THE DIELECTRIC CONSTANT OF GALVINOXYL

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THE DIELECTRIC CONSTANT OF GALVINOXYL

THESIS

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By

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CHAPTER I

INTRODUCTION AND THEORY

Purpose

The molecules in many substances are known to undergo at characteristic temperatures a change in their rotational freedom in the solid state, signifying either a change in structure of the material or the onset of limited rotation of the molecule about some symmetry axis. The purpose of this research was to determine from dielectric constant measurements over the 100°K-420°K temperature range whether or not the organic free radical galvinoxyl\(^1\) and its diamagnetic parent molecule, dihydroxydiphenylmethane, undergo any such transitions.

Capacitance and Dielectric Constant

The electrical capacitance of any isolated two-conductor configuration (usually two parallel plates or two concentric cylinders) is defined as the ratio of the charge \(Q\) on either conductor to the difference of potential \(V\) between them.

When the capacitance is measured with a vacuum (or, for all practical purposes, air) between the plates, a value $C_0$ is obtained. However, if some substance is inserted between the plates, the capacitance is observed to increase. The ratio of these capacitances is defined to be the relative dielectric constant $K$ of the substance:

$$K = \frac{C}{C_0} = \frac{\varepsilon}{\varepsilon_0},$$

where $\varepsilon$ and $\varepsilon_0$ are known as the electric permittivity of the material and of a vacuum, respectively. Thus, the insertion of a dielectric between plates carrying a constant charge reduces the difference of potential from $Q/C_0$ to $Q/KC_0$. An equivalent interpretation is that, in the presence of the dielectric, the potential difference arises from only a fraction of the free charge $Q$, the net charge $Q/K$. The remainder, the polarization charge $Q(1-1/K)$, is neutralized by the "polarization" of the dielectric. This polarization may be visualized as the formation by the applied field of dipole chains with their free ends neutralizing part of the charge on the conductors (see Figure 1).

The role of the various charges may be illuminated via three vector fields $\vec{D}$, $\vec{E}$, and $\vec{P}$ defined in such a way that $Q$, $Q/K$, and $-Q(1-1/K)$, respectively, are the sources. The dielectric displacement vector $\vec{D}$ is defined such that the surface charge density $\sigma$ on the conductor shall be equal to the normal component of $\vec{D}$, i.e., $\sigma = \vec{D} \cdot n$, where $n$ is a unit vector pointing out of the conductor. The displacement.
Fig. 1—Representation of dielectric polarization

O = Net Charge

Polarization Charge

[] = Dipoles
vector has no useful physical significance, but is useful as a computational device. Corresponding to the net charge density $\sigma/K$ is the electric field intensity vector $\vec{E}$ defined such that $\sigma/K = \varepsilon_0 \vec{E} \cdot \hat{n}$ (the factor $\varepsilon_0$ is a feature of the MKS system of units). It is the vector $\vec{E}$ which determines the difference of potential between conductors and so measures force per unit charge. The dielectric surface polarization charge density $\sigma_p = \sigma(1-1/K)$ defines the polarization vector $\vec{P}$ such that $\sigma_p = \vec{P} \cdot \hat{n}$, where $\hat{n}$ is a unit vector pointing out of the dielectric. It follows immediately that $\vec{D} = \varepsilon \vec{E}$ and $\vec{P} = \vec{D} - \varepsilon_0 \vec{E} = (\varepsilon - \varepsilon_0) \vec{E}$ or

$$\vec{P} = (K-1)\varepsilon_0 \vec{E}. \quad (Eq. \ 1)$$

The polarization charges $+PA$ on one surface of the dielectric and $-PA$ on the opposite surface, resulting from a displacement of charge throughout the dielectric, give an electric moment $PAd$ to the dielectric volume, where $d$ is the thickness of the slab. Since $Ad = v$, the volume of the slab, the total electric moment is $Pv$. Thus $P$ is evidently the electric dipole moment per unit volume of dielectric. The polarized slab behaves like an assembly of electric dipoles parallel to one another, where each dipole consists of two equal but opposite electric charges separated by a distance $r$ so that

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\(^2\text{Arthur R. Von Hippel, Dielectric Materials and Applications (Cambridge, Mass., 1954), pp. 3-6.}\)
the dipole moment is \( \mu = e r \), \( e \) being the magnitude of either charge.³

Polarization Mechanisms

The interpretation of \( \mathbf{P} \) as the dipole moment per unit volume provides a link between the macroscopic and the microscopic world. The dipole moment per unit volume may be visualized as resulting from the additive action of \( N \) elementary dipole moments \( \mathbf{\mu} \) so that \( \mathbf{P} = N \mathbf{\mu} \). The average dipole moment of the microscopic constituent may be assumed to be proportional to the local electric field strength \( \mathbf{E}' \) that acts on the particle, provided \( \mathbf{E}' \) is not too large. Thus \( \mathbf{\mu} = \alpha \mathbf{E}' \), where \( \alpha \) is defined as the polarizability and measures the electrical pliability of the particle. Combining these equations with equation 1 gives

\[
\mathbf{P} = (K-1) e_0 \mathbf{E} = N \alpha \mathbf{E}',
\]

(Eq. 2)

which links the macroscopic dielectric constant to the three molecular parameters \( N, \alpha, \) and \( \mathbf{E}' \). The local field \( \mathbf{E}' \) will generally differ from the applied field \( \mathbf{E} \) due to polarization of the surrounding dielectric.

