The Dielectric Properties of Insulating Materials, III
Alternating and Direct Current Conductivity

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This paper deals with the variation of a-c conductivity with frequency and with that of apparent d-c conductivity with charging time for dielectrics exhibiting anomalous dispersion (i.e., having dielectric constants which decrease with increasing frequency). The a-c conductivity of a dielectric exhibiting simple anomalous dispersion approaches a constant limiting value γ_∞ as the frequency increases. The discussion shows that γ_∞ possesses properties similar to those of the conductivity due to free ions, although in most cases it depends upon the motions of polar molecules or bound ions. It is also shown that the apparent conductivity for constant (d-c) potential approaches an initial value as the charging time is diminished. This initial conductivity γ_0 is demonstrated to be equal to the limiting value of the a-c conductivity attained at high frequencies (γ_∞), a relationship which simplifies the description of the behavior of dielectrics exhibiting simple anomalous dispersion. Dielectrics possessing the property of anomalous dispersion then have *two* conductivities: one is due to local motions of polar molecules or bound ions; the other is due to the migration of free ions to the electrodes.

Both γ_0 and γ_∞ refer to methods of measurement. It is to be noted that in many non-homogeneous dielectrics, especially those in which one part is of much higher resistivity than the remainder, both γ_0 and γ_∞ may be a measure of a free ion conductivity. As the equality of γ_0 and γ_∞ is independent of the nature of the polarization responsible for them, experimental agreement between a-c and d-c measurements cannot be used to distinguish whether the dielectric loss in a material is due to polar molecules, to bound ions, or to free ions present in a non-homogeneous dielectric. However, in homogeneous dielectrics γ_0 (or γ_∞) is a conductivity due to polar molecules or bound ions.

INTRODUCTION

THE preceding paper[1] dealt with the dielectric constant, showing mainly how it varies with the frequency of the applied alternating voltage for those dielectrics which behave in the simplest manner, and indicating the general character of the structural features responsible for this behavior. The discussion is extended here to the conductivity,

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[1] Murphy and Morgan, *B. S. T. J.*, *17*, 640 (1938).

which is not less important than the dielectric constant as a property of an insulating material. Though general aspects of the conductivity will be described for the sake of completeness, we wish mainly to show that materials which possess the property of anomalous dispersion may be considered to have *two* quite definite conductivities: one of these is the ordinary d-c conductivity due to free ions or electrons; the other is a special value of the a-c conductivity which will be discussed in this paper. We believe that the recognition of the existence in many materials of two conductivities instead of one is of considerable advantage, particularly in interpreting the behavior encountered in direct-current conductivity measurements on insulating materials, a subject upon which there has existed a considerable divergence of opinion.

The measurement of the direct-current conductivity of an insulating material is usually complicated by the fact that the current which flows when a constant potential is applied does not remain constant but decreases with time. The meaning of this variation of the current is open to more than one interpretation. Some investigators consider that its final value, approached asymptotically, and perhaps not closely approximated until a constant potential has been applied for an hour or more, is the proper basis for the calculation of the true conductivity of the material. Other investigators, notably Joffé, consider that the current/time curve should be extrapolated toward the instant of applying the voltage in order to obtain the proper value of the current to use in calculating the true conductivity. On this account the terms *initial conductivity*, *final conductivity* and *true conductivity* frequently appear in papers on the conductivity of insulating materials. While it has been usual to take either the initial or the final conductivity as the true conductivity, rejecting the other, it is shown here that with certain exceptions both conductivities are true conductivities in the sense that they are independent properties of the material having a different, though related, physical significance.

The relationships which will be brought out here depend in an essential way on the nature of the variation of a-c conductivity with frequency for materials which possess the property of anomalous dispersion. The a-c conductivity of a dielectric exhibiting simple anomalous dispersion increases as the frequency increases until the frequency is high as compared with the reciprocal of the relaxation-time; it then approaches asymptotically a constant limiting value. It is shown here that this limiting value of the conductivity, which will be referred to as the *infinite-frequency conductivity*, is a true conductivity of the material, analogous to the ordinary d-c conductivity, and that it is equal to the initial conductivity obtained by extrapolating the apparent d-c conductivity towards the instant of applying the measuring voltage. We believe that this relationship considerably simplifies the description of the meaning of certain types of measurements upon dielectrics.

In spite of the fact that several terms are already used to distinguish different conductivities, there remains some ambiguity in the meaning of these terms. For example, the physical meaning of the term d-c conductivity when applied to a dielectric is vague. Moreover, it will be evident in the later discussion that the initial conductivity will depend upon free ions for some materials and upon polar molecules for other materials. To avoid this confusion we have found it convenient to use two terms which refer to the nature of the conduction processes rather than to the method of measurement: these are *free ion conductivity* and *polarization conductivity.* The first is the ordinary conductivity due to the drift of free electrons or ions to the electrodes; the second is a conductivity determined by the energy dissipated as heat by the polarization currents in the dielectric. The latter bears the same relation to the neutral polarizable aggregates in the material, which carry the polarization currents, as does the free ion conductivity to the free ions in the dielectric. The terms free ion conductivity and polarization conductivity, or some other terms having approximately the same meaning, are essential to the discussion as they refer unambiguously to two distinct properties of the material, while the terms initial, final, true, infinite-frequency, a-c and d-c conductivity all refer to different methods of measuring these two properties of the material.

The current flowing in a dielectric to which a constant potential is applied often decreases with time for periods of the order of a few minutes or longer measured from the time of applying the potential. This decreasing current is variously referred to as a *residual charging current*, an *absorption current*, an *anomalous conduction current* or an *irreversible absorption current*, depending upon the interpretation given to the phenomenon. We have already indicated that these residual currents complicate the measuring technique in the determination of the d-c conductivity of insulating materials. The most definite kinds of residual currents are those which are simply a manifestation of the structural characteristics which give rise to anomalous dispersion of the dielectric constant. These residual currents and the residual charges associated with them will be referred to here as the *direct-current counterparts of anomalous dispersion* to indicate that they are not independent properties of the material, but necessary requirements of the existence of anomalous dispersion occurring at sufficiently low frequencies. The information obtainable from the study of such residual currents is the same in kind as that obtainable from the study of dielectric constant and conductivity by means of alternating currents; the residual phenomena, however, provide data regarding polarizations having relaxation-times which are too long for convenient investigation by alternating current methods. Residual currents of this kind have no significance in principle which is different from that of low-frequency a-c measurements.

CONDUCTIVITY AND DIELECTRIC LOSS

The conductivity of a material is usually thought of as a property which depends upon the ease with which electric charge can be transferred through the material by the application of an electric field, though it is recognized that a dissipation of electrical energy as heat occurs in the material through which the current is passing. In these terms we think of the conductivity as a quantity proportional to the current per unit voltage gradient, which in turn is proportional to the number of charge carriers, their mobility, and the magnitude of the charge borne by each carrier. For conductors it does not matter whether we define the conductivity, γ, as the factor by which the voltage gradient, E, must be multiplied to give the current density, I,

$$I = \gamma E \tag{1}$$

or as the factor by which the square of the voltage gradient must be multiplied to give the heat, W, developed per second in a unit cube of the material,[2]

$$W = IE = \gamma E^2, \tag{2}$$

for the heat developed by a given voltage is proportional to the current, no matter of what material the conductor is composed. This is due to the fact that the energy obtained by the moving charges from the applied electric field is dissipated continuously to the surrounding molecules or lattice structure as heat, and the electrons or ions then drift with constant average velocity in the direction of the applied field, developing heat at a rate proportional to the current.

However, the proportionality between current and heat developed which is characteristic of conductors does not obtain in dielectrics. When an alternating current flows in a dielectric it dissipates some electrical energy as heat; however, the amount is generally much smaller than would be dissipated by an equal current flowing in a

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[2] Cf. for example, Mason and Weaver, "The Electromagnetic Field," Chicago (1929), p. 233.

conductor and, unlike conductors, the ratio of heat developed to current flowing varies with the material. This is due to the fact that most of the current flowing in a dielectric under ordinary conditions is a polarization current, or rather a sum of several polarization currents of different types, and in general a polarization current dissipates less energy as heat than an equal current flowing in a conductor. In fact a part of the current flowing in a dielectric—the optical polarization current—passes through the dielectric material without developing any heat in it at the ordinary frequencies of electrical transmission. Electrical energy can be transmitted through a good dielectric in a suitable range of frequencies with very little loss; in other words, the dielectric is transparent to currents which have a suitable frequency of alternation. In these circumstances the conductivity of the material as measured on a bridge would be very small though the current density per unit voltage gradient might be quite large. Evidently, then, the view of conductivity as simply a measure of the ease of transfer of electric charge through a material is not in general suitable for application to dielectrics.

The fact is that the *complex* conductivity represents the ease of displacement of electric charge in a dielectric while its real part (i.e., the a-c conductivity as measured on a bridge or equivalent measuring device) is the quantity to which the rate of heat development in the material is proportional. Therefore, in dealing with alternating currents flowing in dielectrics it is usually more convenient to regard the a-c conductivity as the factor which determines the rate of dissipation of electrical energy as heat in the material, rather than as a quantity which is proportional to the current density per unit voltage gradient or to the ease of displacement of electric charge in the material. In a later part of the discussion, however, it will be shown that the limiting high-frequency value of the a-c conductivity may be thought of as representing ease of displacement of electric charge, too, as in a conductor.

The heat developed in a dielectric by polarization currents is called *dielectric loss* and is analogous to the Joule heat developed by free electrons or ions in a conductor; however, it is a property of neutral aggregates of particles, such as polar molecules, rather than of free ions. In the case of a polarization due to polar molecules, for example, the equilibrium distribution of the orientations of the molecules is slightly changed by the application of an electric field. The dielectric constant depends upon the difference between the distribution of orientations with and without the applied field, while the dielectric loss represents the part of the energy of the applied field which is dissipated as heat because of the "friction" (i.e., the molecular equivalent of macroscopic friction) which the molecules experience as they change from the one equilibrium distribution of orientations to the other. Evidently, the dielectric loss may be quite as characteristic of the structure of the material as is the dielectric constant.

In an ideal insulating material there would be no free ion conduction, but in actual materials there are some free ions or electrons and these produce Joule heat as they drift towards the electrodes in the applied field. The total heat developed is the sum of the dielectric loss and the Joule heat; and, as the latter is proportional to the d-c or free ion conductivity, the dielectric loss is proportional to the total a-c conductivity (as measured on a bridge for example) less the d-c conductivity.

