 1)}{(\epsilon + 2)} .$$

It is sometimes convenient to use the polarizability and the dielectric

constant interchangeably in the qualitative discussion of the magnitude of the dielectric polarization. In dealing with alternating currents the fact that polarizations of the absorptive type require a time to form which is often of the same order of magnitude as, or greater than, the period of the alternations, results in the polarization not being able to form completely before the direction of the field is reversed. This causes the magnitude of the dielectric polarization
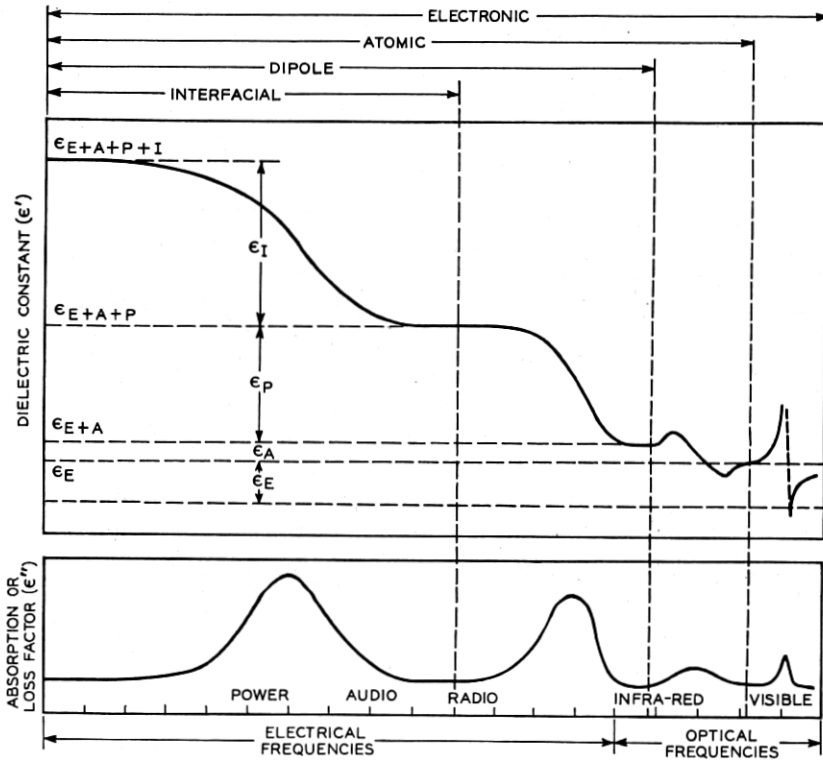

Fig. 1—Schematic diagram of variation of dielectric constant and dielectric absorption with frequency for a material having electronic, atomic, dipole and interfacial polarizations.

and dielectric constant to decrease as the frequency of the applied field increases. An example of this variation of the dielectric constant with frequency is shown in the radio and power frequency section of the curve plotted in Fig. 1. It is often convenient to refer to the mid-point of the decreasing dielectric constant-frequency curve as the *relaxation-frequency;* this frequency f_m is very simply related to the relaxation-time τ, for the theory of these effects shows that $f_m = 1/2\pi\tau$.

Various types of polarization can be induced in dielectrics: There should be an electronic polarization due to the displacement of electrons with respect to the positive nuclei within the atom; an atomic polarization due to the displacement of atoms with respect to each other in the molecule and in certain ionic crystals, such as rock salt, to the displacement of the lattice ions of one sign with respect to those of the opposite sign; dipole polarizations due to the effect of the applied field on the orientations of molecules with permanent dipole moments; and finally interfacial (or ionic) polarizations caused by the accumulation of free ions at the interfaces between materials having different conductivities and dielectric constants.

Electronic Polarizations

A classification of dielectric polarizations into rapidly-forming or instantaneous polarizations and slowly-forming or absorptive polarizations has been made. Instantaneous polarizations may be thought of as polarizations which can form completely in times less than say 10^{-10} seconds, that is, at frequencies greater than 10^{10} cycles per second or wave-lengths of less than 1 centimeter, and so beyond the range of conventional dielectric constant measurements. The *electronic polarizations* are due to the displacement of charges within the atoms, and are the most important of the instantaneous polarizations. The polarizability per unit volume due to electronic polarizations may be considered to be a quantity which is proportional to the number of bound electrons in a unit volume and inversely proportional to the forces binding them to the nuclei of the atoms.