The polarization of the dielectric may arise from several polarization mechanisms. When the electric field is applied to the dielectric, electrons are displaced with respect to their nuclei, producing an induced electronic

³Charles P. Smyth, Dielectric Behavior and Structure (York, Pa., 1955), p. 3.
polarization. When atoms of different types form molecules, their electrons are normally not shared symmetrically and the atoms acquire charges of opposite polarity. The electric field acting on these net charges will tend to change the equilibrium positions of the atoms or groups of atoms with respect to each other and produces an induced atomic polarization. The asymmetric charge distribution between unlike partners of a molecule gives rise to a permanent dipole moment, which exists even in the absence of an external field. Such permanent moments experience a torque in the presence of an applied field which tends to orient them in the direction of the field, thus producing an orientation polarization. These three polarization mechanisms are due to the charges that are locally bound in the molecules. In addition, charge carriers may exist that can migrate through the dielectric. When such charges are impeded at an interface or at the surface of the dielectric, a macroscopic field distortion results in a space-charge or interfacial polarization and causes an increase in the capacitance which is indistinguishable from a real rise of the dielectric constant. These four polarization mechanisms are characterized phenomenologically by an electronic polarizability $\alpha_e$, an atomic polarizability $\alpha_a$, an orientation or dipole polarizability $\alpha_d$, and a space-charge polarizability $\alpha_s$. If these mechanisms act independently of one another, the total polarizability is $\alpha = \alpha_e + \alpha_a + \alpha_d + \alpha_s$, where each term may again represent a
sum of contributions. How these four effects vary with temperature and frequency and thus shape the response characteristics of dielectrics will be examined later.

Relationship Between Polarizability and Dielectric Constant

It would be desirable to eliminate N and $E'$ from Eq. 2 since only $\alpha$ contains the primary information on polarization. In a gas under low pressure the local field $E'$ should be identical with the externally applied field $E$. However, for gases at high pressure, liquids, or solids the local field at a molecule may be greatly modified by the polarization of the surroundings.

Consider a reference molecule X surrounded by an imaginary sphere of such extent that outside of the sphere the dielectric can be treated as a continuum (see Figure 2). Assume that the molecules within the sphere are removed while the polarization outside remains frozen. Then the field at X would arise from the net charge $\frac{Q}{\kappa}$ on the plates ($E_1$) and from the free ends of the dipole chains that line the cavity walls ($E_2$). The molecules inside the sphere contribute an additional field $E_3$. Hence the local field $E'$ is $E_1 + E_2 + E_3$. By definition the field due to the free charges on the electrodes is $E$, giving $E_1 = E$. To calculate $E_2$ recall that the charge density $\sigma_p$ lining the cavity stems from polarization charges and is determined by the normal component of

\[4\text{Von Hippel, op. cit., pp. 18, 19.}\]
Fig. 2—Model for calculation of internal field.
the polarization $P$ through $\sigma_p = P \cdot n = P \cos \theta$. A simple calculation gives $E_2 = P/3\varepsilon_0 = E(K-1)/3$. Calculation of $E_3$ due to molecules inside the sphere requires information on the geometrical arrangement and polarizability of the molecules. When the molecules have no permanent dipole moment or when they are arranged in complete disorder or in cubic or similar highly symmetrical arrays, $E_3$ is approximately zero. Under these circumstances

$$E' = E + \frac{P}{3\varepsilon_0} = E(K+2)/3,$$  \hspace{1cm} (Eq. 3)

and $E'$ is known as a Mosotti field. Combining Eq. 2 with Eq. 3 gives the relation between polarizability per unit volume $N_a$ and the relative dielectric constant $K$ as

$$\frac{N_a}{3\varepsilon_0} = \frac{K-1}{K+2}.$$

The number of molecules per unit volume $N$ can be replaced by the number of molecules per mole $N_o$ by the equation $N_o = \frac{N M}{\rho}$, where $M$ designates the molecular weight and $\rho$ the density. The polarizability per mole $\Pi$ is then defined to be

$$\Pi = \frac{N_o \alpha}{3\varepsilon_0} = \frac{(K-1)M}{(K+2)},$$

which is the famous Debye equation, where $\alpha$ is the total polarizability involving a dipole moment factor. The

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5ibid., p. 20.
6ibid.
7ibid.
8ibid., p. 21.
polarizability $c$ is now given in terms of easily obtained macroscopic parameters.

The Debye equation can be applied to gases under low pressures, to nonpolar liquids, and to dilute solutions of polar molecules in nonpolar solvents. However, since the interference of neighboring molecules, including dipole-dipole interactions, was not incorporated into the equation, it cannot be applied with any particular success to pure polar liquids or to solids. In any case it serves to illuminate the general relationship of various polarization parameters.\(^9\)

Temperature and Frequency Dependence of Dielectric Constant

The dependence of the various polarization mechanisms upon temperature and frequency will now be considered. In the case of the induced moments, a charge is displaced from its equilibrium position. If a charge $e$ is acted upon by a field $E'$, then it experiences a force $E'e$, which displaces it in the direction of the field until balanced by a restoring force $kr$, where $r$ is the displacement and $k$ is the elastic restoring constant. An electric moment $\mu = er$ is created by the displacement.\(^10\) Thus from $E'e = kr$ and $r = \mu/e$, $\mu = E'e^{2/r}$. Clearly, the induced polarization exhibits no temperature dependence.