To give the discussion a more concrete basis, let us consider a dielectric which has a dielectric constant ϵ' and a loss-factor ϵ'' (or in other words which has a complex dielectric constant $\epsilon' - i\epsilon''$). Let it be contained in a parallel-plate condenser having a plate separation of d centimeters, and area A cm^2 for one surface of one of the plates. If a potential difference V is maintained between the plates of this condenser, a charge q per unit area will appear on either plate and a polarization P will be created in the dielectric. The current flowing in the leads to this condenser is Adq/dt, if we assume for the present that the conductivity due to free ions may be neglected. The conductivity is then given by

$$\gamma = \frac{1}{E}\frac{dq}{dt}, \tag{3}$$

where $E = V/d$. The charge q can be calculated from the dielectric constant of the material by means of relations which are provided by the general theory of electricity, namely

$$\epsilon E = D, \tag{4}$$

$$D = E + 4\pi P, \tag{5}$$

$$D = 4\pi q \text{ (for a parallel-plate condenser).} \tag{6}$$

So (3) becomes

$$\gamma E = \frac{dq}{dt} = \frac{1}{4\pi}\frac{dD}{dt} = \frac{\epsilon}{4\pi d}\frac{dV}{dt}, \tag{7}$$

where all of the electrical quantities are expressed in electrostatic units. When the applied potential is alternating, V may be expressed as the real part of $V = V_0 e^{i\omega t}$, where V_0 is the amplitude. The dielectric constant may then be written as the complex quantity $\epsilon' - i\epsilon''$, as shown in the preceding paper. The current density in the dielectric is then

$$\frac{dq}{dt} = i\omega(\epsilon' - i\epsilon'')\frac{V_0}{4\pi d}e^{i\omega t} \tag{8}$$

$$= \left(\frac{\epsilon''\omega}{4\pi} + i\frac{\epsilon'\omega}{4\pi}\right)E_0 e^{i\omega t} \tag{8a}$$

$$= (\gamma' + i\gamma'')E_0 e^{i\omega t}, \tag{8b}$$

where $\gamma' \equiv \epsilon''\omega/4\pi$ and $\gamma'' \equiv \epsilon'\omega/4\pi$. It is evident that $\gamma' + i\gamma''$ $(= \gamma)$ is the complex conductivity.

The dielectric constant and conductivity for alternating currents are determined by measurements, made with bridges or by other means, which give the admittance or impedance of the condenser containing the dielectric at the particular frequency at which the measurement is made. This admittance[3] may be expressed in terms of the equivalent parallel capacitance (C_p) and conductance (G_p) and an alternative expression for (8) is then

$$\frac{dq}{dt} = \frac{0.9 \times 10^{12}}{A}(G_p + iC_p\omega)V_0 e^{i\omega t}, \tag{9}$$

where G_p is expressed in mhos (or reciprocal ohms) and C_p in farads and 0.9×10^{12} is the ratio of the farad to the electrostatic unit of capacitance and also of the mho to the e.s.u. of conductance.

By comparing (9) with (8), (8a) and (8b) we obtain expressions for γ', ϵ'' and ϵ' in terms of the quantities C_p and G_p as directly measured on a bridge or similar arrangement. However, the expressions obtained are briefer if we make use of the fact that, when expressed in farads, the capacity C_0 of the empty condenser is

$$C_0 = \frac{A}{4\pi d \times 0.9 \times 10^{12}}. \tag{10}$$

Then it is evident that

$$\epsilon' = C_p/C_0, \tag{11}$$

$$\epsilon'' = G_p/C_0\omega, \tag{12}$$

$$\gamma' = G_p/4\pi C_0 \tag{13}$$

$$= \epsilon''\omega/4\pi = \epsilon'' f/2. \tag{13a}$$

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[3] Measurements on a series bridge give directly the equivalent series resistance R_s and capacitance C_s. These data can be converted into equivalent parallel conductance and capacitance by the general relationships

$$C_p = \frac{C_s}{1 + (\omega R_s C_s)^2}; \qquad G_p = \frac{\omega^2 R_s C_s^2}{1 + (\omega R_s C_s)^2}.$$

In equations (11) to (13*a*) ϵ', ϵ'' and γ' are expressed in e.s.u., while C_p and C_0 are expressed in farads and G_p in mhos. The substitution of the frequency, f, for ω in (13*a*) depends upon the fact that $f = 2\pi\omega$.

While it is usual to express ϵ' and ϵ'' in e.s.u., it is more convenient for most purposes to have γ' in the units ordinarily used for specific conductance: thus when expressed in $\text{ohm}^{-1}\cdot\text{cm}^{-1}$

$$\gamma' = \frac{\epsilon''\omega}{4\pi \times 0.9 \times 10^{12}} = \frac{\epsilon'' f}{1.8 \times 10^{12}}, \tag{14}$$

$$= \frac{8.85 \times 10^{-2}}{C_{0\text{ mmf}}} G_p = \frac{d}{A} G_p, \tag{14a}$$

where $C_{0\text{ mmf}}$ is the capacitance in micromicrofarads.

By expressing equation (8) in the equivalent polar form certain quantities appear which are closely related to γ', ϵ' and ϵ'' and which are commonly used in describing the characteristics of dielectrics. The polar form is

$$\gamma = \gamma_0 e^{i\theta},$$

where $\gamma_0 = (\gamma'^2 + \gamma''^2)^{1/2}$, a quantity which is a measure of the amplitude of the complex current in the dielectric for unit voltage gradient, while $\theta = \tan^{-1} \gamma''/\gamma'$ is its phase angle. It is customary to use the *loss angle* which is defined as $\left(\frac{\pi}{2} - \theta\right) \equiv \delta$, rather than the phase angle in the description of dielectric properties. It is evident that $\delta = \tan^{-1} \gamma'/\gamma'' = \tan^{-1} \epsilon''/\epsilon'$ and that

$$\tan \delta = G_p/C_p\omega. \tag{15}$$

Similarly, the power factor is given by

$$\cos \theta = \gamma'/(\gamma'^2 + \gamma''^2)^{1/2}$$
$$= \epsilon''/(\epsilon'^2 + \epsilon''^2)^{1/2} = G_p/(G_p^2 + C_p^2\omega^2)^{1/2}. \tag{16}$$

When the current given by (8) is multiplied by the voltage, $E_0 \cos \omega t$, we obtain the instantaneous power, and from this the mean power $\overline{W}$ can be obtained by integration over a whole number of half periods. We then obtain

$$\overline{W} \text{ per second} = \gamma' \left(\frac{E_0}{\sqrt{2}}\right)^2 = \frac{\epsilon''\omega}{4\pi}\left(\frac{E_0}{\sqrt{2}}\right)^2 \tag{16a}$$

and

$$\overline{W} \text{ per cycle} = \frac{\epsilon''}{2}\left(\frac{E_0}{\sqrt{2}}\right)^2. \tag{16b}$$

This demonstrates the statements made earlier that γ' is proportional to the heat developed per second and ϵ'' to that developed per cycle in the dielectric. In the above equations $\overline{W}$ is in ergs per second or per cycle when E_0, γ', and ϵ'' are in e.s.u.

It can be seen from equation (8) that the total current flowing in the dielectric has a dissipative and a non-dissipative part: ϵ' is proportional to the non-dissipative part, and ϵ'' to the dissipative part. The loss-angle, ϵ''/ϵ', may be interpreted as the ratio of the dissipative to the non-dissipative current and the power factor as the ratio of the dissipative current to the total current.

THE FREQUENCY-DEPENDENCE OF CONDUCTIVITY

When the dielectric with which we are dealing possesses the property of anomalous dispersion, the expression for the loss factor ϵ'' as a function of frequency is

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)\omega\tau}{1 + \omega^2\tau^2}, \tag{17}$$

as was shown in the preceding paper. Substituting this expression for ϵ'' in (14) we obtain:

$$\gamma' = \frac{\epsilon''\omega}{4\pi} = \frac{1}{4\pi} \cdot \frac{(\epsilon_0 - \epsilon_\infty)\omega^2\tau}{1 + \omega^2\tau^2} \tag{18}$$

$$= \frac{1}{4\pi \times 0.9 \times 10^{12}} \cdot \frac{(\epsilon_0 - \epsilon_\infty)\omega^2\tau}{1 + \omega^2\tau^2}, \tag{18a}$$

where γ' is expressed in e.s.u. in (18) and in $\text{ohm}^{-1}\cdot\text{cm}^{-1}$ in (18*a*), and ϵ_0 is the static dielectric constant, ϵ_∞ the infinite-frequency dielectric constant and τ is the relaxation-time.

Differentiation of (18) with respect to frequency shows that γ' has no maximum when plotted against frequency; *the conductivity of any dielectric to which (18) applies should always increase with frequency, where it changes at all.* On the other hand, differentiation of (17) with respect to ω shows that the dielectric loss-factor has a maximum which occurs when $\omega\tau = 1$. The dielectric constant ϵ' is given by

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2\tau^2} \tag{19}$$

and it will be seen that it shares with the conductivity the property of having no maximum when plotted against frequency. In Fig. 1 schematic curves are drawn which show the differences in the frequency dependence of γ', ϵ'' and ϵ' for a material having an absorptive polarization of relaxation-time τ. The conductivity goes up as the dielectric constant goes down, as if the one were being transformed into the other.