The effect of number of electrons and binding force is illustrated by a comparison of the values for the polarizability per unit volume of different gases; for the number of molecules per unit volume is independent of the composition of the gas. Thus, although a c.c. of hydrogen with two electrons per molecule has the same number of electrons as a c.c. of helium, which is an atomic gas with two electrons per atom, the quantity $\epsilon - 1$, that is the amount by which the dielectric constant is greater than that of a vacuum, is nearly four times as large for hydrogen as for helium. This shows that in hydrogen the electrons are in effect less tightly bound to the nucleus than in helium, resulting in a larger induced polarization. Nitrogen has a larger dielectric constant than either hydrogen or helium because it has 14 electrons per molecule. Some of these are tightly bound as in helium and some are more loosely bound as in hydrogen.

The dielectric constant of *liquid* nitrogen is 1.43, which is much higher than the value 1.000600 for the gas. This is due to the fact

that the number of molecules, and consequently of bound charges, per unit volume is much greater in the liquid than in the gas. However, the molar polarization, a quantity which is corrected for variations in density, is the same for liquid as for gaseous nitrogen.

The time required for the applied field to displace the electrons within an atom to new positions with respect to their nuclei is so short that there is no observable effect of time or frequency upon the value of the dielectric constant until frequencies corresponding to absorption lines in the visible or ultra-violet spectrum are reached. For convenience in this discussion the frequency range which includes the infra-red, visible and ultra-violet spectrum will be called the *optical frequency range* while that which includes radio, audio and power frequencies will be called the *electrical frequency range*. For all frequencies in the electrical range the electronic polarization is independent of frequency and for a given material contributes a fixed amount to the dielectric constant, but at the frequencies in the optical range corresponding to the absorption lines in the spectrum of the material, the dielectric constant, or better the refractive index, changes rapidly with frequency, and absorption appears. (The justification for using refractive index n and dielectric constant ϵ interchangeably for the qualitative discussion of the properties of dielectric polarizations follows from the relation, $\epsilon = n^2$, which is known as Maxwell's rule. This is a general relationship based upon electromagnetic theory and is applicable whenever ϵ and n are measured at the same frequency no matter how high or low it may be.)

The electronic polarization of a molecule may be regarded as an additive property of the atoms or of the atomic bonds in the molecule, and may be calculated for any dielectric of known composition with sufficient accuracy for most purposes. Within any one chemical class of compounds such as, for example, the saturated hydrocarbons or their simple derivatives, in which all of the bonds are $C-H$, $C-C$ or $C-X$, the calculated values agree with the measured to within a few per cent. For other classes of compounds—for example, benzene, in which there are both single and double bonds such calculations must be corrected for the fact that some of the valence electrons have their binding forces and hence their polarizabilities altered in the double bond as compared to the single bond. Such values of electronic polarization, usually called atomic refractions, have been determined for all of the different types of bonds from the vast amount of experimental study of refractive indices of organic and inorganic compounds.

In some materials the electronic polarization is the only one of importance. For example, in benzene the dielectric constant is the

same at all frequencies in the electrical range and is equal to the square of the optical refractive index.   This must mean that the only polarizable elements of consequence in C_6H_6 are electrons which are capable of polarizing as readily in the visible spectrum, where the refractive index is measured, as at lower frequencies where dielectric constant is measured.   The refractive index in the visible spectrum provides the means of determining the magnitude of electronic polarizations, for other types of polarization are usually of negligible magnitude when the frequency of the impressed field lies in the visible spectrum.   For materials having only electronic polarizations the dielectric properties are very simply dependent upon the chemical composition and the temperature, and are independent of frequency in the electrical frequency range.   In many materials, however, there are also other polarizations which can form at low frequencies but not at high; these are characterized by more complex dielectric behavior.

Atomic Polarizations

Included among the polarizations which may be described as instantaneous by comparison with the order of magnitude of the periods of alternation of the applied field in the electrical frequency range are those arising from the displacement of the ions in an ionic crystal lattice (such as rock salt) or of atoms in a molecule or molecular lattice. In some few materials, for example the alkali halides, sufficient study has been made of the infra-red refractive index to provide data on the atomic polarizations, but for most substances little is known about them.   What is known has in part been inferred from infra-red absorption spectra and in part from the infra-red vibrations revealed by studies of the Raman effect.