\(^10\) Ibid., p. 3.
In the case of the permanent dipoles, the orientation of dipoles by the applied field is opposed by the thermal agitation of the molecules. In the presence of a field, a dipole has a potential energy $W = -\vec{\mu} \cdot \vec{E}$ which depends on its orientation relative to the field. When a large number of molecules with a distribution of energies are in statistical equilibrium, the number possessing a particular energy $W$ is proportional to $e^{-W/kT} = e^{\vec{\mu} \cdot \vec{E}/kT}$, where $k$ is Boltzman's constant and $T$ is the absolute temperature. Upon calculation of the polarization produced by orientation of dipoles, one obtains an approximate expression of $P_d = \frac{N\mu^2}{3kT} E$. It is evident that this contribution to the polarization due to the orientation of permanent dipoles is temperature dependent.

Above some frequency of alternating applied field there will certainly be an observable lag in the polarization behind the driving field for any of the various polarization mechanisms. This lag is due to the relaxation time of the pertinent physical process. The relaxation time measures the lag in the response of a system to an applied stimulus. The existence of relaxation becomes apparent when its rate is the same order of magnitude as the frequency of the applied field since at a much greater frequency the system is almost completely unable to respond to the applied field.

The relaxation time for displacement of the electrons in an atom is approximately $10^{-15}$ seconds, corresponding to ultraviolet frequencies. Displacement of atoms, giving rise to atomic polarization, requires about $10^{-12}$ to $10^{-14}$ seconds and corresponds to infrared frequencies. The relaxation time for the orientation polarization process depends upon the frictional resistance of the medium to a change in molecular orientation. For a gas the time is on the order of $10^{-12}$ seconds. For liquids the time varies from $10^{-10}$ to $10^{-6}$ seconds depending on the viscosity of the liquid. For solids the time range is from the order of $10^{-5}$ seconds to several seconds.\(^\text{12}\) The reasons for using a frequency of 1000 Hz in this research are listed in Chapter III of this report.

The well-known Maxwell relation states that the square of the index of refraction $n$ of a nonabsorbing, nonmagnetic material is equal to the relative dielectric constant at any given frequency; i.e., $K = n^2$.\(^\text{13}\) The refractive index is ordinarily measured for visible light, the refraction of which is due primarily to the displacement of electrons. At such frequencies $n^2 = K_E$, where $K_E$ is the dielectric constant due to electronic polarization $P_E$. The atomic polarization $P_A$ is generally small, and $n$ can be extrapolated to infinite

\(^{12}\text{Smyth, op. cit., pp. 52, 53.}\)

\(^{13}\text{Von Hippel, op. cit., p. 11.}\)
wavelength, which is practically equivalent to the frequency used in measuring $K$, by use of a dispersion formula.\textsuperscript{14} Thus, the part of the dielectric constant produced by induced polarization is approximately equal to $n^2$. A value of $K$ much larger than $n^2$ indicates the presence of dipole rotation.

If a molecule possesses a permanent dipole moment, the contribution of the permanent moment to the polarization of the material is generally larger (though of the same order of magnitude) than that of the induced dipole. The moment of the permanent dipole is commonly about 100,000 times the induced moment, but thermal agitation almost completely destroys the permanent moment alignment. Thus, the orientation produced by an ordinary field of 1 e.s.u. (300 volts per cm.) is so small that the complete orientation of only one molecular dipole in every hundred thousand plus the very small charge shift responsible for the induced moment would produce the observed dielectric constant.\textsuperscript{15}

Dielectric Behavior of Solids

When molecules with strong fields of force around them are brought close together as in solids, neighboring molecules interfere with one another in such a way as to restrict the orientation of permanent dipoles in an alternating field.\textsuperscript{16}

\textsuperscript{14}Smyth, \textit{op. cit.}, p. 13.
\textsuperscript{15}\textit{Ibid.}, pp. 13, 16.
\textsuperscript{16}\textit{Ibid.}, p. 15.
In the case of nonpolar materials, the dielectric constant-temperature curve usually shows only a slight drop at the melting point due to the decrease in the number of molecules per unit volume. In the case of polar substances, the molecules acquire rotational freedom upon melting and $P_M$ changes abruptly from zero to a value often many times that of $P_E + P_A$. A slight increase in dielectric constant with increasing temperature at low temperatures and a more pronounced rise just below the melting point are typical. An impure sample of a polar substance may show a considerable increase in dielectric constant and an apparent conductance as the melting point is approached, presumably because of the separation of a small amount of a liquid phase and consequent interfacial polarization. Some substances exhibit an effect known as "premelting" in which an occasional molecule acquires sufficient freedom through loosening of the molecular lattice to permit its orientation in the applied field as the melting point is approached.\(^{17}\)

The restriction of molecular orientation in solids normally reduces or eliminates the orientation polarization and reduces the dielectric constant, generally to a value between 2 and 3.\(^{18}\) However, in some solids dipolar molecules have been observed to possess sufficient orientational

\(^{17}\)Ibid., p. 139.