The most interesting feature of (18) is that as the frequency increases γ' approaches a limiting value, and that this limiting value,

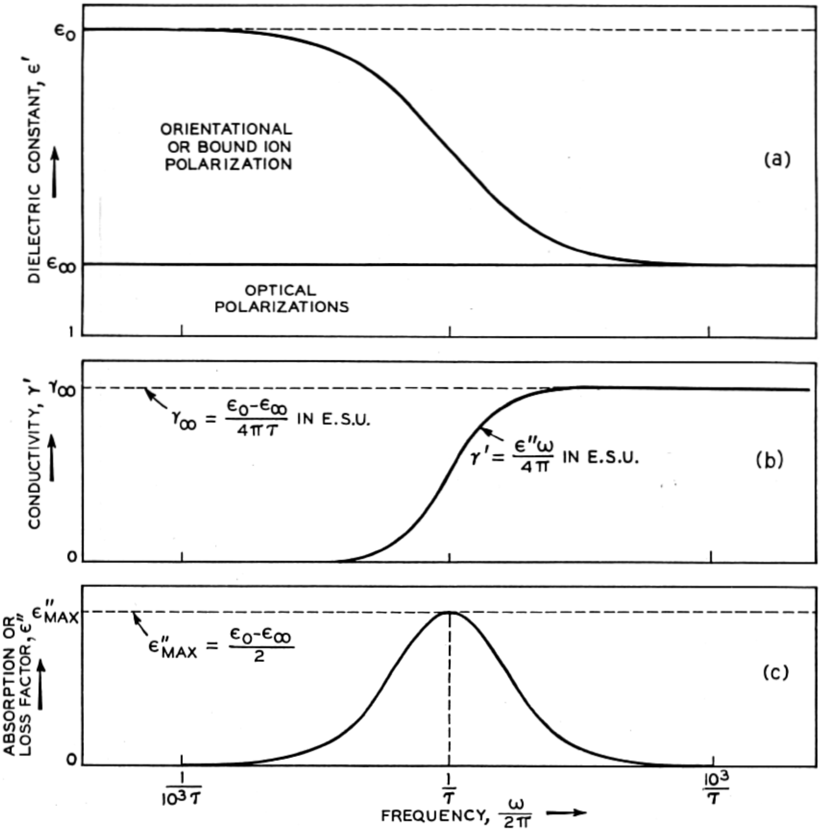

Fig. 1—Schematic diagram comparing the frequency dependence of dielectric constant (ϵ'), loss factor (ϵ'') and conductivity (γ'). This applies to a polarization having a single relaxation-time (τ). The frequency in cycles per second is $\omega/2\pi$.

which will be designated as γ_∞, has the value

$$\gamma_\infty = \frac{\epsilon_0 - \epsilon_\infty}{4\pi\tau} \tag{20}$$

$$= \frac{\epsilon_0 - \epsilon_\infty}{4\pi \times 0.9 \times 10^{12}\tau}, \tag{20a}$$

where (20) gives γ_∞ in e.s.u. and (20a) in ohm$^{-1}\cdot$cm^{-1}. The conthe dependence of conductivity on frequency in terms of the displacement and velocity of a single bound ion. As we are not concerned here with very high frequencies, we may employ the abbreviated equation of motion given in equation (17) of the preceding paper to discuss the motion of the bound ion of this model; this equation is

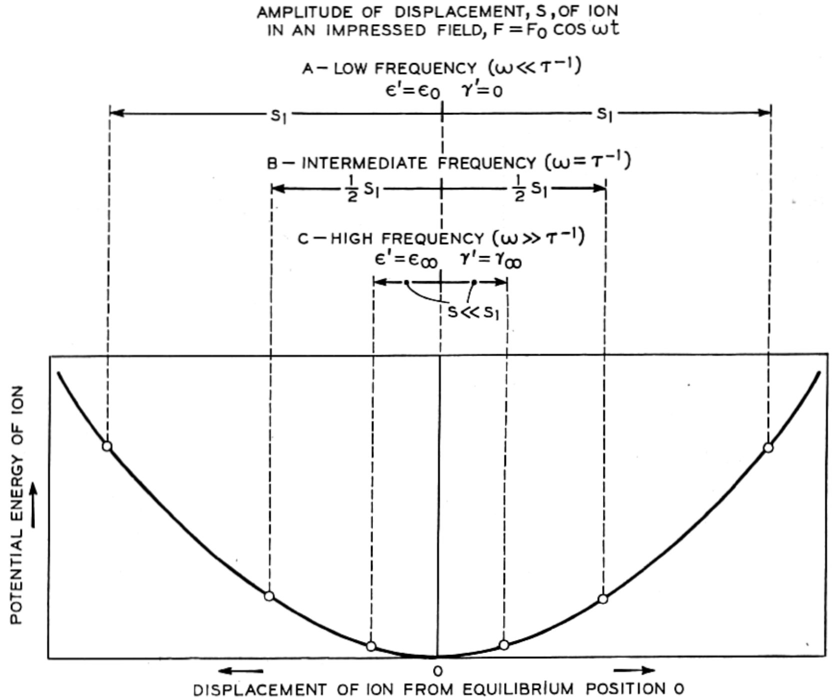

Fig. 3—The mechanism of anomalous dispersion illustrated by a simple model.

The model consists of a single bound ion. The potential energy of this ion increases when it is displaced from its equilibrium position 0. The ion also experiences a frictional force proportional to its velocity, as if it were an ion in solution. The upper part of the diagram shows the way in which the amplitude (s) of displacement of the ion by a given applied field varies with the frequency. It has its maximum amplitude at low frequencies (A in the diagram) and a comparatively negligible amplitude at high frequencies (C in the diagram). In this model the amplitude is a measure of the dielectric constant. The limiting value γ_∞ of the conductivity prevails under the conditions C where the amplitude is comparatively negligible.

$$rv + fs = eF,$$

where $v = ds/dt$.

When a d-c voltage V_1 is applied to this model, it establishes a field F_1 which displaces the bound ion to a new equilibrium position s_1 if the field is allowed to act upon the ion for a sufficient time. The new equilibrium position s_1 of the ion corresponds to the static value P_1 of the polarization of the model. When the voltage is varying with the time according to $V = V_0 \cos \omega t$, the greatest amplitude which the displacement can have is s_1, and in general the amplitude will fall short of this value by an amount which increases with increasing frequency. The value s_1 is then closely approached only when the frequency is low as compared with the reciprocal of the relaxation-time, because at high frequencies the applied field reverses its direction before the ion has had time to reach s_1. At sufficiently low frequencies, namely where ω is negligible by comparison with $1/\tau$, the frictional dissipation of energy by the moving ion is so small that there is practically no difference between the instantaneous position of the ion when the voltage has any given value and the position it would finally attain upon reaching equilibrium for that voltage. The ion then moves through a succession of near-equilibrium positions, as in a reversible process in thermodynamics. The dielectric constant has its static value and the conductivity is zero unless there is a d-c conduction component in the total conductivity.

At the high-frequency extremity of a dispersion region we see that the situation is simply reversed: the alternations in the direction of the applied field are so rapid that the bound ion does not have time to move an appreciable distance from its equilibrium position before the direction of the applied field is reversed (*C*, Fig. 3). The amplitude of the displacement of the ion by the applied field is then small as compared with s_1 and the dielectric constant of the material receives practically no contribution from the bound ion of this model in these circumstances. However, though the amplitude of motion of the ion shrinks to a small fraction of s_1, its velocity is comparatively high and independent of frequency. The conductivity γ_∞ is proportional to the average velocity of the bound ion of the model under these conditions.

As the restoring force is proportional to the displacement, its effect upon the motion of the ion is negligible by comparison with that of the applied force when the displacement s is small as compared with s_1. On this basis, the fact that the conductivity is an increasing function of frequency may be attributed to the decrease in the influence of the restoring forces as the frequency increases. In fact, when the amplitude of displacement is very small as compared with s_1, the ion moves as if the only force opposing the applied force were the frictional force; that is, its average velocity is the same as that of a free ion subjected to the same applied field and the same friction.

For many of the purposes of this discussion we could use a model of the dielectric consisting of an air capacity C_s in series with a resistance

R_s both being shunted by a second air condenser C_∞. In this equivalent circuit, C_s and R_s refer to the polarizations responsible for anomalous dispersion, and C_∞ to the optical polarizations. The frequency-dependence of the equivalent parallel capacitance and conductance of this network is

$$C_p = C_\infty + \frac{C_0 - C_\infty}{1 + \omega^2 T^2} \tag{21}$$

and

$$G_p = \frac{(C_0 - C_\infty)\omega^2 T}{1 + \omega^2 T^2}, \tag{22}$$

where $C_0 \equiv C_s + C_\infty$ and $T \equiv C_s R_s$. In the above expressions $(C_0 - C_\infty)$ and T are analogous respectively to $\epsilon_0 - \epsilon_\infty$ and τ in equations (17) and (19).

The physical basis for the infinite frequency conductivity in this model depends upon the fact that at high frequencies the impedance of C_s is so low that nearly the whole drop in voltage is over the resistance R_s. This simple network is capable of representing the frequency-dependence of materials exhibiting anomalous dispersion due to a polarization having a single relaxation-time. In fact, when the frequency is sufficiently high that it is in the range where the conductivity is independent of frequency, the required network becomes even more simple, for it then reduces to C_∞ shunted by R_s, where the magnitude of C_∞ corresponds to ϵ_∞ and that of R_s to $1/\gamma_\infty$.

POLARIZATION CONDUCTIVITY

The operation of the models which have been discussed above provides a basis for interpreting the physical nature of γ_∞. The essential characteristics brought out by these models are listed below. They show the justification for considering γ_∞ to be a conductivity in the same sense as the ordinary d-c conductivity.

(1) To obtain γ' in an actual measurement on a dielectric, we subtract the d-c conductivity γ_f from the total a-c conductivity. There is then no contribution from free ion conduction in γ' and consequently none in γ_∞, its limiting value at high frequencies. Polar molecules or other polarizable aggregates in the dielectric must then be the origin of γ_∞.

(2) In the second place γ_∞ is independent of frequency, a property which puts it on the same footing as the d-c or free-ion conductivity in at least one respect.

(3) Earlier in this paper it was mentioned that the heat developed in a conductor for a given voltage is proportional to the *total* current,

but that in dielectrics this proportionality does not in general prevail. The current in a dielectric is complex and heat is developed only by its dissipative component. If the expressions for ϵ' and ϵ'' given in (17) and (19) are substituted in (8) we see that when ω becomes large by comparison with $1/\tau$, i.e., when γ' becomes γ_∞, the imaginary component of the current reduces to $\epsilon_\infty\omega/4\pi$; this is the optical polarization current. If it is subtracted from the total current given by (8), the remaining current contains no imaginary component. This current then develops as much heat in the dielectric as would a current of the same magnitude flowing in a conductor.

(4) In connection with the foregoing we see that unlike lower values of γ' the infinite-frequency conductivity γ_∞ is a measure of the ease with which electrical charge can be displaced in the material by a unit applied field. This characteristic of γ_∞ agrees with our usual conception of the physical basis of the conductivity of an electrolyte or a metal. (We assume in this connection that the optical polarization current $\epsilon_\infty\omega/4\pi$ may be neglected in comparison with the current responsible for γ_∞. Where this is not the case, appropriate modifications in the above statements are required.)

