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I. DETERMINATION OF DIELECTRIC PROPERTIES UNDER CONSTANT VOLUME CONDITIONS

By

Andrew Gilchrist

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By

Robert H. Cole

III. DIELECTRIC CONSTANTS OF LIQUID AND SOLID HYDROGEN SULFIDE

By

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DETERMINATION OF DIELECTRIC PROPERTIES UNDER
CONSTANT VOLUME CONDITIONS

ABSTRACT

The complex dielectric constant of glycerol has been determined as a function of frequency, (15 c.p.s. to 5 Mc.p.s.), temperature, (-40°C to -60°C) and pressure, (0-15,000 p.s.i.). By combining this data with the requisite PVT data, it is hoped to be able to calculate the dielectric relaxation time for glycerol, as a function of temperature at constant volume. Results so far obtained show that the relaxation time and the equilibrium dielectric constant increase with pressure, and that the rate of increase is greater at lower temperatures.

The description of the apparatus includes the design of a thermostat which may be kept to within 0.01°C at any temperature in the range -40°C to -60°C .

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DETERMINATION OF DIELECTRIC PROPERTIES UNDER
CONSTANT VOLUME CONDITIONS

By

Andrew Gilchrist

The majority of the work done on this contract has been concerned with the temperature dependence of dielectric properties at atmospheric pressure; measurements made at different temperatures are thus on samples at different molar volumes. However, the results of theories of the liquid state concerning rates of molecular rotation are in many cases more easily expressed using molar volume and temperature as the independent state parameters. For this reason measurements of the temperature dependence of dielectric properties made (or corrected to) constant volume are desirable. This section of the report describes the progress made in making such measurements.

Preliminary measurements have so far been made on glycerol over the temperature range, $-60^{\circ}\text{C}.$ to $-40^{\circ}\text{C}.$; corresponding atmospheric pressure measurements have previously been described.¹

1. D. W. Davidson and R. H. Cole, J. Chem. Phys., 19, 1484 (1952)

The Experimental Method.

One possible method of operation at constant volume over a temperature range is to seal off a quantity of the substance to be examined in a constant volume vessel, at the lowest working temperature. Then measurements are taken over the temperature range without unsealing the vessel. If glycerol is sealed in a vessel at $-60^{\circ}\text{C}.$, a pressure of about 6Kp.s.i. (6,000 p.s.i.) is developed on warming to $-40^{\circ}\text{C}.$. This direct approach has not been used as it has been

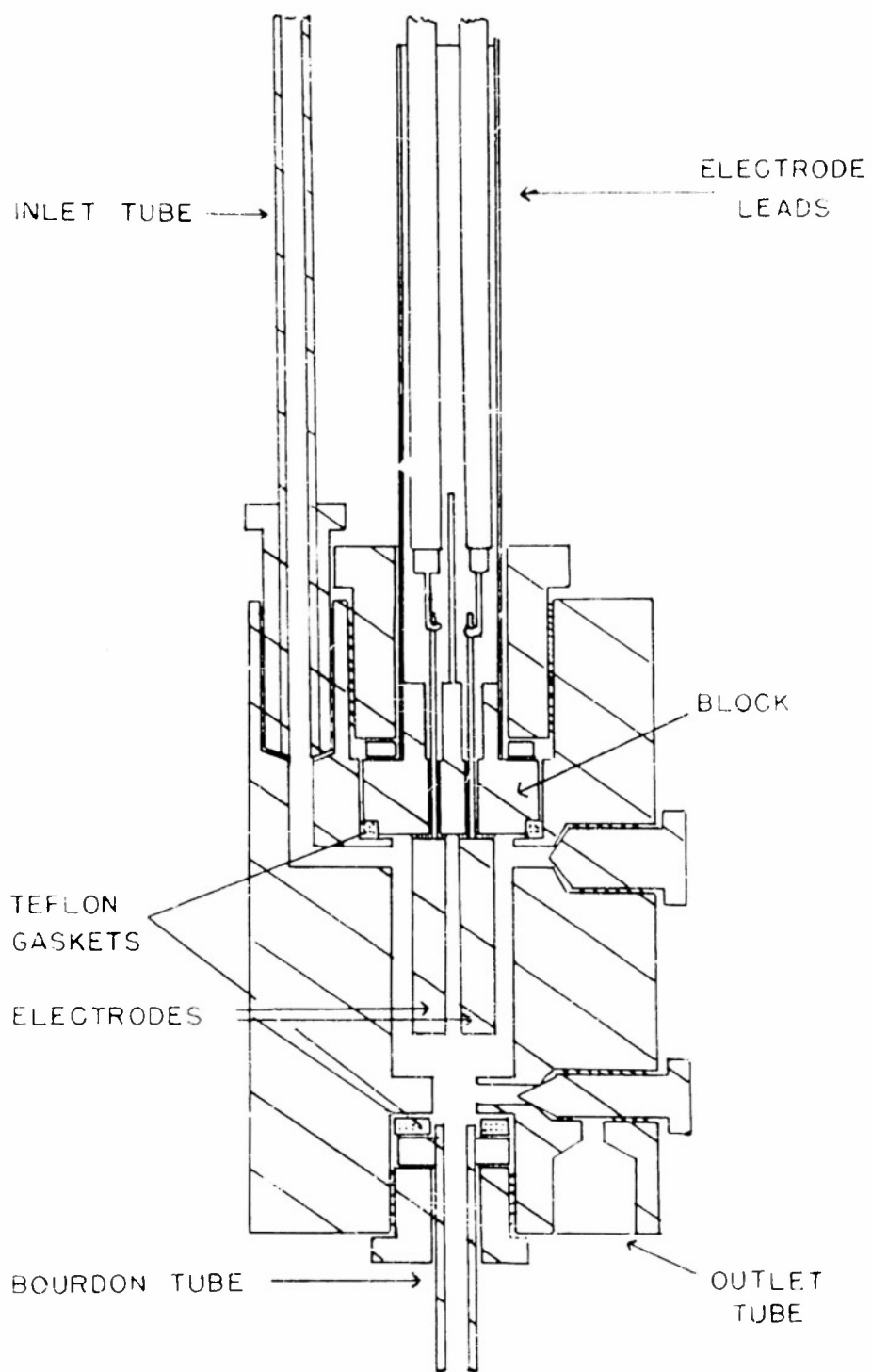
found simpler, experimentally, to measure the variation of dielectric properties with pressure at a series of temperatures within the range mentioned. The pressure range must clearly extend to 6 Kp.s.i., and in fact it has been extended much further so that the effect on dielectric properties, of reduced molar volumes, may be studied. These results are to be combined with the pertinent PVT data to calculate the temperature dependence of dielectric properties, corrected to constant molar volume.