\(^{18}\)Ibid., p. 132.
freedom to give dielectric constants of perhaps 10 to 60, comparable to those in the liquid state. In such cases the solid is said to be in a rotator phase. The molecules do not rotate freely as in a gas but merely have sufficient energy to permit a fairly frequent passage over the potential barriers hindering rotation.

Almost all organic substances have an index of refraction below 1.7. Since $n^2$ is approximately equal to the portion of the dielectric constant caused by induced polarization, a value for $K$ above approximately 3.0 generally indicates that some dipole rotation is occurring and that a transition point does exist at some temperature.

**Dielectric Constant and Loss**

For frequencies below the frequency corresponding to the relaxation time for any polarization process, the particles involved are able to respond easily to the applied field and to move in phase with it. For frequencies above the relaxation frequency, the particles can not easily follow the variations in the applied field and their contribution to the dielectric constant is therefore much reduced. This situation is somewhat analogous to the case of a driven

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19 Ibid., pp. 134-189.
20 Ibid., p. 132.
harmonic oscillator. For frequencies below the normal frequency of vibration of the mass-spring system, the mass stays in phase with the driving force and oscillates with essentially the same amplitude as the driving displacement. For frequencies above the normal frequency, the mass moves 180 degrees out of phase with the driving force and with very small amplitude. For a driving force frequency equal to the normal frequency of the system, resonance occurs and the amplitude of vibration is quite large, and there is significant energy transfer from the driving to the driven system. Theory predicts that the dielectric constant of a substance will obey a dispersion relation of the form

\[ K' = K'_\infty + \frac{K'_0 - K'_\infty}{1 + \omega^2 \tau^2} \]

for dipole rotation and that the loss factor (corresponding to energy losses in the dielectric) will exhibit a resonance type peak in accordance with

\[ K'' = \frac{(K'_0 - K'_\infty) \omega \tau}{1 + \omega^2 \tau^2} . \]

The dissipation factor (which is measured directly by a capacitance bridge—see Chapter II) is defined as the loss factor divided by the dielectric constant and is thus given by

\[ \frac{K''}{K'} = \frac{(K'_0 - K'_\infty) \omega \tau}{K'_0 + K'_\infty \omega^2 \tau^2} . \]

In these equations, $K_0$ means the static field value, $K_\infty$ means the contribution from electronic and atomic polarization, $\tau$ is the relaxation time for orientation polarization, and $\omega$ is the frequency of the driving field. The dielectric constant and dissipation factor are shown plotted against $\omega \tau$ in Figure 3.

In a solid-solid transition the substance changes from a configuration permitting dipole rotation to a configuration in which dipole rotation ceases. At some point in the transition the relaxation frequency of the molecules will equal the frequency of the applied field, and the dissipation factor will exhibit a peak.

Correlation with Other Measurements

Evidence of molecular rotation in the solid state through dielectric constant measurements can generally be correlated with the measurements of certain other parameters.

1. The additional degree of molecular freedom will be reflected in the specific heat of the substance. The thermal energy of solids as evidenced by their specific heats is due mainly to the translational vibrations of atoms, ions, or molecules about fixed points in the crystals or in the molecules, although rotational vibration or free rotation of a molecule may play a part. Thus, at the transition temperature $T_t$, where rotation of polar molecules begins, the
Fig. 3—Dielectric constant, loss factor, and dissipation factor in normalized form vs. $\omega \tau$. 
specific heat will rise, just as the dielectric constant does. 23

2. Nuclear magnetism measurements may give information concerning molecular rotation. According to Smyth

The magnetic dipolar broadening of nuclear resonance absorption lines is reduced by molecular motion in the crystal lattice. In some cases, it has been possible to relate observed line structure and transitions in the line width to the existence and frequency of certain types of hindered rotational motion in the solid state. Relatively low-frequency motion of the order of $10^5$ cycles suffices to narrow the width of an absorption line from its value in the absence of that motion. 24

3. X-ray analysis will indicate a change in the lattice structure from one arrangement to another in which the molecules may be able to rotate, as, for example, from an orthorhombic lattice to a cubic lattice. 25

4. Specific volume and thermal expansion measurements should indicate any general loosening of the structure which could accompany an increased mobility of its units. 26

23 Smyth, op. cit., p. 140.
24 Ibid., pp. 132, 133.
25 Ibid., p. 141.
CHAPTER II
APPARATUS AND PROCEDURE

Description of Apparatus

In this research the dielectric constant of several test samples and of the various organic substances to be tested was measured at a frequency of 1000 Hz. The basic component of the measuring system was a capacitance bridge. A sine-wave generator was used to provide the 1000 cycle signal of approximately 10 volts to the bridge, and an oscilloscope was used as the null detector. (See Figures 4 and 5.)