(5) It is characteristic of a dielectric that when the charged particles which form part of its structure are displaced by a force of external origin, there is a restoring force tending to return them to their initial positions. On the other hand, in an ideal conductor there are, by definition, no restoring forces of this kind. The above discussion of the model shows that in a dielectric possessing the property of anomalous dispersion it is possible to make the influence of the restoring forces on the motion of a bound ion negligible in comparison with that of the applied force by sufficiently increasing the frequency above the value corresponding to the reciprocal of the relaxation-time. This is the condition which prevails when γ' equals γ_∞. Thus at low frequencies ($\omega \ll \tau^{-1}$) the part of the dielectric structure which is responsible for anomalous dispersion behaves as a dielectric; whereas at high frequencies ($\omega \gg \tau^{-1}$) it behaves as a conductor. A result of this is that a dielectric exhibiting anomalous dispersion of the simple kind conforming to equation (39) of the preceding paper will behave in an electric circuit like a pure capacity shunted by a pure resistance over the whole of that range of frequencies where ϵ' and γ' are both practically independent of frequency and equal respectively to ϵ_∞ and γ_∞. Pure ice, for example, behaves in this manner over a considerable range of frequencies. (See Figs. 2 and 4.)

(6) The average velocity of the bound ion of our model becomes independent of frequency when ω is large as compared with $1/\tau$. This

constant velocity is equal to that which a free ion would have under the same voltage gradient if it were moving in a medium subjecting it to the same frictional resistance as is experienced by the bound ion of our model.

(7) In ordinary electrolytic conduction the conductivity is usually represented as the product of three factors: the number of ions per unit volume; their valence or charge per ion; and the average mobility of each ion, i.e., the average distance which an ion drifts per second in the direction of the applied field. The above statement refers to one species of ion; when two or more species are present in the solution, the total current or conductivity is the sum of the currents or conductivities contributed by each type. The infinite-frequency conductivity γ_∞ may also be represented as the product of three factors similar in physical meaning to those just mentioned as applying to conduction by ions in solution. Thus reference to Table I, Item 2, will show that

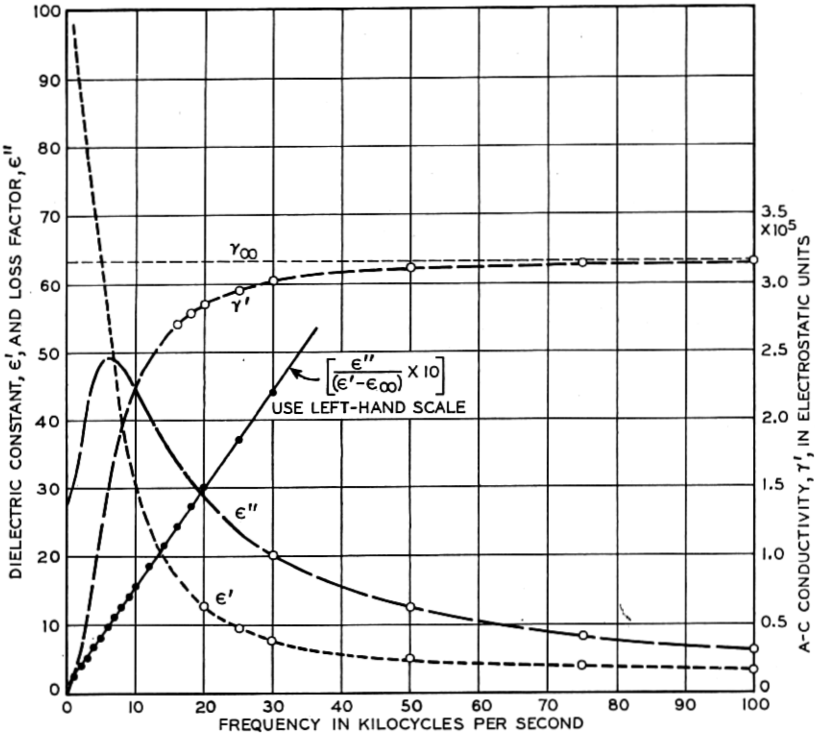

Fig. 4—Dependence of ϵ', ϵ'', γ' and $\epsilon''/(\epsilon' - \epsilon_\infty)$ upon frequency for ice at $-2.6°$ C.

for the model we have employed to illustrate this discussion,

$$\gamma_\infty = \frac{1}{4\pi} \cdot \left(\frac{\epsilon_\infty + 2}{3} \right)^2 \cdot \frac{ne^2}{r} \cdot \tag{23}$$

The factors in this expression may be seen to have the following general significance: the quantity e is the charge on each bound ion; n is the number of bound ions per unit volume; and $e/4\pi r$ is a measure of the mobility per ion. This mobility does not refer to the motion of an ion which is free to move through the dielectric from one electrode to the other but to the mobility of a bound ion in small, local translational motions or the rotational mobility of a polar molecule. The remaining factor $\left(\frac{\epsilon_\infty + 2}{3} \right)^2$ is not of direct significance in the present connection.[5]

We see then that γ_∞ is also analogous to ordinary electrolytic conduction in that its physical mechanism may be represented as depending upon a mobility, a concentration and a factor such as dipole moment or charge per bound ion. The latter factor has a function in this mechanism which is similar to that of the valence or charge per ion in electrolytic conduction.

These considerations indicate that although γ_∞ is a property of polarizable units such as polar molecules it has the usual attributes of a conductivity due to free ions or free electrons. A dielectric which exhibits simple anomalous dispersion conforming to equations (17) and (19) then has *two* conductivities. One of these is the conductivity due to free ions; this will be called the *free ion conductivity* and designated throughout this paper by γ_f. The other is a conductivity which is a characteristic of the polarizable complexes responsible for anoma-

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[5] When $\epsilon_\infty = 1$, equation (23) reduces to

$$\gamma_\infty = \frac{ne^2}{4\pi r},$$

showing thereby that the factor $\left(\frac{\epsilon_\infty + 2}{3} \right)^2$ would be absent if the material possessed no optical polarizations. Evidently γ_∞ depends upon the optical refractive index $\sqrt{\epsilon_\infty}$, as well as upon the characteristics of the absorptive polarization. In mixtures it may be possible to vary these two factors independently. Since optical polarization currents make no *direct* contribution to the energy dissipation in the dielectric, even up to the highest radio frequencies, it is interesting to observe that they make an *indirect* contribution according to equation (23). Their indirect action takes place by virtue of their effect on the actual internal field which acts upon each polarizable aggregate in the dielectric. The effect of the interaction of the optical polarization with the absorptive polarizations is to increase the apparent mobility of the polarizable complexes responsible for anomalous dispersion.

lous dispersion; this will be called the *polarization conductivity*[6] and designated by γ_{pol} in this paper.

The magnitude of the polarization conductivity of a material is proportional to the number of polarizable units of structure such as polar molecules or bound ions per unit volume which contribute to anomalous dispersion. It also depends upon the mobility which these polarizable units have in the local translational or rotational motions in which they engage in consequence of thermal agitation. It finally depends upon the permanent dipole moment of the polar molecules or upon the charges upon the bound ions.

The concentration of ions able to contribute to conduction in dielectrics is generally low because in many cases the free ion conductivity depends mainly upon a small percentage of impurity in the material. On the other hand, the concentration of polarizable units which are able to contribute to the polarization conductivity may be much larger and in fact even equal to the total number of molecules per unit volume. Consequently, the polarization conductivity γ_{pol} may often be more reproducible in measurements upon different specimens of the same dielectric than is the free ion conductivity.[7] It may well be that in many materials diffusion coefficients, thermal conductivity, mechanical dissipation and other similar properties which might be expected on theoretical grounds to be related to electrical conductivity will bear a simpler or more easily demonstrated relationship to polarization conductivity than to free ion conductivity.

An example of the advantage of using the infinite-frequency conductivity instead of the d-c conductivity appears in measurements of the conductivity of ice. In Fig. 5 the infinite-frequency conductivity (or polarization conductivity) of ice is plotted against the reciprocal of the absolute temperature, using unpublished data of the writers. The data for γ_∞ are reproducible and the curve shows a relation similar to that usually observed for the d-c conductivity of solids. Direct-current measurements on the same specimens on the other hand yielded very erratic results. It may be seen from Fig. 5 that the polarization conductivity is much higher than the d-c conductivity.

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[6] We suggest for this conductivity the name polarization conductivity because it is a property of polarizable units of structure. In cases where the polarization is due to the change of orientation of polar molecules, we might instead refer to it as an *orientational conductivity* or a *polar molecule conductivity*, contrasting it thereby with the translational aspect of ordinary conduction by free ions. As ions which are loosely bound to some stationary or moving unit of the dielectric structure are often capable of producing anomalous dispersion, at least two types of polarization conductivity are possible; these may be described as the orientational conductivity and the bound ion conductivity.

[7] Joffé has obtained evidence that the initial conductivity, which we show here to be in some cases a polarization conductivity, is often superior in reproducibility to the final conductivity. (Cf. Reference 15.)

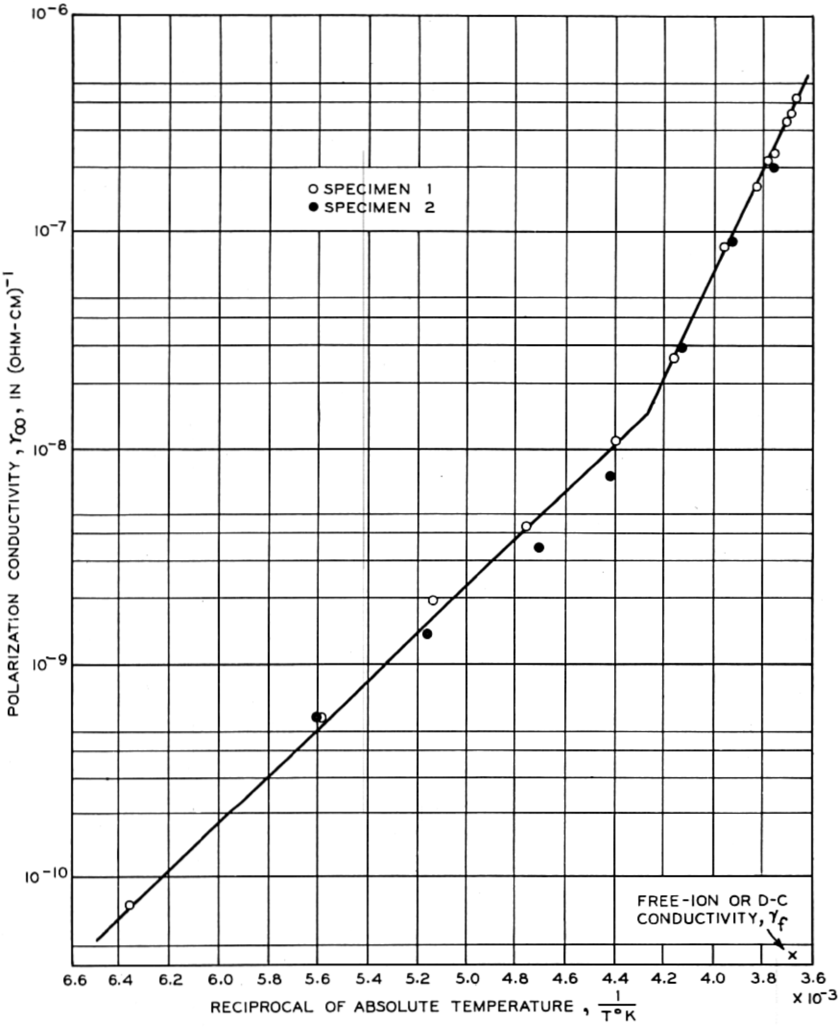

Fig. 5—An illustration of polarization conductivity. The temperature-dependence of the polarization conductivity of pure ice in the range − 0.8° C to − 190° C. The free-ion (or d-c) conductivity is also shown for a single temperature.