Atomic polarizations are distinguished from electronic polarizations by being the part of the polarization of a molecule which can be attributed to the relative motion of the atoms of which it is composed. The atomic polarizations may be attributed to the perturbation by the applied field of the vibrations of atoms and ions having their characteristic or resonance frequencies in the infra-red.   Atomic polarizations may be large for substances such as the alkali halides and other inorganic materials, but are usually negligible for organic materials. The exact value of the time required for the formation of atomic polarizations is unimportant in the electric range of frequencies with which we are primarily concerned.   The essential thing is that atomic polarizations begin to contribute to ϵ(or n^2) at frequencies below approximately 10^{14} seconds—that is, in the near infra-red and that below about 10^{10} cycles per second, where the optical and electrical

frequency ranges merge, atomic polarizations contribute a constant amount to ϵ(or n^2) for a given material. The atomic polarization is determined as the difference between the polarization which is measured at some low infra-red or high electric frequency and the electronic polarization as determined from refractive index measurements in the visible spectrum.

The electronic and atomic polarizations are considered to comprise all of the so-called instantaneous polarizations; that is, the polarizations which form completely in a time which is very short as compared with the order of magnitude of the periods of applied fields in the electrical range of frequencies.

The Debye Orientational Polarization

The remaining types of polarization are of the "absorptive" kind, characterized by relaxation-times corresponding to "relaxation-frequencies" in the electrical range of frequencies. These polarizations include the important type which is due to the effect of the applied field on the orientation of molecules with permanent electric moments, the theory of which was developed by Debye. Among the other possible polarizations of the absorptive type are those due to inter-facial effects or to ions which are bound in various ways.

Debye,[2] in 1912, suggested that the high dielectric constant of water, alcohol and similar liquids was due to the existence of permanent dipoles in the molecules of these substances. The theory which Debye based upon this postulate opened up a new field for experimental investigation by providing a molecular mechanism to explain dielectric behavior which fitted into and served to confirm the widely held views of chemical structure. Debye postulated that the molecules of all substances except those in which the charges are symmetrically located possess a permanent electric moment which is characteristic of the molecule. In a liquid or gas these molecular dipoles are oriented at random and therefore the magnitude of the polarization vector is zero. When an electric field is applied, however, there is a tendency for the molecules to align themselves with their dipole axes in the direction of the applied field, or, put in another way, to spend more of their time with their dipole axes in the direction of the field than in the opposite direction. This dipole polarization is superimposed upon the electronic and atomic polarizations which are also induced by the field. The theory as developed by Debye accounts for the observed difference between the temperature and frequency dependence of the dipole polarizations and the instantaneous polarizations. While the latter are present in all dielectrics, the dipole polarizations can

[2] P. Debye, *Phys. Zeit.*, *13*, 97, (1912); *Verh. d. D. phys. Ges.*, *15*, 777 (1913).

occur only in those made up of molecules which are electrically asymmetrical.

Polar molecules (that is molecules with permanent electric moments) are, by definition, those in which the centroid of the negative charges does not coincide with the centroid of the positive charges, but falls at some distance from it. All materials must be classed either as polar or non-polar, the latter class including those which are electrically symmetrical. Some simple examples of non-polar molecules

METHANE
(CH_4)

CARBON TETRACHLORIDE
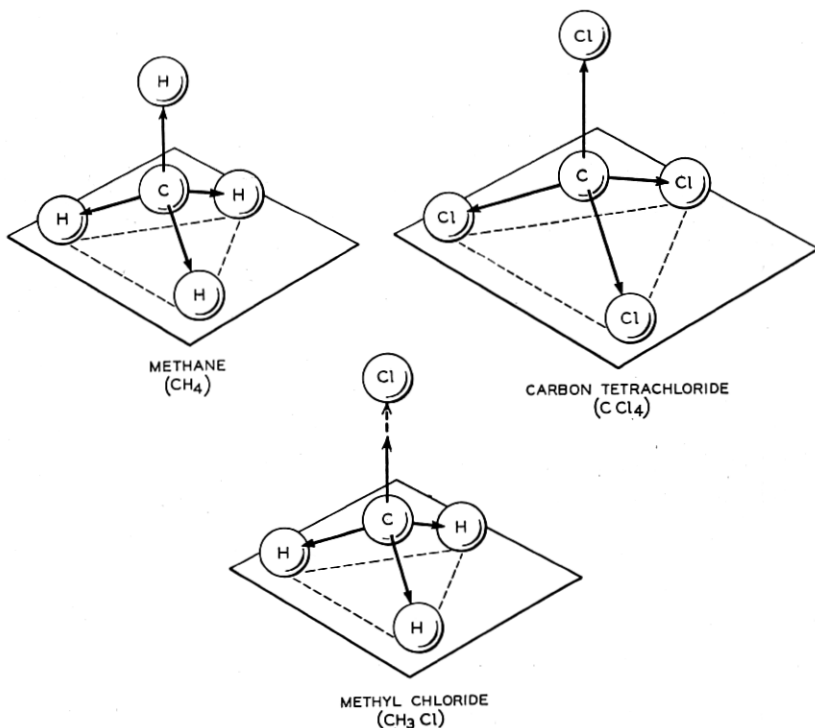($C Cl_4$)