A typical bridge, the Schering bridge, is shown in Figure 5. Such a bridge consists of equal ratio arms $R_A$ and $R_B$, a variable air capacitor $C_N$, and a balancing capacitor $C_T$. A substitution method of measurement is used because of its greater accuracy over direct measurement. The measuring cell with the dielectric specimen is connected in parallel with the standard capacitor $C_N$ and the bridge balanced, then disconnected, and the bridge rebalanced. The capacitance $C_p$ of the specimen is the difference of the two readings of the standard capacitor.\footnote{Von Hippel, \textit{op. cit.}, p. 55.} Great care must be
Fig. 4--D.C. null detector, potentiometer, capacitance bridge, frequency generator (top), and oscilloscope.

Fig. 5--Schematic of a Schering bridge
taken to keep the leads to the measuring cell in the same position at all times since any change in the separation of these leads causes a change in the measured capacitance.

In any real capacitor there is a loss current which flows across the capacitor due to a migration of charge carriers or energy losses in the dielectric, giving a resistive element to the capacitance measurement. The arms A and B and the arms N and T (see Figure 5) are both a.c. voltage dividers for the generator voltage. The condition for a null is $\frac{Z_A}{Z_B} = \frac{Z_N}{Z_T}$, where $Z_A$, $Z_B$, $Z_N$, and $Z_T$ are the impedances of the four arms. In addition, for the detector to measure a null, the voltage at points a and b must be in phase. In the bridge shown in Figure 5 the resistive balance is provided by the variable capacitor $C_B$ in parallel with $R_B$. The resistive control $C_B$ can then be calibrated directly in terms of a dissipation factor, which is defined as the loss current across the measuring cell divided by the charging current.\(^2\)

The bridge used could not be balanced for a capacitance value below about 100 pf. Thus, an 82 pf capacitor was inserted in parallel with the measuring cell, and all subsequent capacitance values listed which are above 100 pf include this additional capacitance. The bridge could be adjusted with an accuracy of ±0.05 pf, and the values obtained were accurate to within 0.5 pf as stated on the bridge.

\(^2\)Ibid.
Description of Measuring Cell

The capacitor used as a measuring cell consisted of two concentric brass cylinders, with the inner cylinder as the high potential electrode, the outer one being grounded (the ground connection was provided through the thermocouple). The inner cylinder had a diameter of 1/4 inch, while the outer cylinder had an inside diameter of 3/8 inch, making the spacing between them 1/16 inch. Both cylinders were 2 1/2 inches long. The cylinders were held in place by a Fiberglas frame measuring 1 1/2 inches in diameter and 3 1/8 inches long (see Figure 6). The ends of the outer cylinder were beveled in an attempt to reduce the edge capacitance due to the fringing field at the ends of the plates. The error due to the fringing field was virtually eliminated by using a specimen of known dielectric constant to calculate the capacitance $C_{L+E}$ due to leads and the fringing field.

The capacitance of the capacitor with air between the plates is $C_0 + C_{L+E} = C'_0$, where $C'_0$ is the measured capacitance. For the standard dielectric, paraffin with a dielectric constant of 2.25 was melted and poured between the plates of the capacitor. The capacitance of the capacitor with the paraffin is $C_S + C_{L+E} = C'_S$, where $C'_S$ is the measured capacitance of the specimen. From $K = 2.25 = \frac{C_S}{C_0} = \frac{C'_S}{C'_0 - C_{L+E}} = \frac{127.60 - C_{L+E}}{117.35 - C_{L+E}}$, the value of $C_{L+E}$ was determined to be 109.0 pf.

For convenience in loading the dielectric specimen into the capacitor, a two-piece filler cap was devised (see Figure 7).
Fig. 6—Measuring cell

Fig. 7—Loading apparatus
A screw through one end of the capacitor frame held the inner cylinder in place during filling. The Fiberglas cap at the other end was removed and replaced by the filler cap. The top piece of the filler cap had a funnel-shaped hole to facilitate loading and was grooved on the bottom so as to stay centered on the lower piece. The specimen was poured into the capacitor until the capacitor was completely filled. The capacitor was then tapped to insure even, compact distribution of the specimen. Next, the top piece of the filler cap was removed, with any of the dielectric specimen remaining in the funnel hole falling onto the lower portion. This excess dielectric specimen was scraped into a trench in this portion of the filler cap. This piece of the cap was then removed, and the excess dielectric was returned to its container. Throughout the loading process a small pin placed in the groove in the inner cylinder kept this groove free of any dielectric. The Fiberglas cap was then replaced, and a screw through the center of this cap provided the electrical contact to the center plate.

Means of Temperature Variation

Determination of temperature over the entire range of measurement was made with a copper-constantan thermocouple, the voltage of the thermocouple being determined with a potentiometer.
For the measurements at temperatures below room temperature, 100°K to 298°K, a double-Dewar system was used (see Figure 8). The jacket of the inner Dewar was provided with a stopcock so that the pressure in the jacket could be varied. A partial vacuum was produced in this jacket with a mechanical forepump. Liquid nitrogen was then introduced into the outer Dewar. The inside of the inner Dewar was thus cooled very slowly, the rate being controlled by the pressure in the inner Dewar wall, and measurement of the dielectric constant of the specimen could easily be made as the specimen cooled. No attempt was made to hold the temperature at a constant value over a long period of time.

For measurements above room temperature, 298°K to 420°K, the capacitor was placed in a small furnace (see Figure 9). Again, no attempt was made to hold the temperature constant at any point. In each case the temperature was allowed to increase up to approximately 10°K below the melting point of the specimen.