Types of Infinite-Frequency Conductivity

In Table I of the preceding paper there were listed several types of polarization capable of yielding anomalous dispersion curves distinguishable from each other only by the values of the constants. Corresponding to each is a different expression for the polarization conductivity and these expressions are listed in Table I of this paper.

This list shows that there are at least three main types of infinite-frequency conductivity. The first of these is the type which depends upon the change of the orientation of polar molecules according to the Debye theory. This type of polarization conductivity is of more theoretical interest than any of the others and perhaps also of more practical importance; as already mentioned, it may be described as an orientational conductivity to emphasize that no translational mobility is necessary for it to occur.

TABLE I

EXPRESSIONS FOR THE CONSTANT VALUE γ_∞ APPROACHED BY THE A–C CONDUCTIVITY AS THE FREQUENCY INCREASES

Type of Polarization	
1. The Orientational Polarization due to Polar Molecules	$\gamma_\infty = \dfrac{L\mu^2}{12\pi\eta a^3} \cdot \left(\dfrac{\epsilon_\infty + 2}{3}\right)^2$
2. A Distortional Polarization having a Relaxation-Time given by $\tau = r/f$	$\gamma_\infty = \dfrac{ne^2}{4\pi r} \cdot \left(\dfrac{\epsilon_\infty + 2}{3}\right)^2$
3. Polarizations due to Spatial Variations of Conductivity and Dielectric Constant	
(*a*) A two-layer dielectric, layers 1 and 2 having respectively static dielectric constants ϵ_1 and ϵ_2 and free-ion conductivities γ_1 and γ_2	$\gamma_\infty = \dfrac{(\epsilon_1\gamma_2 - \epsilon_2\gamma_1)^2}{(\epsilon_1 + \epsilon_2)^2(\gamma_1 + \gamma_2)}$
(*b*) Special case of (3*a*) where γ_1 is much larger than γ_2	$\gamma_\infty = \left(\dfrac{\epsilon_2}{\epsilon_1 + \epsilon_2}\right)^2 \gamma_1$
(*c*) Special case of (3*b*) where $\epsilon_1 \backcong \epsilon_2$	$\gamma_\infty = \gamma_1/4$
(*d*) Special case of (3*a*) consisting of a high resistance transition layer at the dielectric/electrode interface, where γ_1 is the conductivity of the dielectric	$\gamma_\infty = \gamma_1$
(*e*) Conducting spheres dispersed in an insulating medium of the same dielectric constant	$\gamma_\infty = p\gamma_1$

Note: The infinite-frequency conductivity γ_∞ is given here in e.s.u. (See equation 20.) In Table I of the preceding paper (*B. S. T. J.*, *17*, 640 (1938)) the values of $(\epsilon_0 - \epsilon_\infty)$ and τ are given for the polarizations listed above; the expressions given there for τ should be divided by 4π in the case of Items 3*a*, *c*, *d* and *e*, as should also the expressions for $\epsilon_0 - \epsilon_\infty$ in the case of Item 2. The quantities which appear in the above Table are defined in an appendix to the preceding paper. γ_1 and γ_2 are expressed in e.s.u. in this table.

The remaining members of the list of Table I originate in the properties of ions rather than those of molecules. These ions must be more or less bound in order to have an infinite-frequency conductivity differing from the zero-frequency conductivity.[8] The nature and

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[8] It will be recalled that the terms infinite-frequency and zero-frequency are not used here in their general meaning but merely as a convenient way to indicate opposite directions of extrapolation of dispersion curves. They refer respectively to the high-frequency extremity of a dispersion curve where γ' becomes practically independent of frequency and to the low-frequency extremity where the dielectric constant becomes practically independent of frequency.

strength of the binding forces may vary widely amongst the types of polarization which have an infinite-frequency conductivity. An ion will be regarded as bound if its potential energy increases when it is displaced from an equilibrium position by an applied field.[9]

Included among the infinite-frequency conductivities which depend upon the presence of ions in the dielectric is a type for which macroscopic inhomogeneities in the dielectric are responsible; for example, a two-layer or multiple layer laminated dielectric, or a dielectric in which space-charges [10] form because of spatial variations in its resistivity or because of a transition layer of high resistance at the contact between dielectric and electrode. Examples of the infinite-frequency conductivity due to this type of mechanism are given in Items *3a*, *b*, *c* and *d* of Table I.

This type of infinite-frequency conductivity is of little interest in principle, but in practice there may be many instances in which the measurement of the infinite-frequency conductivity provides a convenient means of determining the conductivities of the constituents of these non-homogeneous systems. For example, when one layer of a two-layer dielectric has a much higher conductivity than the other, γ_∞ assumes a value which is related simply to the free ion conductivity of the layer which has the higher conductivity (see Item *3b*, Table I). If the dielectric constants of the two layers are equal, γ_∞ is equal to one-quarter of the conductivity of the high-conductivity layer. The conductivities γ_1 and γ_2 of the two layers are considered in the present connection to be free ion conductivities. A more complicated situation is possible where γ_1 and γ_2 are in part polarization conductivities due to polar molecules or bound ions.

The special case of a space-charge caused by a thin layer of high resistance at one or both of the electrodes is of interest in connection with the methods recommended by Joffé for the measurement of the true conductivity of crystals. This will be discussed in more detail later but for the present it may be noted that the infinite-frequency

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[9] It is necessary to confine the application of the last statement to direct voltages or to frequencies lower than those for which γ' is equal to γ_∞. When the frequency is high enough for the latter condition to prevail the amplitude of displacement of the ion becomes so small that the applied field produces no appreciable increase in the average potential energy of the ion; this is illustrated in Fig. 3 at *C*.

[10] The external effects of a space-charge occurring in a dielectric because of spatial variations in its resistivity may be reproduced by a uniformly distributed polarization of suitably adjusted magnitude and relaxation-time. Several different polarizations of different magnitudes and relaxation-times would in some instances be required. In referring to such a space-charge as a polarization we may think of the term as applying to the uniform distribution of polarization which could replace the space-charge in its external effects.

conductivity for this system has the simple value

$$\gamma_\infty = 1/4\pi C_0 R = \gamma_1$$

as shown in Item 3*d*, Table I. Here γ_1 is the free ion conductivity of the main part of the dielectric, R is its resistance and $4\pi C_0 (= A/d)$ is the ratio of thickness to length of specimen. (In Table I of the preceding paper the symbol C_∞ is used in place of C_0.) *The infinite-frequency conductivity in a non-homogeneous system of this type is a free-ion conductivity.*

Bound ions may also be distributed with macroscopic uniformity in a dielectric. An example of this type of bound ion conductivity[11] is one due to conducting particles dispersed uniformly in a relatively non-conducting medium. This is the case referred to in Item 3*e* of Table I. Macroscopic uniformity is obtained in this case by the random distribution of a large number of particles. However, there are some general experimental indications that the distribution of bound ions may in some materials depend upon the basic internal structure of the dielectric and involve some regular geometrical configuration repeated throughout the material.

In certain dielectrics which absorb an appreciable amount of water when in a humid atmosphere, conduction takes place in aqueous conduction paths permeating the solid. Examples of these materials are cotton, paper, silk and wool. This property is probably shared by many other polymeric substances. The water in these materials is distributed in minute capillaries, the dimensions and other characteristics of which probably determine the form and distribution of the conduction paths.[12] There exists in these materials a condition capable of producing a bound ion conductivity inasmuch as there are indications that the conducting paths are not of uniform cross-sectional area. Evidence for the existence of a bound ion conductivity in the kind of material to which we have just referred is provided, for example, by conductivity measurements on cotton.[13] Raw cotton contains salts which can be removed by extraction leaving the material otherwise practically unchanged. These salts are likely to be distributed in the material with macroscopic uniformity as they form part of its natural structure. The fact that the removal of these salts decreases the

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[11] As already mentioned we shall call any infinite-frequency conductivity which is caused by a macroscopically uniform distribution of bound ions a *bound ion conductivity*. In some places this term will be applied to any conductivity due to bound ions irrespective of whether or not that conductivity is the limiting high-frequency value.

[12] One of the basic structural units of cellulose and other similar materials is the *micelle*. This usually contains a large number of molecules and the capillaries we refer to may correspond to the intermicellar spaces.

[13] Murphy, *Journal of Physical Chemistry*, *33*, 200 (1929).

dielectric loss indicates that the material possessed a bound ion conductivity before the salts were removed.

Some of the materials belonging to the class of dielectrics which we have just discussed are closely related in chemical and in physical structure to compounds which are important biologically and in the study of plant and seed structure. Many are also of commercial importance as insulating materials.

It is not necessary that the conduction paths be composed of aqueous solutions: in some materials plasticizers or products of pyrolysis are sufficiently conducting for this purpose. The dielectric behavior of certain plastics may be interpreted as evidence for the existence of such non-aqueous conduction paths in the material, producing a free ion conductivity, a bound ion conductivity and a contribution to the dielectric constant. Imperfections of structure occurring in crystals are able to produce a bound ion conductivity and there is experimental evidence that these imperfections do occur.[14] The regular lattice ions in an ionic crystal have too high a binding energy, and dissipate too little energy in their motions in a radio frequency electric field to produce a bound ion conductivity.

The polarization which is responsible for the bound ion conductivity is of the interfacial, or Maxwell-Wagner, type. This type of polarization may be of importance in materials with a cellular structure and in materials which may be described as interstitially conducting dielectrics.