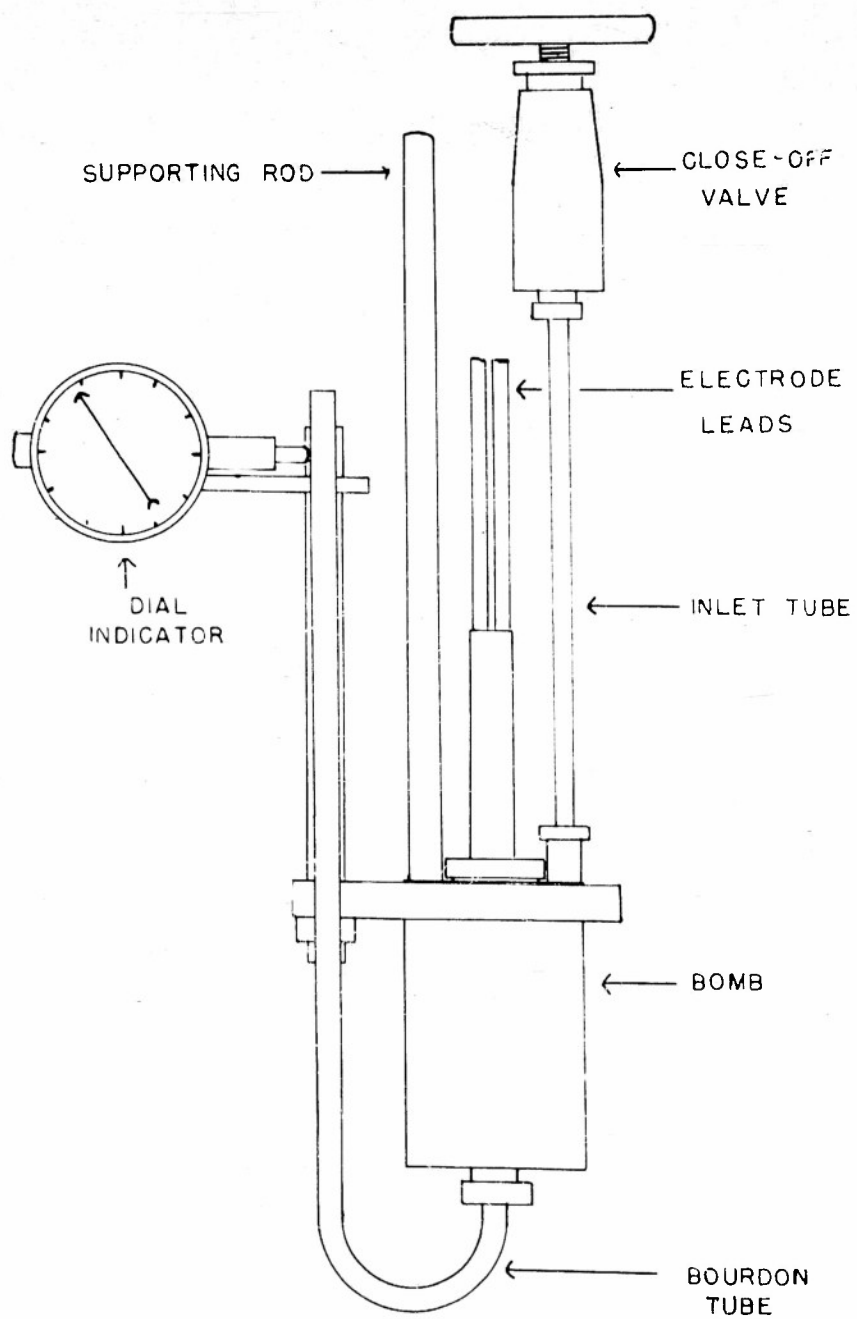
The Apparatus.