It was found that the back of the furnace got hotter than the front and that the top got hotter than the bottom. Thus, the measuring cell was placed at a slight incline with the front higher than the rear so that the front and rear would be at the same temperature.
Fig. 8--Double-Dewar system and cell suspension apparatus

Fig. 9--Furnace and measuring cell
CHAPTER III

CALCULATIONS AND MEASUREMENTS

Calculation of Dielectric Constant

As indicated previously, the capacitance $C_{L+E}$ due to the leads and the fringing field was determined by measuring the capacitance of the cell filled with paraffin and using the equation

$$K = \frac{C_s' - C_{L+E}}{C_0' - C_{L+E}}, \quad \text{(Eq. 4)}$$

where $C_s'$ and $C_0'$ are the measured capacitances with the specimen and air, respectively, as the dielectric. Knowing $C_{L+E}$, one could determine $K$ for any substance by measuring $C_s'$ and $C_0'$ and applying equation 4. Thus, the air capacitance $C_0'$ of the capacitor was measured over the entire temperature range of interest, and the results are shown in Figure 10. The changes observed are not from a change in the dielectric constant of air but rather from changes in the measuring cell itself. (At room temperature the dielectric constant of air is only 0.00054 above a value of 1.000, which is the value defined for a vacuum, so the dielectric constant of air cannot decrease by more than 0.00054 and no significant increase would be expected from a temperature increase of only 125°C.)
Fig. 10—Air capacitance of capacitor as a function of temperature
These changes would then be incorporated into the value of $C_{L+E}$ and $C_0 = C_0' - C_{L+E}$, the denominator of Eq. 4, should be constant ($C_0 = 8.35 \text{ pf}$). Thus, the value of 109.0 pf for $C_{L+E}$ was corrected by an appropriate amount $\Delta C$ at each temperature reading (see Figure 10). For example, at 150°K the capacitance measured for a specimen was increased by 0.58 pf, and at 410°K the capacitance was reduced by 0.60 pf. This correction has been made for the curves shown for the various substances. In most cases the values indicated are a composite of several measurements, and, unless otherwise indicated, the values of dielectric constant above room temperature are those obtained as the temperature increased and those below room temperature are the ones obtained as the temperature decreased.

Preparatory Measurements

Reasons for Picking Borneol

In order to test the apparatus, measurements were made on borneol (see Figure 11). Borneol was picked because it is a solid at room temperature and because it has two transitions—one above room temperature at 343-348°K and one below room temperature in the range of 173-223°K as reported by W. A. Yager and S. O. Morgan in 1935\(^1\) (see Figure 12).

Fig. 11--Structure of borneol

Fig. 12--Accepted data for borneol--curve represents d-borneol and points represent l-borneol.
The dielectric constant has a value of 3.67 at 348°K and at 343°K it drops to a value of 3.02, which is still larger than the square of the refractive index (n² = 2.5). Thus, one expects another transition, which occurs between 123°K and 173°K and lowers K to a value approximately equal to n². The upper transition is apparently due to a change in the crystalline structure, while the lower transition point represents a cessation in the rotation of the hydroxyl group.²

The fact that borneol is optically active (occurrence of dextrorotatory and levorotatory forms) turned out to be an unfortunate factor. No definite transition temperature could be found for the lower transition—only the general range of 173-223°K pertaining to several different substances.³ Both transitions are affected by the amount of d-borneol and l-borneol in a mixture of d- and l-borneol, known as dl-borneol. According to theory (which has now been substantiated for many substances) there should be absolutely no difference in the physical properties of pure d- and pure l- forms of any substance.⁴ This is reasonable since no difference should exist in the structure or fields.

²Ibid., p. 2076.

³Ibid.

surrounding each molecule in the two molecular forms. This is borne out by measurements made by White, Biggs, and Morgan on \( l \)-borneol,\(^5\) which were then compared with the measurements made by Yager and Morgan for \( d \)-borneol. The transition point was exactly the same as that for \( d \)-borneol (see Figure 12). However, different mixtures may very well exhibit slightly different properties since different molecules may be surrounded by slightly different force fields. Such a variation in the properties of a substance is illustrated by the range of values for transition temperature (340.7-345.5\( ^0\)K) reported by O. Hassel and J. A. Hveding for three different samples of borneol.\(^6\) Also, the transition in \( d \)-camphor has been found to be displaced to a substantially lower temperature in \( dl \)-camphor.\(^7\)

Results on Borneol

In the present experiments a value of 338-345\( ^0\)K was obtained for the upper transition temperature and a value of 161-189\( ^0\)K was obtained for the lower transition temperature of the sample (see Figure 13). Both of these values were considered reasonable, with any difference from a

\(^5\)Ibid.

\(^6\)O. Hassel and J. A. Hveding, "Rotational Transitions of Crystals Determined by the Differential Thermoanalyzer," Archives der Mathematische Naturvidenskab, XLV, No. 2 (1941), 1-11, cited in Chemical Abstracts, 36 (1941), 5072\(^2\).

\(^7\)White and Bishop, op. cit., p. 12.
Fig. 13—Dielectric constant and dissipation factor vs. temperature for borneol
particular accepted value being accounted for by a difference in composition.