In the above discussion we have outlined the character of three widely different types of infinite-frequency conductivity:

(*a*) An orientational conductivity depending upon the small changes which an applied field produces in the average orientation of polar molecules.

(*b*) A bound ion conductivity depending upon the displacement of uniformly distributed bound ions.

(*c*) An infinite-frequency conductivity which is proportional to the free ion conductivity of one of the constituents of a dielectric consisting of two or more layers of widely different conductivities.

THE RELAXATION-TIME

The relaxation-time is closely related to the infinite-frequency conductivity. This may be seen by reference to equation (20), which shows that the relaxation-time is given by

$$\tau = \frac{\epsilon_0 - \epsilon_\infty}{4\pi\gamma_\infty}. \tag{24}$$

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[14] See, for example, A. Smekal, *Zeits. f. techn. Physik*, *8*, 561 (1927).

This equation shows that specifying the values of τ and $(\epsilon_0 - \epsilon_\infty)$ gives as much information as specifying γ_∞ and $(\epsilon_0 - \epsilon_\infty)$. In some applications there are advantages in using τ but in other applications greater simplicity of description is gained by using γ_∞.

There are several convenient ways of calculating the relaxation-time. The more familiar ones depend upon the position of maxima which occur in certain dielectric properties when they are plotted against the frequency: there are maxima in the loss factor vs. frequency curve, in the tangent of the loss angle vs. frequency curve and in the power factor vs. frequency curve. As these maxima occur at different frequencies, the corresponding expressions for the relaxation-time are also different. They are listed in Table II. It will be observed that the simplest of these formulae for the relaxation-time is the one involving the maximum in the loss factor.

TABLE II

List of Formulae for Calculating the Relaxation-Time (τ)

1. The frequency at which the maximum in loss factor (ϵ'' or $\epsilon' \tan \delta$) occurs is $\omega_{\max(1)}$	$\tau = 1/\omega_{\max(1)}$
2. The frequency at which the maximum in loss angle (ϵ''/ϵ' or $\tan \delta$) occurs is $\omega_{\max(2)}$	$\tau = \sqrt{\frac{\epsilon_\infty}{\epsilon_0}}\frac{1}{\omega_{\max(2)}}$
3. The frequency at which the maximum in power factor $\epsilon''/(\epsilon'^2 + \epsilon''^2)^{1/2}$ occurs is $\omega_{\max(3)}$	$\tau = \sqrt{2}\sqrt{\frac{\epsilon_\infty}{\epsilon_0}}\frac{1}{\omega_{\max(3)}}$
4. The quantity $\epsilon''/(\epsilon' - \epsilon_\infty)$ is a linear function of ω	$\tau = \frac{d}{d\omega}(\epsilon''/(\epsilon' - \epsilon_\infty))$
5. The relaxation-time is proportional to the ratio of the absorptive part $(\epsilon_0 - \epsilon_\infty)$ of the static dielectric constant to the infinite-frequency conductivity (γ_∞)	$\tau = (\epsilon_0 - \epsilon_\infty)/4\pi\gamma_\infty$

Note: An example of the application of these formulae is provided by the curves of Fig. 4. The value of τ for ice at −2.6°C is 25.8 microseconds as calculated from the position of the maximum in ϵ'', 24.6 microseconds as calculated from $(\epsilon_0 - \epsilon_\infty)/4\pi\gamma_\infty$, where γ_∞ is in e.s.u., and 23.1 microseconds as calculated from the slope of $\epsilon''/(\epsilon' - \epsilon_\infty)$.

The function $\epsilon''/(\epsilon' - \epsilon_\infty)$ is a linear function of ω with slope equal to τ. This property provides an alternative method of calculating the relaxation-time. An example of its application to an actual material is provided by the data for ice plotted in Fig. 4.

It is interesting that $\epsilon''/(\epsilon' - \epsilon_\infty)$ has no maximum while ϵ''/ϵ' has a maximum. The physical basis of this is that in subtracting ϵ_∞ from ϵ' we remove the contribution to ϵ' made by optical polarizations. What is left represents only the dielectric constant due to the polarization responsible for anomalous dispersion. Consequently the tangent of the loss angle of the polarization current responsible for anomalous dispersion has no maximum when plotted against the frequency and its behavior is, therefore, in contrast with the tangent of the loss angle of the *total* polarization current, i.e., the sum of the optical polarization current and the absorptive polarization current.

From the above discussion it will also be evident that the physical basis for the maximum in tan δ is different from that of the maximum in ϵ''. As we have just shown, the maximum in ϵ''/ϵ' (= tan δ) depends upon the inclusion of optical polarizations in ϵ'. On the other hand, there would be a maximum in ϵ'' even if the part of the dielectric constant which is due to optical polarizations (ϵ_∞) were neglected or considered to be zero. This will be evident by differentiation of equation (17).

The maximum in ϵ'' is an intrinsic property of the absorptive polarization. The general nature of the mechanism by which it occurs is as follows: ϵ'' is proportional to γ'/ω; as the frequency increases γ'/ω at first increases, but when γ' reaches the constant value γ_∞, further increase in frequency causes γ'/ω to decrease.

The quantity τ which we have discussed here is a property of the dielectric as a whole as we indicated in the preceding paper. This quantity is connected with the relaxation-time τ' of the individual polarizable units by the relation

$$\tau = \frac{\epsilon_0 - 2}{\epsilon_\infty + 2}\tau', \tag{25}$$

when the material is of cubic or isotropic structure. This relationship is a consequence of the fact that the actual force acting upon a particle within a dielectric depends not only upon the applied field of external origin but also upon a force exerted by the polarization induced in the dielectric.

THE RELATIONSHIP BETWEEN DIELECTRIC CONSTANT AND DIELECTRIC LOSS

If $\epsilon'_{\max}$ is the value of the dielectric constant at the frequency where the loss factor ϵ'' is at a maximum when plotted against frequency, we have

$$\epsilon'_{\max} = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2_{\max}\tau^2} = \frac{\epsilon_0 + \epsilon_\infty}{2}, \tag{26}$$

$$\epsilon''_{\max} = \frac{(\epsilon_0 - \epsilon_\infty)\omega_{\max}\tau}{1 + \omega^2_{\max}\tau^2} = \frac{\epsilon_0 - \epsilon_\infty}{2}. \tag{27}$$

By addition and subtraction of (26) and (27) we obtain the following relationships:

$$\epsilon_0 = \epsilon'_{\max} + \epsilon''_{\max}, \tag{28}$$

$$\epsilon_\infty = \epsilon'_{\max} - \epsilon''_{\max}, \tag{29}$$

$$\epsilon_0 - \epsilon_\infty = 2\epsilon''_{\max}. \tag{30}$$

The comparison of the last equation with equation (20) brings out an interesting contrast between the maximum dielectric loss per *cycle* ($\epsilon''_{\max}$) and the maximum dielectric loss per *second* (γ_∞). *The maximum dielectric loss per cycle is completely determined by the difference between the static dielectric constant and the optical dielectric constant.* On the other hand, the dielectric loss per second depends as well upon the relaxation-time. The relaxation-time usually varies rapidly with temperature, whereas ($\epsilon_0 - \epsilon_\infty$) changes comparatively slowly with temperature. The temperature-dependence of the maximum dielectric loss per cycle is related to the polarizability of the material, whereas the temperature variation of the maximum dielectric loss per second is primarily a measure of the change of internal friction with temperature.

In the foregoing we have discussed the conductivity, dielectric loss and relaxation-time of dielectrics which have simple properties with respect to the frequency-dependence of these quantities. However, for many dielectrics, particularly solids, the experimental data are not in agreement with the dispersion formulae for a single relaxation-time which has been discussed here. The explanation usually adopted for this discrepancy is that the polarizations induced in the dielectric possess a distribution of relaxation-times.

THE D-C COUNTERPARTS OF ANOMALOUS DISPERSION

A dielectric so constructed that it exhibits anomalous dispersion under an alternating voltage should show some equally characteristic behavior when a direct voltage is substituted for the alternating one. These characteristics may be described as the d-c counterparts of anomalous dispersion. They include certain definite types of variation of current with time under constant applied potential.

In the appendix the d-c counterparts of anomalous dispersion are derived by employing the model used throughout this paper. This enables us to demonstrate an especially simple relationship between the a-c and d-c conductivity.

Equation (16) of the appendix gives the apparent conductivity as a function of charging time. As it has been assumed that $\epsilon_\infty C_0 R \ll \tau$, the first term of equation (16) will quickly become negligible. Then for charging times, measured from the instant of applying the voltage, such that $\tau \gg t_c \gg \epsilon_\infty C_0 R$, the apparent conductivity $\gamma_c(t_c)$ has the value

$$\gamma_0 = \frac{\epsilon_0 - \epsilon_\infty}{4\pi\tau} = \gamma_\infty. \tag{31}$$

The special value of $\gamma_c(t_c)$ which we have designated as γ_0 in (31) will be called the *initial conductivity.*

Equation (31) states that the infinite-frequency conductivity (γ_∞), *obtained by a-c measurements, is equal to the initial d-c conductivity* (γ_0) *which would be obtained by extrapolating current-time curves toward the instant of applying the voltage.* This relationship, which has not been demonstrated previously to our knowledge, is of interest in connection with the interpretation of conductivity measurements.

The model described in Appendix I and indicated schematically in Fig. 3 illustrates the physical nature of the initial conductivity in a simple manner. When a constant voltage V_1 is applied to a dielectric having the properties of this model an effective impressed field F_1 is established in the dielectric. This displaces the bound ion assumed to be responsible for the polarization in this model. The magnitude of the displacement s of this bound ion depends upon the length of time that F_1 is applied. If it is applied for a time which is much longer than the relaxation-time, s approaches a constant value s_1 corresponding to complete polarization of the dielectric. On the other hand, during that stage of the charging process when the charging time t_c is negligible in comparison with the relaxation time τ and at the same time large as compared with the time constant $\epsilon_\infty C_0 R$, the displacement s is negligible in comparison with s_1. The resultant force tending to displace the ion is then approximately equal to the impressed force; $eF_1 - fs_1 \cong eF_1$.

Near the beginning of the charging process there is a brief interval of time ($\epsilon_\infty C_0 R \ll t_c \ll \tau$), when the motion of the bound ion of our model in the applied field is essentially the same as that of a free ion. During this interval the prevailing conductivity is the initial conductivity defined by equation (31). Although the bound ion of the model is actually subjected to a force tending to restore it to its initial position, this restoring force has not had time during the initial stage of the charging process to build up to a magnitude appreciable in comparison with the applied force. The initial conductivity corresponds to a condition in the dielectric where bound ions act for a brief time as if they were free as far as conduction processes are concerned. The infinite-frequency conductivity corresponds also to this condition. The variation of apparent conductivity with the time of charging is indicated schematically in Fig. 6. As is there shown, there must be an initial stage, always too brief to be detected experimentally, during which the inductance of the circuit and the inertia of the charges cannot be neglected.