METHYL CHLORIDE
($CH_3 Cl$)

Fig. 2—Methane and carbon tetrachloride are non-polar molecules each having four equal vector moments whose sum is zero. Methyl chloride is polar because the sum of the vector moments is not zero.

are H_2, N_2, O_2, CH_4, CCl_4 and C_6H_6. In these molecules each C — H, C — Cl or other bond may be regarded as having a vector dipole moment of characteristic magnitude located in the bond. Where the sum of these vector moments is zero the molecule will be non-polar. Both CH_4 and CCl_4 meet this requirement but CH_3Cl is polar because the C — Cl vector moment is considerably greater than the resultant of the three C — H vectors. (See Fig. 2.) Polar molecules are the rule and non-polar the exception.

In the discussion of dipole polarizations it has frequently been pointed out that non-polar materials usually obey the general relationship $\epsilon = n^2$ whereas for polar materials such as H_2O, NH_3 and HCl this rule is apparently not obeyed. Water, for example, has $n^2 = 1.7$ and $\epsilon = 78$. This apparent discrepancy arises because the refractive index as measured in the *visible* spectrum is usually compared with the dielectric constant as measured in the electric range of frequencies. Non-polar materials usually have only electronic polarizations and these can form both in the optical and in the electrical frequency ranges, but the dipole polarizations can form and contribute to the dielectric constant only in the electrical frequency range; this is the most frequent source of the above mentioned discrepancy. The general relationship $\epsilon = n^2$ should apply for any material at any frequency provided ϵ and n are measured at the same frequency. The refractive index of water when measured with electric waves,[3] for example, at a million cycles, is found to be slightly less than 9, the square of which agrees very well with the observed value $\epsilon = 78$. However, it does not always follow that when $\epsilon > n^2$ the molecules of which the material is composed have permanent dipole moments, for this condition can also result from the presence of any slowly-forming or absorptive polarization or of a large atomic polarization. Experimental investigations based upon the Debye theory have shown, however, that in the case of water and many other familiar compounds the orientation of dipole molecules actually accounts for the high dielectric constant.

The Debye theory shows that the magnitude of the dipole polarization of a material is proportional to the square of the electric moment of the molecule, which, as has been pointed out, may be regarded as the vector sum of a number of constituent moments characteristic of the individual atoms or radicals of which the molecule is composed, or alternatively, of the bonds which bind these atoms into molecules or more complex aggregates. The very great amount of experimental study of the Debye theory has shown that the NO_2 and CN groups have the largest group moments while CO, OH, NH_2, Cl, Br, I and CH_3 have progressively smaller group moments. The value 34 for the dielectric constant of nitrobenzene ($C_6H_5NO_2$), as against 5.5 for chlorobenzene (C_6H_5Cl), 2.8 for methyl benzene ($C_6H_5CH_3$) and 2.28 for benzene (C_6H_6), which is non-polar, are evidence of the large differences in the magnitudes of these group moments and the large part that dipole moments can play in determining the dielectric constant.

[3] Drude, "Physik des Aethers," Stuttgart (1894), p. 486.

Another point regarding molecular structure shown by such studies is that it is not only the presence of polar groups in the molecule but also their position which determines the electric moment of the molecule. This is nicely illustrated by the dichlorobenzenes, of which there are three isomers. As is shown in Fig. 3, ortho-dichlorobenzene, having the two substituent groups in adjacent positions, is the most asymmetrical of the three compounds, and consequently has the high-
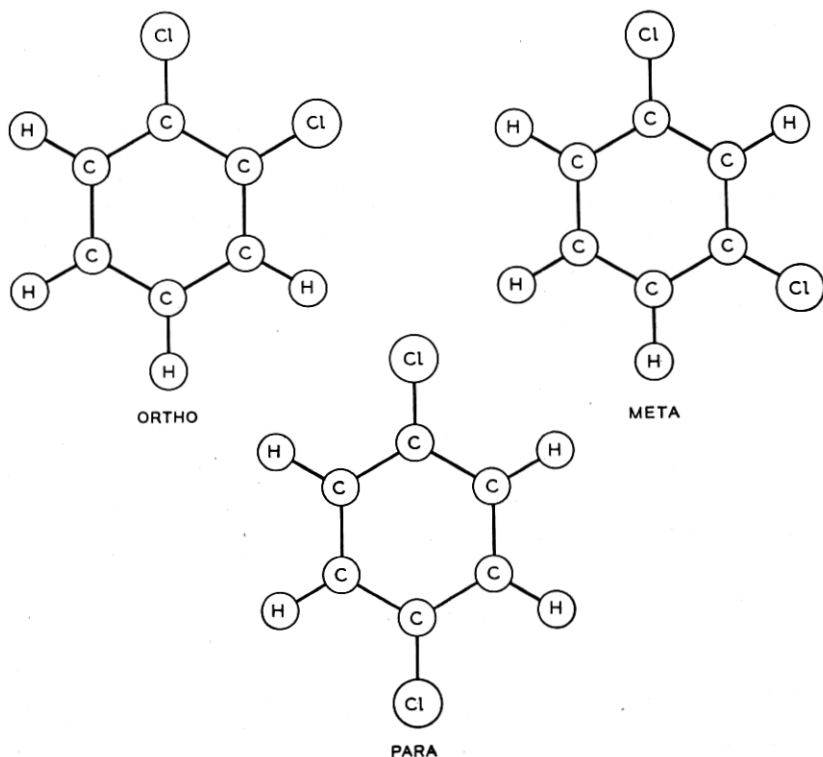