The dielectric cell used in this work consists of a cylindrical bomb (Fig. 1), into the upper part of which is fitted a block carrying two semi-cylindrical stainless-steel electrodes. These are cemented to the block by a thin layer of "Araldite" resin, which is an electrical insulator. Electrode leads are brought through the block and attached to two coaxial leads which are surrounded for some distance from the block by a brass tube; this carries the leads clear of the thermostat bath. A stainless steel Bourdon tube is fitted to the bottom of the bomb (Fig. 2) and the movement of the extended free arm is measured with a dial indicator rigidly attached to the bomb. The inlet tube is fitted at its upper end with a close-off valve, which consists essentially of a piston and cylinder, with a suitable sealing gasket. To generate a given pressure in the bomb, the piston is screwed into the cylinder for the required distance. An outlet tube is provided so that the cell may be flushed with glycerol preparatory to filling it with the proper sample.

The Bourdon tube pressure gauge is calibrated periodically using a dead-weight tester; this consists essentially of a cylinder

- Fig. 1 High Pressure Dielectric Cell.
- Fig. 2 Cell with Associated Apparatus.





and piston which may be fitted in the bomb in place of the electrode block, and a set of weights which are loaded onto the piston. The whole is held in a frame so that the bomb with the gauge may be immersed in the thermostat bath at about $-50^{\circ}\text{C}.$; within a range of $10^{\circ}\text{C}.$ on either side of this temperature, the gauge calibration is effectively independent of temperature.

Results.

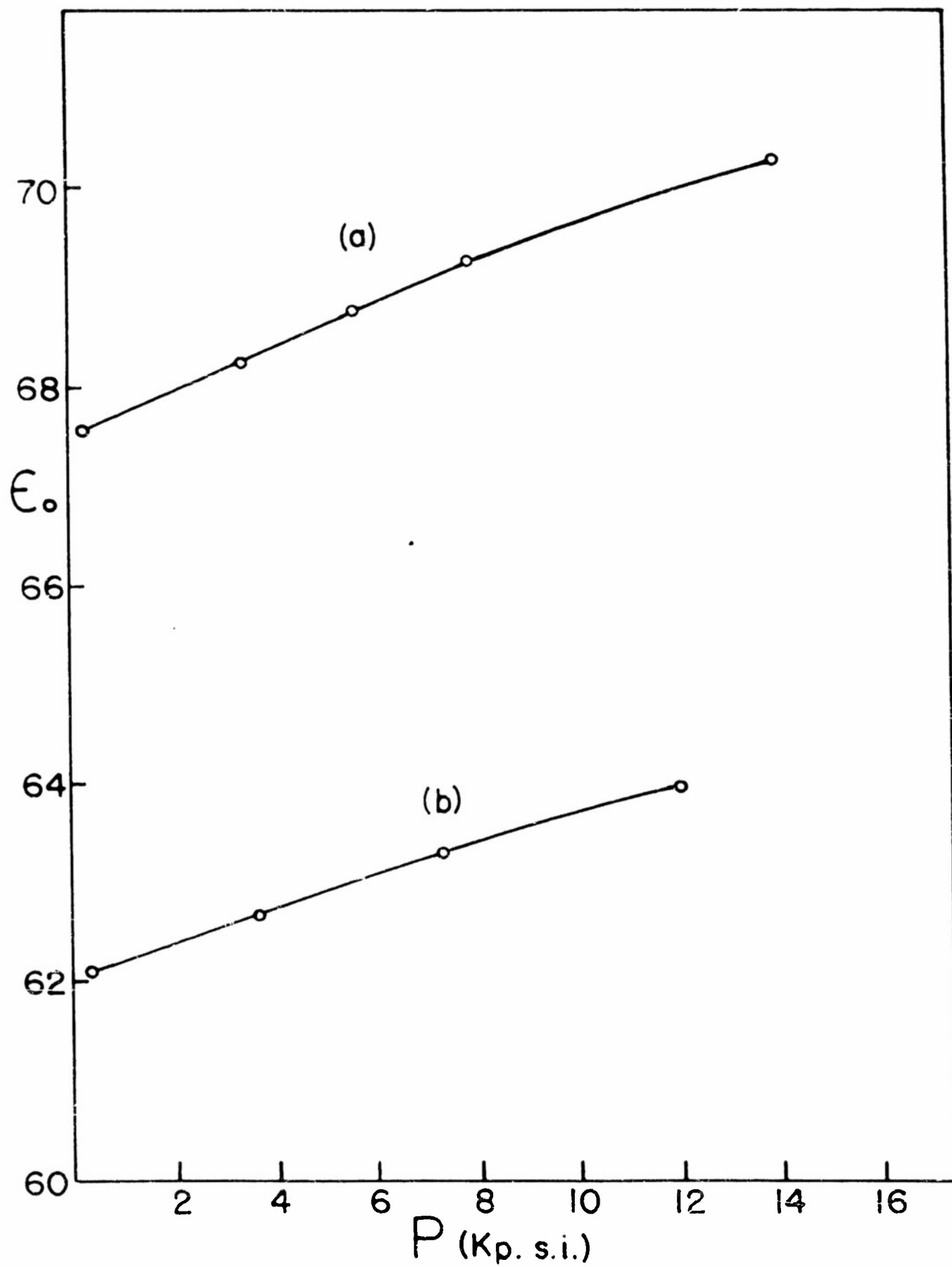
Some preliminary results have been obtained using this apparatus, but no detailed discussion of them has been attempted so far. It is observed that dielectric relaxation times in glycerol increase with pressure at constant temperature and that the enhancement is greater at lower temperatures. A plot of $\log \tau$ against pressure is linear within experimental error. The quantity β , the second parameter in the dispersion equation (Ref. 1) appears to be independent of pressure.