THE TYPES OF INITIAL CONDUCTIVITY

The polarization conductivity γ_{pol} may then be measured in two ways: either as the infinite-frequency conductivity γ_∞ obtained by a-c measurements, or as the initial conductvity γ_0 obtained by d-c measurements:

$$\gamma_{\text{pol}} = \gamma_\infty = \gamma_0.$$

The quantity γ_{pol} *refers to a property of the material, whereas* γ_0 *and* γ_∞ *refer to the methods of measuring this property.*

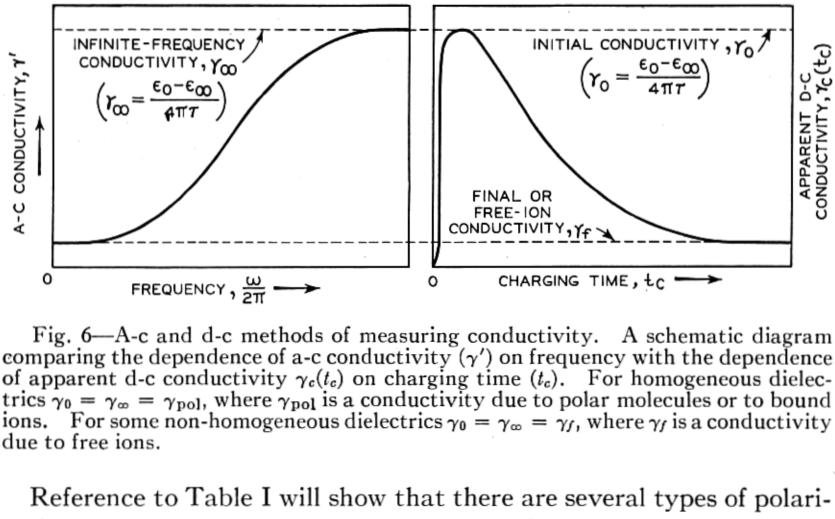

Fig. 6—A-c and d-c methods of measuring conductivity. A schematic diagram comparing the dependence of a-c conductivity (γ') on frequency with the dependence of apparent d-c conductivity $\gamma_c(t_c)$ on charging time (t_c). For homogeneous dielectrics $\gamma_0 = \gamma_\infty = \gamma_{\text{pol}}$, where γ_{pol} is a conductivity due to polar molecules or to bound ions. For some non-homogeneous dielectrics $\gamma_0 = \gamma_\infty = \gamma_f$, where γ_f is a conductivity due to free ions.

Reference to Table I will show that there are several types of polarization which may be responsible for γ_∞. Consequently this will be true also of the initial conductivity. The equality of γ_0 and γ_∞ applies to all of these types of polarization and, therefore, can not be used to distinguish between them. For this reason experimental agreement between a-c and d-c measurements of conductivity does not enable us to distinguish whether we are dealing with polar molecules, bound ions, or free ions in a macroscopically inhomogeneous dielectric. Thus it is clear that when we are dealing with a polarization due to polar molecules, the *initial conductivity is a true polarization conductivity or a specific dielectric loss.* If the polarization is of the bound ion type discussed earlier in this paper, the initial conductivity is also a polarization conductivity. However, if we are dealing with a macroscopically non-homogeneous dielectric such as a two-layer dielectric or a material *which has a high resistance blocking layer at one of the electrodes* γ_0 *is a free ion conductivity.* This is evident from the previous discussion of the significance of γ_∞.

These relationships are of interest in connection with the difficulties encountered in the interpretation of d-c conductivity data which were mentioned in the introduction. They apply especially to the methods recommended by Joffé [15] and by Richardson.[16]

When a constant potential difference is maintained between the plates of a condenser containing a solid dielectric the current observed does not in general remain constant but usually decreases with time. This decrease may continue for several minutes or hours. The study of these residual currents is of importance in connection with the interpretation of conductivity data on dielectrics. The question arises as to how much of the observed behavior of the residual currents which flow in dielectrics under constant potential may be explained as the d-c counterparts of anomalous dispersion. Many materials of practical importance as insulators exhibit a more complicated type of variation with frequency than is indicated by equations (17) and (19) which refer only to the simplest observed type of dispersion. The more complicated types of behavior observed are usually attributed to the presence of polarizations possessing a wide distribution of relaxation-times. However, other processes may also contribute to the deviation of the experimental curves from the theoretical. One of these is electrolysis which produces changes in the composition, and consequently in the conductivity of the material. Another effect which may contribute is a possible lack of constancy of the relaxation-time. It is evident, therefore, that the d-c counterparts of anomalous dispersion due to a polarization of a single relaxation-time should not be expected to explain all of the observed residual phenomena, particularly in solid dielectrics. However, the quantitative relations derived as the d-c counterparts of anomalous dispersion are applicable to some materials, and for those to which they are not quantitatively applicable, may serve as a useful guide in the interpretation of the residual currents. As another section of this paper is planned in which the influence of residual currents upon conductivity measurements will be discussed further, we have included in the appendix some relationships which are useful in the interpretation of the behavior of these currents.

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[15] A. Joffé, *Ann. d. Physik, 72,* 481 (1923); "Physics of Crystals," New York (1928); *Zeits. f. Physik, 62,* 730 (1930). See also Sinjelnikoff and Walther, *Zeits. f. Physik, 40,* 786 (1927).

[16] S. W. Richardson, *Proc. Roy. Soc., 107A,* 102 (1925).

APPENDIX

THE D-C COUNTERPARTS OF ANOMALOUS DISPERSION

Having developed the a-c characteristics of the model, the properties of which were specified in the preceding paper,[17] we now turn to the direct-current characteristics of this model. This involves investigating the characteristics of the currents produced when a constant or direct voltage V_1 is applied to a condenser containing a dielectric having properties which correspond in all respects essential to the discussion to those of the model just described. Let the resistance of the leads to the condenser be R and let the source of the electromotive force V_1 have a negligible internal resistance. These conditions require the following five equations to be satisfied simultaneously:[18]

$$r\frac{dP}{dt} + fP - ne^2F = 0, \tag{1}$$

$$F = E + AP_t, \tag{2}$$

$$P_t = k_iF + P, \tag{3}$$

$$D = E + P_t, \tag{4}$$

$$E = E_1 - CR\frac{dD}{dt}. \tag{5}$$

(Rational e.s.u. are used in these equations for convenience but the final relations are converted into electrostatic units.[19]) P_t denotes the total polarization; it is the sum of the optical polarizations, given by k_iF, and the polarization P which forms comparatively slowly and causes anomalous dispersion. The total displacement D, is given by (4). C_0 is the air capacitance of the condenser. V is the potential drop over the condenser. The separation of the plates of the condenser is d. When the whole drop in potential is concentrated over the condenser the applied field strength E_1 is given by $E_1 = V_1/d$. Equation (5) is obtained by equating the total drop in potential over the leads and the condenser to the applied potential V_1.

Equations (1) to (5) may be combined to give the following:

$$(1 + 2p_0)\tau'CR\frac{d^2D}{dt^2} + \{(1 - p_0)\tau' + CR(1 + 2p_0 + 2p_1)\}\frac{dD}{dt} + (1 - p_0 - p_1)D - (1 + 2p_0 + 2p_1)E_1 = 0. \tag{6}$$

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[17] These properties are also outlined on page 513 of this paper.

[18] Cf. P. Debye, "Polar Molecules," pp. 86–88, where an analogous case is discussed.

[19] For conversion factors see, for example, Mason and Weaver, Reference 2, page 370. The rational electrostatic unit of conductivity is smaller than the e.s.u.; the ratio is 4π. The dielectric constant is unaffected by changing from rational e.s.u. to e.s.u.

In this equation the following abbreviations are used: $\tau' = r/f$, $Ak_i = p_0$, $Ak = p_1$. The last two abbreviations are introduced to facilitate comparison with an analogous derivation given in "Polar Molecules," p. 86. $D = D_0e^{\alpha t}$ is a solution of the homogeneous differential equation obtained by letting $E_1 = 0$, provided that the following equation is satisfied:

$$\alpha^2 + \left\{ \left(\frac{1 - p_0}{1 + 2p_0} \right) \frac{1}{CR} + \frac{(1 + 2p_0 + 2p_1)}{1 + 2p_0} \frac{1}{\tau'} \right\} \alpha + \left(\frac{1 - p_0 - p_1}{1 + 2p_1} \right) \frac{1}{\tau' CR} = 0. \quad (7)$$

As we are interested here only in the special case where $CR \ll \tau'$, the $1/\tau'$ term in the coefficient of α can be neglected in comparison with the $1/CR$ term, and the roots are

$$\alpha = -\left(\frac{1 - p_0 - p_1}{1 - p_0} \right) \frac{1}{\tau'} \text{ or } \alpha = -\left(\frac{1 - p_0}{1 + 2p_0} \right) \frac{1}{CR}$$

to a degree of approximation which improves the larger the ratio τ/CR. The general solution of the non-homogeneous equation (6) is

$$D = D_1 e^{-\left(\frac{1-p_0}{1+2p_0}\right)\frac{t}{CR}} + D_2 e^{-\left(\frac{1-p_0-p_1}{1-p_0}\right)\frac{t}{\tau'}} + \left(\frac{1 + 2p_0 + 2p_1}{1 - p_0 - p_1} \right) E_1 = 0. \quad (8)$$

For the special case of a random or cubic distribution of molecules (in which case $A = 1/3$), Eq. (8) can be simplified by means of the following relationships:

$$(1 + 2p_0)/(1 - p_0) = \epsilon_\infty, \quad (9)$$

$$(1 + 2p_0 + 2p_1)/(1 - p_0 - p_1) = \epsilon_0, \quad (9')$$

$$(\epsilon_\infty + 2)/(\epsilon_0 + 2) = (1 - p_0 - p_1)/(1 - p_0), \quad (10)$$

$$\left(\frac{1 - p_0}{1 - p_0 - p_1} \right) \tau' = \left(\frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \right) \tau' = \tau. \quad (10')$$