A slight temperature hysteresis was observed due to the placement of the thermocouple. The thermocouple was embedded in the outer cylinder of the capacitor and was therefore warmer than the sample as the temperature increased and cooler than the specimen as the temperature decreased. The maximum temperature difference between the two curves amounted to approximately 4°K at the upper transition and 12°K at the lower transition. At the upper transition, the rate of heating was about three times the rate of cooling, so the actual value is nearer the descending temperature curve. At the lower transition, the rate of cooling was about nine times the rate of warming, so the actual is much closer to the ascending temperature curve. Some of the temperature hysteresis at this lower transition point may be normal since such a hysteresis is observed in many substances.

The relationship between the dielectric constant and the dissipation factor at a solid-solid transition is clearly observed at the lower transition point of borneol.

**Form in Which Substances Were Measured**

All substances measured were measured in the solid state only. Generally when measurements are made on a solid,  

8 Yager and Morgan, _op. cit._, pp. 2075, 2076.
the substance is melted and cast into the proper shape or is compressed under very high pressure into the proper form. In these measurements, all substances were left in a loose powdered form since they are to be reused in other experiments. In addition, they undergo an irreversible transition on melting which, at least partially, permanently destroys their paramagnetism. The fact that the samples were in this loose powdery form made the numerical values of their dielectric constants much lower than the actual value, but the qualitative results remained unchanged. The only purpose in these measurements was to determine the presence of any transition points, and this could be adequately done with the samples in the powdered form.

The numerical values obtained in this experiment for borneol were about 58 per cent of the values shown in Figure 12. In addition, measurements were made on powdered sodium chloride and potassium chloride, and the values obtained were 54 per cent and 56 per cent of the accepted values, respectively. This indicates that the filling factor for a powdered sample is generally about 57 per cent of that for a solid block. The values for the other specimen measured would then likely be on the order of 57 per cent of their actual values.

Reproducibility of Results

The numerical values of dielectric constants vary some due to differences in packing of the substance from one run
to the next and due to slight changes in positioning of the leads while the shape of the curve remained essentially the same. Numerical values were generally reproducible to within three per cent.

Reasons for Using 1000 Hz Signal

Some discussion is warranted concerning the frequency of 1000 Hz used in these measurements since it has been stated in Chapter I that the relaxation time for dipole rotation can vary from $10^{-5}$ seconds to several seconds. Smyth gives a list of substances ranging from very simple inorganic substances through benzene-like substances to long-chain fatty acid esters containing 25-30 carbon atoms. The articles on a majority of the substances in this list were checked, and it was found that all of these were run in the frequency range of 3-100 kHz, generally with little dispersion. This indicates that the values obtained were about the same as the static dielectric constant (measured with a static field). Since none of the substances measured here had a particularly large, complex molecular structure, the chances were considered good for measuring any significant changes in structure or rotational freedom.

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9 Smyth, op. cit., pp. 142-150.

Furthermore, the low-frequency measuring technique is rather tedious and apparently rarely used as a result. In the low-frequency range (0-10 Hz) a conventional bridge, such as the Schering bridge described in Chapter II, can no longer be used due to the inconvenient size of the components required and the duration of the induced transients, which may be effective for several tens of cycles of the applied voltage. Thus, various methods are used to measure the charge or discharge current of a dielectric specimen as a function of time.11,12

An examination of the transition points for the organic materials listed by Smyth and of their melting points indicates that the transition point for most organic substances (if they have one) occurs within 20°K below the melting point.

Dielectric Constant of Galvinoxyl

Figure 14 shows the structure of galvinoxyl. The dielectric constant of a sample of galvinoxyl obtained from Aldrich Chemicals was measured over the range of 100°K to 413°K (see Figure 15). The dielectric constant vs. temperature curve is relatively flat up to a point just below the melting point, at which point there is a rapid rise in the dielectric constant, apparently due to pre-melting. No solid-solid transition appears to exist. The

12 Von Hippel, op. cit., p. 47.
Fig. 14—Structure of galvinoxyl
Fig. 15—Dielectric constant and dissipation factor vs. temperature for pure galvinoxyl.
average value of the dielectric constant over the "flat"
portion of the curve is 1.48. This is less than 57 per cent
of 3.0, so no transition is really expected. (As stated
earlier, a value of \( K \) above 3.0 usually indicates that a
transition will occur.) In addition, a flat or gradually
rising curve with increasing temperature generally indicates
that no transitions will occur at a lower temperature since
above a transition the dielectric constant will decrease
with increasing temperature due to increasing thermal agita-
tion of the molecules. Originally, the color of pure
galvinoxyl is deep blue, but upon melting (m.p. is 423\(^{\circ}\)K)
its color changes to a dark brown.