The equilibrium dielectric constant also increases with pressure at constant temperature and the coefficient $\frac{1}{\epsilon_0} \frac{d\epsilon_0}{dT}$, appears to increase at lower temperatures. The value of ϵ_1 , the limiting high frequency dielectric constant for the main dispersion region also has a positive pressure coefficient but our accuracy is not sufficient to determine its magnitude.

Some typical results are shown graphically in Figs. 1 and 2, and expressed in tabular form in Tables ³1 and ⁴2.

Fig. 3 Variation of ξ_c with Pressure.

Fig. 4 Variation of Relaxation Time with Pressure.



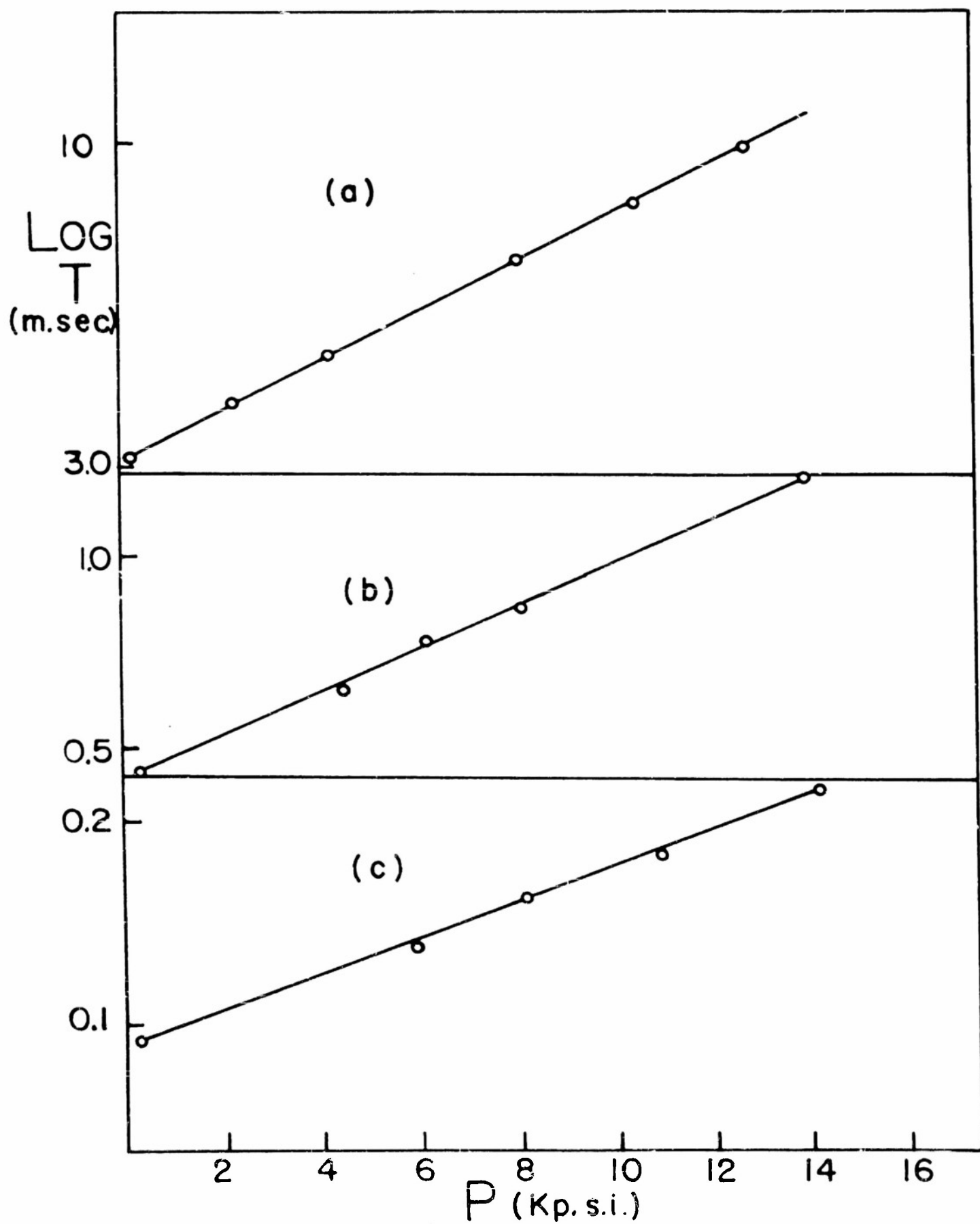


Table 1.

Variation of τ with pressure, at four temperatures.

Temp. °K.	τ . 15 p.s.i.	τ . 10,000 p.s.i.	Ratio
210.6	3.00×10^{-3} sec.	7.8×10^{-3} sec.	2.6
216.8	4.3×10^{-4} sec.	9.7×10^{-4} sec.	2.3
222.8	9.1×10^{-5} sec.	1.73×10^{-4} sec.	1.9
228.8	2.47×10^{-5} sec.	4.6×10^{-5} sec.	1.8

Table 2.

Variation of ϵ_0 with pressure at two temperatures.

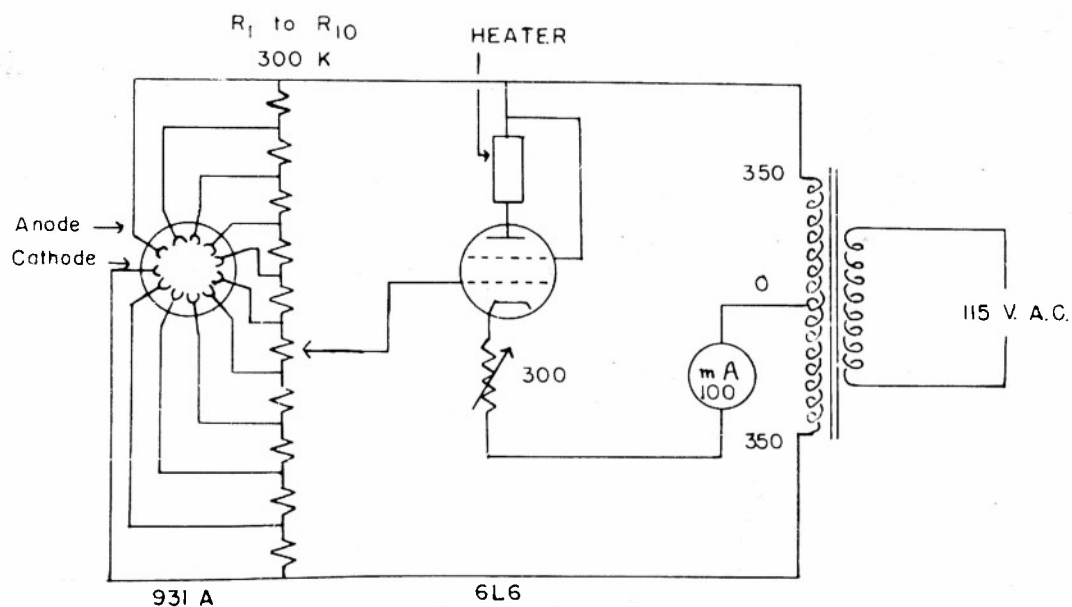
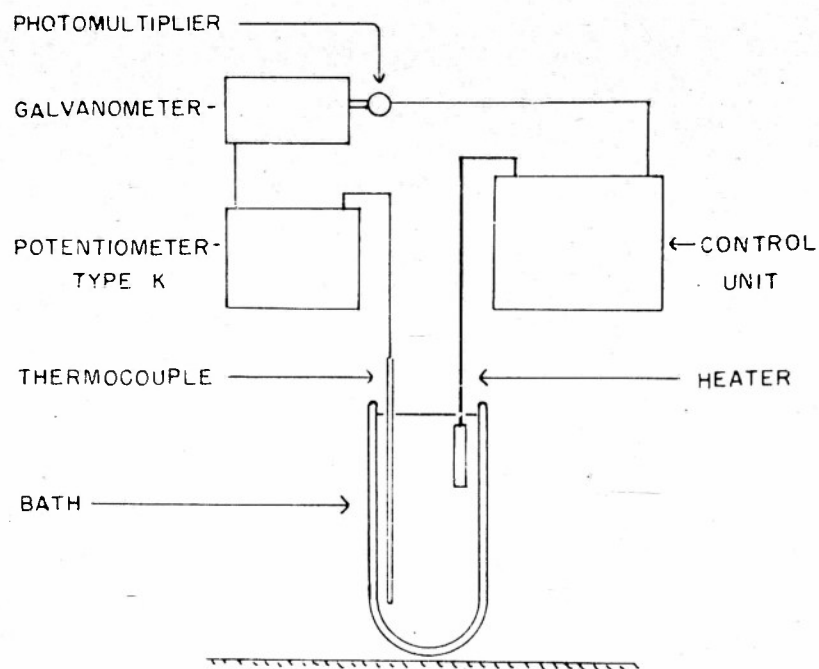
Temp. °K.	at 15 p.s.i.	at 10,000 p.s.i.	Ratio
216.8	67.5	69.65	0.032
228.8	62.1	63.7	0.026