ORTHO

META

PARA

Fig. 3—Ortho dichlorobenzene being the more asymmetrical has a higher electric moment than the meta isomer; the para isomer which is symmetrical has zero electric moment.

est electric moment, $\mu = 2.3$. The meta compound has about the same moment as monochlorobenzene, $\mu = 1.55$. The para compound, however, is symmetrical and has zero electric moment because the Cl atoms are substituted on opposite sides of the benzene ring so that their vector moments cancel. These values of electric moment are reflected in the values of dielectric constant which are respectively 10, 5.5 and 2.8 for the three isomeric dichlorobenzenes.

Dielectric studies of this kind have also shown, for example, that H_2O is not a symmetrical linear molecule, $H - O - H$, but rather a triangular structure $O\diagdown_H^H$. CO_2 on the other hand, being non-polar, is determined to be a linear molecule $O = C = O$. Thus, dielectric measurements interpreted by the Debye theory have become established as one of the standard means of studying molecular structure.

Since dipole polarizations depend upon the relative orientations of molecules, rather than upon the displacement of charges within the atom or molecule, the time required for a polarization of this type to form depends upon the internal friction of the material. Debye expressed the time of relaxation of dipole polarizations in terms of the internal frictional force by the equation:

$$\tau = \frac{\zeta}{2kT} = \frac{8\pi\eta a^3}{2kT},$$

where ζ is the internal friction coefficient, η is the coefficient of viscosity, a the radius of the molecule and T the absolute temperature.[4] This latter expression, because it depends on Stokes' law for a freely falling body, is rigidly applicable only to gases or possibly to dilute solutions of polar molecules in non-polar solvents in which the polar molecules are far enough apart that they exert no appreciable influence on each other.

Applying this equation to the calculation of the relaxation-time of the orientational polarizations in water at room temperature we obtain $\tau = 10^{-10}$ seconds, assuming a molecular radius of 2×10^{-8} cm. and taking the viscosity as 0.01 poises.[5] The relaxation-frequency corresponding to this relaxation-time is about 1.6×10^9 cycles/sec., agreeing with the results of experimental studies on water which show that in the range of frequencies extending from 10^9 to 10^{11} cycles the dielectric constant decreases from its high value to a value approximately equal to the square of the refractive index. Thus the drop in dielectric constant occurs in the frequency range which corresponds to the calculated value of the relaxation-time.

Similar experiments on dilute solutions of alcohols [6] in non-polar solvents yield values of τ of about 10^{-9} seconds. The shortest relaxation-times which dipole polarizations can have are probably not

[4] P. Debye, "Polar Molecules," Chem. Cat. Co., 1929, p. 85.
[5] The viscosity of a liquid in poises is given by the force in dynes required to maintain a relative tangential velocity of 1 cm./sec. between two parallel planes in the liquid each 1 cm.[2] in area and 1 cm. apart, the distance being measured normal to their surfaces.
[6] R. Goldammer, *Phys. Zeit.*, 33, 361 (1932).

much less than the order of 10^{-11} seconds, since in general either the internal friction or the molecular radius of materials having polar molecules will be greater than those of water, resulting in longer relaxation-times. No long-time limit can be placed on the relaxation-times which dipole polarizations may have, for they are limited only by the values which the internal friction can assume. For materials, such as glycerine, which tend to become very viscous at low temperatures the time of relaxation of the dipoles may be a matter of minutes. Studies of the dielectric constant of crystalline solids, to be discussed in a later paper, show also that in some cases polar molecules are able to rotate even in the crystalline state, where the ordinary coefficient of viscosity has no meaning because the materials do not flow. In connection with the dielectric properties we are concerned only with the ability of the polar molecules to undergo rotational motion and it is likely that in these solids, which constitute a special class, the internal frictional force opposing rotation of the molecules is small even though the forces opposing translational motion may be very large. The particular equation for the calculation of the time of relaxation given above obviously does not apply to solids.