Measurements were also made on a second sample of
galvinoxyl obtained from Eastman Chemicals (see Figure 16).
Independent magnetic susceptibility measurements\(^{13}\) indicated
that this particular sample, which had an unusual deep
purple color, was only about 30 per cent paramagnetic. It
is not known whether this low yield was due to poor chemical
preparation or to subsequent partial decomposition. This
sample had a considerably lower melting point than the blue
sample, and the melting occurred over a range of several
degrees (389\(^{\circ}\)K-396\(^{\circ}\)K), indicating that the sample was impure.
However, the sample softened considerably well below 389\(^{\circ}\)K.
The temperature of the sample was allowed to rise to 373\(^{\circ}\)K

\(^{13}\)W. D. Duffy, private communication.
Fig. 16: Dielectric constant and dissipation factor vs. temperature for impure galvinoxyl.
in the capacitance measuring cell. When the cell was cooled and opened, the sample was found to have softened enough to have caked upon cooling but not to have softened enough to sag. The dielectric constant of the purple sample rises a little more steeply with increasing temperature than does the blue sample, and at approximately 373°K it begins a rapid increase with increasing temperature due to considerable loosening of the structure or formation of a small amount of liquid phase and consequent interfacial polarization. No solid-solid transitions occur. The average value of K over the relatively flat portion of the curve is 1.59, which is less than 57 per cent of 3.0, so no transition is expected. The purple sample changed color to dark brown upon melting, as did the blue sample. No subsequent measurements were made on the melted, decomposed products.

The dielectric constants of the two samples of galvinoxyl exhibited basically the same variations with temperature.

Dielectric Constant of Dihydroxydiphenylmethane

Figure 17 shows the structure of dihydroxydiphenylmethane, which is the diamagnetic parent molecule of galvinoxyl. Its dielectric constant was measured over the range of 100°K to 429°K (see Figure 18). From 100°K to 298°K the dielectric constant rose slowly with increasing temperature for each specimen measured. From 298°K to 429°K,
Fig. 17--Structure of 3,3',5,5'-tetra-tert-butyl-4,4'-dihydroxydiphenylmethane.
Fig. 18--Dielectric constant and dissipation factor vs. temperature for dihydroxydiphenylmethane.
a fresh specimen exhibited a very slight rise in dielectric constant up to 373°K where a greater increase began due to premelting. A specimen which had previously been run from 298°K to 377°K and then from 298°K to 100°K and back to 298°K exhibited a hump in the dielectric constant between 298°K and 369°K when it was again run in the range of 298°K to 419°K (dotted line in Figure 18). Above 369°K the curve was the same as that for the fresh specimen. The mechanism causing the difference was not determined.

Dihydroxydiphenylmethane does not exhibit as great an increase in dielectric constant due to premelting as does galvinoxyl. The dielectric constant is shown for a small region above the melting point. The small decrease from 419°K to 425°K is due to the shrinkage of the dielectric away from the inner plate during melting. The dielectric constant then increases considerably due to the increased dipole rotation.

No transitions were found over the temperature range measured, and no large transitions would appear likely to occur at lower temperatures. The average value of K over the "flat" portion of the curve is 1.72, which is approximately 57 per cent of 3.0. This is probably slightly larger than the square of the refractive index for this substance. This could be caused by a larger filling factor for this powder than that estimated from other powdered substances, or it could indicate the presence of hindered rotation of
molecules or atomic groups in the substance, with the rotation decreasing gradually with decreasing temperature and finally giving a small transition at some temperature below 100°K. Further experiments would have to be done to determine definitely the behavior.

The color of dihydroxydiphenylmethane changes from yellow-orange to amber upon melting (m.p. is 419°K).

Concluding Remarks

The capacitance bridge used was sensitive enough to measure any significant changes in the dielectric constant of the substances since a change of 0.01 (approximately 0.07 per cent) in the dielectric constant could be detected. There was virtually no variation in the lead capacitance for the leads in the Dewar since they were held rigid by steel wire rods. However, some variation (as much as 0.5 pf) did occur in the lead capacitance for the furnace from one run to the next, and some improvement could probably be made there.

A lucite holder was originally used in the measurements below room temperature, but it eventually cracked. Upon review of the data on the lower transition point of borneol, the transition was observed to be sharper with the Lucite holder than with the Fiberglas holder. This was apparently caused by a more uniform cooling of the sample when the Lucite was used.
The dielectric constants of galvinoxyl and dihydroxydiphenylmethane both rise very gradually with increasing temperature up to just below their melting points, where a large rise in the dielectric constant occurs due to pre-melting. This gradual rise of the dielectric constant with temperature generally suggests that no transitions exist for either substance below the lowest temperature measured (100°K) since above a transition point the dielectric constant usually decreases due to increasing opposition to dipole rotation by thermal agitation. However, this rise could also indicate (particularly in dihydroxydiphenylmethane with the higher dielectric constant) the presence of hindered rotation of molecules or atomic groups, with the rotation decreasing with decreasing temperature and ending with a small transition below 100°K. The data gathered in this experiment alone are insufficient for drawing definite conclusions about the behavior of the substances below 100°K. The variations in dielectric constant of galvinoxyl and dihydroxydiphenylmethane appear to be very similar over the temperature range measured here. However, the inability to compare the values of dielectric constant accurately to the refractive index makes it impossible to conclude definitely whether any molecular freedom exists in dihydroxydiphenylmethane that does not exist in galvinoxyl which could be related to their dia- or para-magnetism.
Further measurements should be made to determine the dielectric constant of solid pressed blocks of each substance at room temperature and these values compared with the square of the refractive index, or the dielectric constant of pressed or powdered samples should be measured below 100°K.
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