A Thermostat Control.

A thermostating device has been built to be used in conjunction with the apparatus already being used by this department for temperature measurement. This apparatus consists of a thermocouple connected to a potentiometer and lamp-and-scale galvanometer. The device uses a photomultiplier tube mounted in front of the galvanometer scale, to control the current through a vacuum tube; a thermostat heater is connected in the anode circuit of this tube. (Fig.5) The entrance slit of the photomultiplier is so mounted that when the galvanometer is undeflected very little light passes through the slit, and correspondingly little current flows through the heater. Should the potentiometer become unbalanced by virtue of the bath becoming colder, the galvanometer is deflected in such a sense that more light falls on the photomultiplier and the heater current increases.

This device has been used to control a bath at temperatures within the range -60°C. to -40°C. by immersing a cold finger in the

Fig. 5 Diagram of the Low-temperature Thermostat.
(above) Block Diagram.
(below) Circuit of Control Unit.



bath as well as a heater. The cold finger is filled with dry ice and the thermal conductivity to the bath is adjusted so that it abstracts heat from the latter at the rate of 5 to 10 watts. This loss is then made up by the controlled heater. The sensitivity of the system is such that a deflection of the galvanometer caused by a change in bath temperature of 0.01°C . produces a change in the heater output of about 5 watts.

The unit is presently in use on the high pressure project and gives temperature control to within 0.01°C ., except in so far as variations in the standard cell and ice-junction of the thermocouple necessarily go undetected; but these are probably very small.

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ON THE ANALYSIS OF DIELECTRIC RELAXATION MEASUREMENTS

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ABSTRACT

Convenient methods of analysing dispersion and loss satisfying the Debye equations are described and illustrated. The similarities and differences of the Fuoss-Kirkwood and circular arc representations of symmetrical, non-Debye type dispersions are considered. Interpretations given by various writers to the asymmetric dispersion found by D. W. Davidson and the writer for glycols are discussed. Finally, the possibilities and limitations of reduced representations of dielectric measurements are examined.

I. INTRODUCTION

The purpose of this paper is to discuss methods of analyzing dielectric dispersion data and questions of interpretation of such measurements. The contributions to these subjects in what follows have developed from various investigations in the Brown laboratories, and the illustrative examples are largely drawn from this work on dielectric properties of a number of relatively simple liquids and solids. The methods and conclusions are, however, relevant to much other research, both on dielectric relaxation and on other broadly similar relaxation phenomena. It has therefore seemed appropriate to present this material separately rather than piecemeal in reports of results for particular systems.