In discussing the three types of polarizations which have been considered thus far, it has been pointed out that the magnitude of the dielectric constant depends upon the polarizability of the material. Each type of polarization makes a contribution to the dielectric constant if the measuring frequency is considerably below its relaxation-frequency. However, if the frequency of the applied field used for measuring the dielectric constant is too high the presence of polarizations with low relaxation-frequencies will not be detected. Thus the refractive index of water in the visible spectrum is 1.3 and therefore gives no evidence whatever of the presence of permanent dipoles. This is due to the fact that the H_2O molecules do not change their orientations rapidly enough to allow fields which alternate in direction as rapidly as those of light to cause an appreciable deviation from the original random orientation which prevails in the absence of an applied field.

The band of frequencies in which the dielectric constant decreases with increasing frequency because of inability of the polarization to form completely in the time available during a cycle, is called a region of absorption or of *anomalous dispersion*. The discussion of this characteristic of dielectric materials forms an important part of dielectric theory. The term anomalous dispersion is no doubt usually thought of in connection with the anomalous dispersion of light: when the refractive index of light decreases with increasing frequency the

material is said to display anomalous dispersion in the range of frequencies concerned. However, in a paper published in 1898 Drude [7] applied this term to the decrease of dielectric constant with increasing frequency in the electrical range of frequencies. The justification for this extension of the original application of the term is very direct for electromagnetic theory shows that the dielectric constant and the refractive index of a material are connected by the general relationship $\epsilon = n^2$ whatever the frequency of the electromagnetic disturbance. As the dispersion of light by a prism is due to the variation of its refractive index with frequency, the use of the expression *anomalous dispersion* to refer to the decrease of dielectric constant with increasing frequency is consistent and has become generally accepted.

Interfacial Polarizations

The polarizations thus far considered are the main types to be expected in a *homogeneous* material. They depend upon the effect of the applied field in slightly displacing electrons in atoms, in slightly distorting the atomic arrangement in molecules and in causing a slight deviation from randomness in the orientation of polar molecules. The remaining types of polarization are those resulting from the *heterogeneous* nature of the material and are called *interfacial polarizations*. Interfacial polarizations must exist in any dielectric made up of two or more components having different dielectric constants and conductivities except for the particular case where $\epsilon_1\gamma_2 = \epsilon_2\gamma_1$, γ being the conductivity [8] and the subscripts referring to the two components. Heterogeneity in a dielectric may be due to a number of causes, and in the case of practical insulating materials is probably the rule rather than the exception. Impregnated paper condensers and laminated plastics are obvious examples of heterogeneous dielectrics. Paper is itself a heterogeneous dielectric, consisting of water and cellulose. In all probability the plastic resins are also heterogeneous, and certainly so if they contain fillers. Ceramics, being mixtures of crystalline and glassy phases, are also heterogeneous.

The simplest case of interfacial polarization is that of the *two-layer* dielectric, that is, a composite dielectric made up of two layers, the dielectric constants and conductivities of which are different. Maxwell showed that in such a system the capacity was dependent upon the charging time. This is due to the accumulation of charge at the interface between the two layers, for this charge must flow through a

[7] P. Drude, *Ann. d. Physik, 64,* 131 (1898), "Zur Theorie der anomalien elektrischen Dispersion."

[8] In this expression γ represents the total a.c. conductivity, a quantity which depends on the frequency.

layer of dielectric whose resistance may be high enough that the interface does not become completely charged during the time allowed for charging.   For the alternating current case this implies a decrease of capacity with increasing frequency, which is equivalent to the anomalous dispersion which has been described for the case of dipole polarizations.   It should be particularly emphasized that the term *anomalous dispersion* describes a type of variation of dielectric constant with frequency which can be produced by a number of different physical mechanisms.