Equation (8) then becomes

$$D = D_1 e^{-t/\epsilon_\infty CR} + D_2 e^{-t/\tau} + \epsilon_0 E_1 \quad (11)$$

and introducing the initial conditions, $t = 0$, $D = 0$; $t = 0$, $\dfrac{dD}{dt} = E_1/CR$, we obtain,

$$D = \epsilon_0 E_1 - \epsilon_\infty E_1 e^{-t/\epsilon_\infty CR} - (\epsilon_0 - \epsilon_\infty) E_1 e^{-t/\tau}. \quad (12)$$

Let q_c be the charge per unit area on either of the condenser plates at any stage of the charging process, that is, at any time t_c after the instant at which the voltage was applied. On converting (12) into e.s.u., we have for the charge at any time during the charging process:

$$q_c = \frac{D_c}{4\pi} = \frac{\epsilon_0 E_1}{4\pi} - \frac{\epsilon_\infty}{4\pi} E_1 e^{-t_c/\epsilon_\infty C_0 R} - \frac{(\epsilon_0 - \epsilon_\infty)}{4\pi} E_1 e^{-t_c/\tau}. \tag{13}$$

Therefore the ballistic or d-c dielectric constant at any time of charging t_c, is

$$\epsilon(t_c) = \frac{D_c}{E_1} = \epsilon_0 - \epsilon_\infty e^{-t_c/\epsilon_\infty C_0 R} - (\epsilon_0 - \epsilon_\infty) e^{-t_c/\tau}. \tag{14}$$

The d-c dielectric "constant" appears in this equation as a function of the charging time. Its dependence on charging time is analogous to the dependence of the a-c dielectric "constant" on frequency. The static dielectric constant ϵ_0 is obtained when charging has been continued until $t_c \gg \tau$, that is, when t_c is infinite the dielectric constant has its static value ($t_c = \infty$, $\epsilon(t_c) = \epsilon_0$) and when t_c is zero the dielectric constant is zero ($t_c = 0$, $\epsilon(t_c) = 0$).

The charging *current* is obtained by differentiation of (13) and is

$$\dot{q}_c = \frac{\dot{D}_c}{4\pi} = \frac{E_1}{4\pi C_0 R} e^{-t_c/\epsilon_\infty C_0 R} + \left(\frac{\epsilon_0 - \epsilon_\infty}{4\pi\tau} \right) E_1 e^{-t_c/\tau}. \tag{15}$$

The charging current per unit voltage gradient, or the apparent conductivity $\gamma_c(t_c)$, is

$$\gamma_c(t_c) = \frac{\dot{q}_c}{E_1} = \gamma_R e^{-t_c/\epsilon_\infty C_0 R} + \gamma_\infty e^{-t_c/\tau}, \tag{16}$$

where $\gamma_R \equiv (4\pi C_0 R)^{-1}$ and $\gamma_\infty = (\epsilon_0 - \epsilon_\infty)/4\pi\tau$. (It will be noticed that if we define a quantity $G_R \equiv 1/R$, it follows that $(4\pi C_0 R)^{-1} = G_R \cdot d/A = \gamma_R$ since $4\pi C_0 = A/d$. The quantity γ_R is the specific conductance which a fictitious material must possess if it were put in a condenser of geometric capacitance C_0 and required to conduct the same current as C_0 when in series with an external resistance R.)

At any stage of the charging process such that t_c is large as compared with $\epsilon_\infty C_0 R$, but at the same time small as compared with τ the apparent conductivity given by (16) reduces to

$$\gamma_c(t_c) = \gamma_\infty.$$

This value of $\gamma_c(t_c)$, where $\epsilon_\infty C_0 R \ll t_c \ll \tau$, will be designated by γ_0 and called the *initial conductivity*. Using this terminology we see that the *initial conductivity* γ_0 *as determined by d-c measurements equals the infinite-frequency conductivity* γ_∞ *as determined by a-c measurements.*

If t_d represents the time measured from the instant that the voltage is abruptly reduced to zero, and q_d, D_d, $\dot{q}_d$ represent respectively the charge, displacement, and discharge current at time t_d, we have for discharging after *complete* charging

$$q_c(t_d) = \frac{D_d}{4\pi} = \frac{\epsilon_\infty E_1}{4\pi} e^{-t_d/\epsilon_\infty C_0 R} + \frac{(\epsilon_0 - \epsilon_\infty)}{4\pi} E_1 e^{-t_d/\tau} \tag{17}$$

or

$$\epsilon(t_d) = \epsilon_\infty e^{-t_d/\epsilon_\infty C_0 R} + (\epsilon_0 - \epsilon_\infty) e^{-t_d/\tau}. \tag{17a}$$

At the end of the charging process (cf. (13)) or the beginning of the discharge process (cf. (17)) the charge per unit area per unit applied field strength is $\epsilon_0/4\pi$.

The discharge current for *complete* charge is obtained by differentiating (17) with respect to the time:

$$\dot{q}_d = \frac{\dot{D}_d}{4\pi} = -\frac{E_1}{4\pi C_0 R} e^{-t_d/\epsilon_\infty C_0 R} - \frac{(\epsilon_0 - \epsilon_\infty) E_1}{4\pi\tau} e^{-t_d/\tau} \tag{18}$$

or

$$\gamma_d(t_d) = \frac{\dot{D}_d}{4\pi E_1} = \gamma_R e^{-t_d/\epsilon_\infty C_0 R} + \gamma_\infty e^{-t_d/\tau}. \tag{18a}$$

Comparison of (18) and (15), or (18*a*) and (16), shows that for complete charging (that is, t_c effectively infinite or $t_c \gg \tau \gg \epsilon_0 C_0 R$) the charging current vs. time curve is identical, except for direction, with the discharge current vs. time curve. *This is true only of the curves for complete charging and is not true if the polarized condition in the dielectric is not fully formed and the polarization currents are not zero.*

The discharge-current time curve for *incomplete* polarization of the dielectric is not as simple as for complete polarization. When the charging process is broken off before completion, the initial conditions for the discharge are not the same as when charging is complete. The charge at time t_d during a discharge following a charging process which is broken off at t_c is

$$\begin{aligned} q_d = \frac{D_d}{4\pi} = \frac{\epsilon_\infty E_1}{4\pi} e^{-t_d/\epsilon_\infty C_0 R} - \frac{\epsilon_\infty E_1}{4\pi} e^{-(t_c+t_d)/\epsilon_\infty C_0 R} \\ + \left(\frac{(\epsilon_0 - \epsilon_\infty)}{4\pi} E_1 e^{-t_d/\tau} - \frac{(\epsilon_0 - \epsilon_\infty)}{4\pi} E_1 e^{-(t_c+t_d)/\tau} \right). \end{aligned} \tag{19}$$

This is an example of the *superposition principle for residual charges.*

The discharge current for incomplete charge is given by

$$- \dot{q}_d = \frac{-\dot{D}_d}{4\pi} = \frac{E_1}{4\pi C_0 R} e^{-t_d/\epsilon_\infty C_0 R} - \frac{E_1}{4\pi C_0 R} e^{-(t_c+t_d)/\epsilon_\infty C_0 R} + \left(\frac{\epsilon_0 - \epsilon_\infty}{4\pi\tau}\right) E_1 e^{-t_d/\tau} - \left(\frac{\epsilon_0 - \epsilon_\infty}{4\pi\tau}\right) e^{-(t_c+t_d)/\tau}. \quad (20)$$

Or if

$$\frac{-\dot{D}_d}{4\pi} = -\dot{q}_d \equiv I_d$$

$$I_d = \gamma_R E_1 e^{-t_d/\epsilon_\infty C_0 R} - \gamma_R E_1 e^{-(t_c+t_d)/\epsilon_\infty C_0 R} + \gamma_\infty E_1 e^{-t_d/\tau} - \gamma_\infty E_1 e^{-(t_c+t_d)/\tau}. \quad (20a)$$

Equation (20) or (20*a*) is an example of the superposition principle for the residual currents in a dielectric having a single absorptive polarization with a relaxation-time τ. It is evident that in the early stages of the charging process the electronic or instantaneous polarizations responsible for ϵ_∞ have the same external effect as an absorptive polarization because of the fact that the current by which they are formed must flow through the lead resistance R. Thus the condenser acts as though it contained a polarization yielding a dielectric constant with a relaxation-time $\epsilon_\infty C_0 R$.

As the time-constant $\epsilon_\infty C_0 R$ is generally small, the first two terms on the right of (20*a*) may usually be neglected and we have

$$I_d = \gamma_\infty E_1 e^{-t_d/\tau} - \gamma_\infty E_1 e^{-(t_c+t_d)/\tau}. \quad (21)$$

The first term on the right of (21) is the discharge current corresponding to the discharge of the condenser after the residual polarizations have been *fully* formed. The second term gives the value which the charging current would have if the charging process were continued for the interval of time $t_c + t_d$ instead of being discontinued after t_c seconds. When the charging time is large as compared with τ the second term may be neglected and the magnitude of the discharge current is the same function of the discharge time as is the charging current of the charging time; the charging curve and discharge curve can then be superimposed on one another if we disregard the direction of the current. There is only one complete charging current curve and *only one discharging current curve corresponding to complete polarization of the dielectric at any given applied potential. There is, however, an infinite number of discharge curves corresponding to incomplete polarization of the dielectric*, that is, to any time of charging which is shorter than that necessary for complete polarization.

The superposition principle states that any of these discharge curves may be derived from the discharge curve for complete polarization by subtracting from its ordinates the values which the charging current would have if it had continued during the discharge. From the method of deriving equation (21) it is clear that the superposition principle is a necessary consequence of an assumed exponential growth and relaxation of the residual polarizations, as required by the theory of simple anomalous dispersion. If these in fact do not vary exponentially with the time, whatever function they do follow appears in general to obey an empirical superposition rule. Reference to (20*a*) will indicate that if there are m polarizations of different relaxation-times which are quite far apart, each polarization will simply contribute two terms to the expression for I_d; that is,

$$I_d = \sum_{j=1}^{m} \left(\gamma_{\infty j} E_1 e^{-t_d/\tau_j} - \gamma_{\infty j} e^{-(t_c+t_d)/\tau_j}\right) \\ + \gamma_R E_1 e^{-t_d/\epsilon_\infty C_0 R} - \gamma_R e^{-(t_c+t_d)/\epsilon_\infty C_0 R}. \quad (22)$$

Thus, the existence of the superposition principle for residual currents as an empirical law suggests that the individual polarizations actually vary exponentially with the time, though direct measurement of the total discharge current seldom gives a single exponential curve. This is, however, not the only possible interpretation.