We shall be concerned with the frequency and temperature dependence of dielectric behavior in alternating electric fields. The relaxation effects arising from failure of the polarization to reach equilibrium with the applied

field are conveniently described by the complex dielectric constant

$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ where ϵ' represents the polarization in phase with the assumed sinusoidal field of frequency $f = \omega / 2\pi$, and ϵ'' the component with phase difference of $\pi/2$ which expresses the energy absorption (dielectric loss). The variation of these quantities with frequency is of the general form shown in Fig. 1; a logarithmic scale of frequency permits representation of the significant range of variation of ϵ' and ϵ'' more compactly and symmetrically than other possible scales. The effect of temperature is quite generally to change the range of dispersion to lower frequencies at lower temperatures, and the limiting dielectric constants ϵ_0 and ϵ_∞ realized at very low and high frequencies are also temperature dependent.

The projection of the curve $\epsilon^*(\omega)$ on the ϵ' -log f plane as indicated in Fig. 1 is the familiar sigmoid dispersion curve; the projection on the ϵ'' -log f plane is the bell-shaped absorption curve. An alternative representation is the projection on the ϵ'' - ϵ' plane. The usefulness for dielectric data of this complex plane locus has been discussed by K. S. Cole and the writer¹.

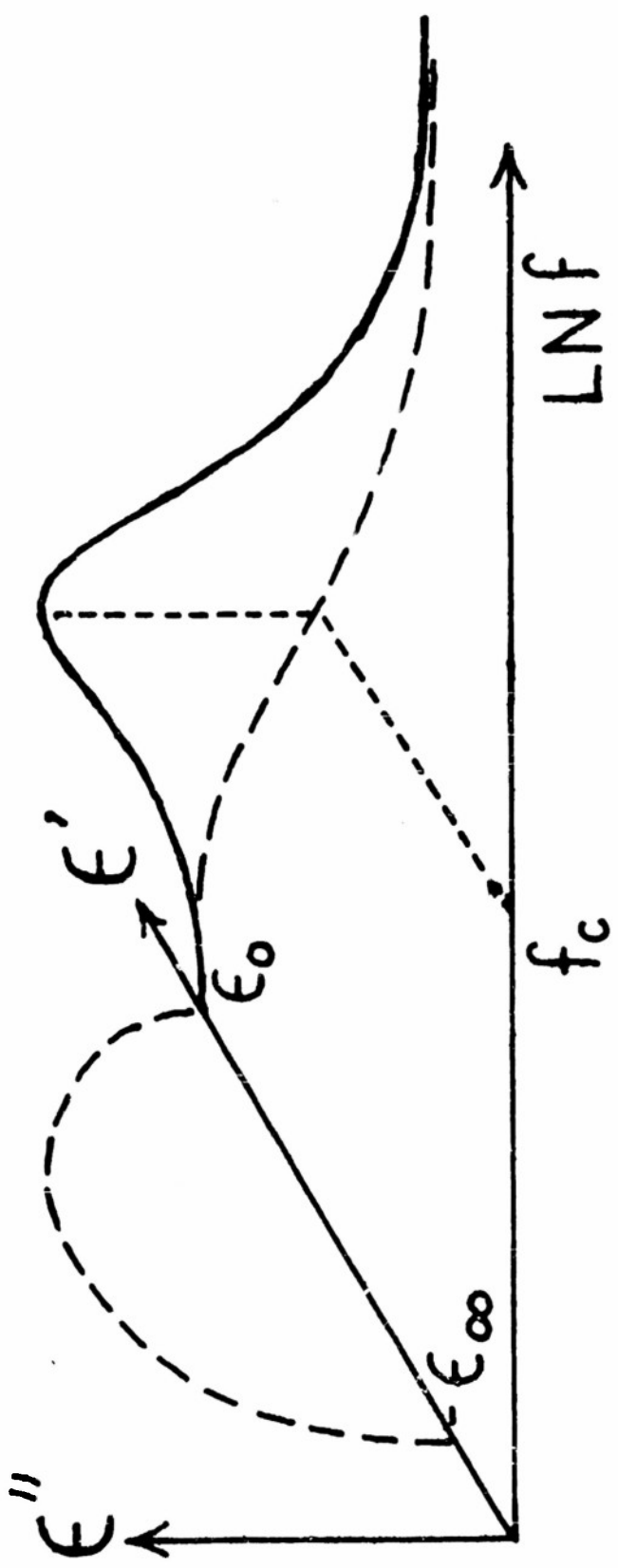
1. K. S. and R. H. Cole, J. Chem. Phys., 9, 341 (1941).

In Fig. 1 as it is drawn, the projection is the semicircle predicted for simple relaxation processes. In other cases, relaxation data do not conform to this locus but may often be fitted quite accurately by a circular arc as an asymmetric curve of simple functional form. Questions arising in connection with these empirical results are discussed in what follows.