The two-layer dielectric is of less interest than a generalization of this type of polarization which includes heterogeneous systems composed of particles of one dielectric dispersed in another.   This type of heterogeneous dielectric is of considerable importance since such systems represent the actual structure of many practical dielectrics. Such a generalization of the two-layer dielectric has been made by K. W. Wagner [9] who developed the theory for the case of spheres of relatively high conductivity dispersed in a continuous medium of low conductivity.   The conditions for the existence of an interfacial polarization are, as in the two-layer case, that $\epsilon_1\gamma_2 \neq \epsilon_2\gamma_1$, where the symbols have the significance just given.   This type of polarization, which is variously referred to as an interfacial polarization, an ionic polarization and a Maxwell-Wagner polarization, shows anomalous dispersion like other absorptive polarizations.   When the particle size is small as compared with the electrode separation it may be treated as a uniformly distributed polarization.

The magnitude and time of relaxation of interfacial polarizations are determined by the differences in ϵ and γ of the two components. There is a widely prevalent opinion that this type of polarization always has such long relaxation-times as to be observed only at very low frequencies.   While this is true for mixtures of very low-conductivity components, the general equations show that for the case where one component has a high conductivity—for example equal to that of a salt solution—the dispersion may occur in the radio frequency range.

Several special types of interfacial polarization have been proposed to explain the dielectric properties of various non-homogeneous dielectrics where something regarding the nature of the inhomogeneity is known.   The dielectric constant of cellulose, for example, receives a contribution from an interfacial polarization due to the water and dissolved salt which it contains.   Experimental evidence indicates that an aqueous solution of various salts is distributed through the

[9] K. W. Wagner, *Arch. f. Elektrotechn.*, 2, pp. 374 and 383.

cellulose in such a way as to form a reticulated pattern which may correspond to the pattern formed by the micelles or to some feature of it. An interesting feature of this structure is that the conductance of the aqueous constituent can be changed by varying the moisture content or the salt content of the material and the effect on the dielectric constant observed.[10]

Frequency Dependence of Dielectric Constant

As has been pointed out, each of the different types of polarization may contribute to the dielectric constant an amount depending upon the polarizability and its time of relaxation. The upper curve in Fig. 1 shows schematically the variation of the dielectric constant (or of the square of the refractive index) for a hypothetical material possessing an interfacial polarization with relaxation-frequency in the power range, a dipole polarization with relaxation frequency in the high radio frequency range and atomic and electronic polarizations with dispersion regions in the infra-red and visible respectively. If polarizability were plotted, instead of ϵ (or n^2), the curves would be of the same general form but of different magnitudes, because of a relationship between the two given earlier.

At the low-frequency side of Fig. 1, the dielectric constant curve has its highest value, usually called the static or zero-frequency dielectric constant. Here all of the polarizations have time to form and to contribute their full amount to the dielectric constant. With increasing frequency ϵ begins to decrease as the relaxation-frequency of the *interfacial* polarization is approached and reaches a constant lower value (called the infinite-frequency dielectric constant) when the applied frequency is sufficiently above the relaxation-frequency of the polarization that it has not time to form appreciably. It is this decrease of ϵ with frequency which is called anomalous dispersion. The horizontal arrows across the top of Fig. 1 indicate the frequency region in which the various types of polarizations indicated are able to form and contribute to the dielectric constant.

At still higher frequencies we see that ϵ again decreases as the relaxation-frequency of the *dipole* polarization is approached, and again reaches a constant lower value as the frequency becomes too high for the field to affect appreciably the orientation of dipoles. This second region of anomalous dispersion is similar to the first, which was due to interfacial polarizations. It has been shown as occurring at a higher frequency, but it should be emphasized that the frequency ranges chosen to illustrate anomalous dispersion in Fig. 1

[10] Murphy and Lowry, *Jour. Phys. Chem., 34,* 594 (1930).

are purely arbitrary.   Anomalous dispersion due to dipole polarizations has been observed at power frequencies while that due to interfacial polarizations has been observed at radio frequencies.   The two types of polarizations may in fact give rise to anomalous dispersion in the same frequency range in a given dielectric.

Proceeding to still higher frequencies in Fig. 1 other regions of dispersion appear in the infra-red and visible spectrum.   These regions show a combination of normal optical dispersion, in which the dielectric constant, or better now the refractive index, increases with frequency, and anomalous dispersion in which it decreases.   The dispersion in the visible range of frequencies is predominantly normal (anomalous dispersion being confined to relatively narrow frequency bands) whereas in the electrical range the reverse is true, normal dispersion not being observed; the infra-red represents an intermediate region.   Dipole and interfacial polarizations are not represented in the dispersion in the optical range, the dielectric constant (or refractive index) in the visible being due to electronic polarizations and in the infra-red to electronic and atomic polarizations.

The curves plotted in Fig. 1 are merely schematic and the relative magnitudes of the different contributions to the dielectric constant are therefore arbitrary.   However, experimental results indicate that the contribution ϵ_E of the electronic polarization to the dielectric constant is limited to values between 2 and 4 except for certain inorganic materials, since very few organic solids or liquids are known which have refractive indices in the visible spectrum which are greater than 2 or less than 1.4.   The contribution ϵ_A of atomic polarizations to the dielectric constant is in general small and is usually negligible, as has been indicated on the curve, although the possibility exists of special cases occurring in which the infra-red refractive indices are very high.   The contributions ϵ_P and ϵ_I of dipole and interfacial polarizations to the dielectric constant may vary greatly from one material to another, depending upon the symmetry of the molecule and the physical structure of the dielectric.   From the above mentioned limitations on the contribution to the dielectric constant which can be expected from electronic and atomic polarizations, it is apparent that the explanation of values of ϵ higher than 3 to 4, at least in organic materials, requires the existence of some absorptive polarization such as arises from dipoles or interfacial effects.   Thus all of the liquids which have high dielectric constants such as H_2O (78), alcohol (24), nitrobenzene (34) have been shown to contain polar molecules.

The lower part of Fig. 1 shows a maximum in the *absorption* for each type of dielectric polarization.   The absorption, at least in the

electrical frequency range, is due to the dissipation of the energy of the field as heat because of the friction experienced by the bound charges or dipoles in their motion in the applied field in forming the polarizations. The theory of dispersion shows that the dielectric constant and absorption are not independent quantities but that the absorption curve can be calculated from the dielectric constant vs. frequency curve and vice versa. The absorption maximum is greatest for those materials showing the greatest change in dielectric constant in passing through the dispersion region. Thus a material having a high dielectric constant must have a large dielectric loss at the frequency at which ϵ has a value half way between its low and high-frequency values.

Though the quantum theory is necessary for the explanation of many optical and electrical phenomena a simple explanation, sufficient for our purposes, of the general form of the curves of dielectric constant vs. frequency in the infra-red and visible spectrum may be given in terms of the Lorentz theory of optical dispersion. In this theory the form of the dispersion curves depends upon the variation with frequency of the relative importance of the inertia of the typical electron and of the frictional forces and restoring forces acting upon it. For electronic polarizations the frictional or dissipative force is negligible, except in the narrow frequency interval included in the absorption band, and the inertia and restoring force terms predominate. For the atomic polarizations the frictional force is larger and the absorption region extends over a wider interval of frequencies. For dipole and interfacial polarizations the influence of inertia is entirely negligible as compared with the frictional or dissipative forces so that in effect these polarizations may be thought of as aperiodically damped.

Temperature Dependence of Dielectric Constant

The dielectric constant of a material is a constant only in the exceptional case. Besides the variation with frequency which has been considered the dielectric constant varies with temperature. Electronic polarizations may be considered to be unaffected by the temperature. The refractive index does indeed change with temperature but this is completely accounted for by the change of density, and the molar refraction is independent of temperature. The atomic and ionic vibrations are, however, affected by temperature, the binding force between ions or atoms being weakened by increased temperature. This factor of itself would yield a positive temperature coefficient for the atomic polarizations but the decrease in density with the increase in temperature acts in the opposite direction. The result is that calculation of the temperature coefficient of atomic polarizations

usually yields zero or slightly positive values. What experimental data there are indicate small positive temperature coefficients for atomic polarizations.

One of the principal achievements of the Debye theory of dipole polarizations has been the manner in which it explains the large negative temperature coefficients of polarization of many liquids. Debye showed that the variation of polarization with temperature could be expressed by the relation $P = A + (B/T)$, in which the constant A is a measure of the instantaneous polarizations which are independent of temperature and B is a measure of the dipole polarizations. In a liquid or gas the molecules are continuously undergoing both translational and rotational motion, and the result of this thermal motion is to maintain a random orientation of molecules. The action of the electric field in aligning the dipoles is opposed by the thermal motion which acts as an influence tending to keep them oriented at random. As the temperature decreases, the thermal energy becomes smaller and the dipole polarization becomes larger, resulting in a negative temperature coefficient of dielectric constant.

The effect of temperature upon interfacial polarizations has not been experimentally investigated to an extent at all comparable with that of dipole polarizations. However, interest in the interfacial or ionic type of polarization has increased considerably in the past few years, and it has applications of some importance. Among these is diathermy which is becoming of considerable importance as a therapeutic agency.

The foregoing qualitative description of the behavior of the dielectric constant and the type of information regarding molecular structure which has been derived from it will be followed in the next section by the derivation of some of the quantitative relationships which are common to all polarizations of the absorptive type.