II. SIMPLE RELAXATION THEORY

It is a common characteristic of dielectric and other relaxation theories based on simple molecular or macroscopic models that they predict a rate of change

Fig. 1. The curve $\epsilon^*(\omega)$ in $\epsilon' - \epsilon'' - \log \omega$ space.



of polarization, or other response, which is proportional to the difference of the polarization from its equilibrium value. In such cases the complex dielectric constant, or its steady state analogue for an alternating field, is expressed by an equation of the form

$$\epsilon^* = \epsilon_{\infty} + (\epsilon_0 - \epsilon_{\infty}) / (1 + i\omega T_0). \quad (1)$$

In this equation, the relaxation time T_0 is related to the kinetics of the relaxation process of the particular model, and is analogous to the reciprocal of a rate constant in first order chemical kinetics.

An equation of the form (1) was obtained by Debye²

2. P. Debye, Polar Molecules (Dover Publications, New York, 1929).

from his model for polar liquids of spherical polar molecules reaching equilibrium subject to brownian diffusion and viscous damping; the result (1) for dielectric relaxation is often referred to as the Debye equation. This description is appropriate and convenient, but it is important to recognize that equations of the same form result for models of such diverse systems and phenomena as two-phase suspensions of dielectrics, paramagnetic relaxation, viscoelastic polymers, and various other physical and biological relaxation effects.

In the dielectric case, it has been perhaps remarkable that the majority of examples of dispersion have failed to conform to the frequency or true dependence corresponding to Eq. (1), but in the last few years adequate data have been obtained to demonstrate its validity for a number of liquids and solids of relatively simple molecular constitution. Because of this and the fact that the first order result is the simplest significant one, adequate means of testing its validity and of determining the parameters ϵ_0 , ϵ_{∞} and T_0 if it is valid are

two problems of importance.

The obvious and direct means of testing (1) is to compare experimental values of ϵ' and ϵ'' as a function of frequency with the functions required by Eq. (1):

$$\begin{aligned}\epsilon'(\omega) &= \epsilon_{\infty} + (\epsilon_0 - \epsilon_{\infty}) / [1 + (\omega T_0)^2] \\ \epsilon''(\omega) &= (\epsilon_0 - \epsilon_{\infty}) \omega T_0 / [1 + (\omega T_0)^2].\end{aligned}\quad (2)$$

Direct tests of these equations can be made by curve fitting with proper choice of the three adjustable parameters ϵ_0 , ϵ_{∞} , and T_0 , but there is considerable trial and error if ϵ_0 and ϵ_{∞} are not known from measurements over a considerable frequency range. Variants of this procedure involve, for example, plotting $\epsilon''/(\epsilon' - \epsilon_{\infty})$, which should equal ωT_0 from (2), against frequency, but ϵ_{∞} must be known or trial values assumed. Two alternative procedures which avoid use of trial values of any of the parameters are very useful in practice, as described below.

The first is to employ the complex plane locus of ϵ'' versus ϵ' , which if Eqs. (1) and (2) are valid is a semicircle with center on the real axis and intercepts on this axis at ϵ_0 and ϵ_{∞} as indicated in Eq. (1). This representation is a very useful one whether or not the actual data conform to such a semicircle, and if they do the determination of the best semicircle is surprisingly sensitive. The intercepts of a satisfactory fit give ϵ_0 and ϵ_{∞} directly, but the value of T_0 is not accurately determined from the plot, although it can often be estimated with fair accuracy from the interpolated frequency of the midpoint of the semicircle.

Alternative graphical or analytical methods, which have been found extremely useful and convenient in this laboratory, can be based on the real and imaginary parts of Eq. (1) obtained after multiplication by $(1 + i\omega T_0)$. These are

$$\epsilon' = \epsilon_0 - \tau_0 (\omega \epsilon''), \quad (3)$$

$$\epsilon' = \epsilon_\infty + (1/\tau_0)(\epsilon''/\omega). \quad (4)$$

The advantage of the equations is that they are linear relations in the measured quantities ϵ' , $\omega \epsilon''$, and ϵ''/ω , and from them, if they are satisfied, the parameters ϵ_0 , ϵ_∞ , τ_0 can be derived as intercepts and slopes without using assumed values.

Two examples of the use of Eqs. (3) and (4) are shown in Figs. 2 and 3. In Fig. 2 measurements by Mr. Walter Dannhauser in this laboratory for n-butyl alcohol are plotted. For the plot on the left of data at -76°C , excellent straight line fits are obtained over most of the frequency range of the measurements (15 c/s to 3 Mc/s), and the slopes of these straight lines for the two plots give a relaxation time $\tau_0 = 1.37 \times 10^{-7}$ sec.

The data at -106°C plotted at the right in Fig. 2 show significant deviations from linearity at frequencies above 100 kcs. These result from a second dispersion of the form first reported for n-propyl alcohol³,

3. D. W. Davidson and R. M. Cole, J. Chem. Phys. 20, 1389 (1952).

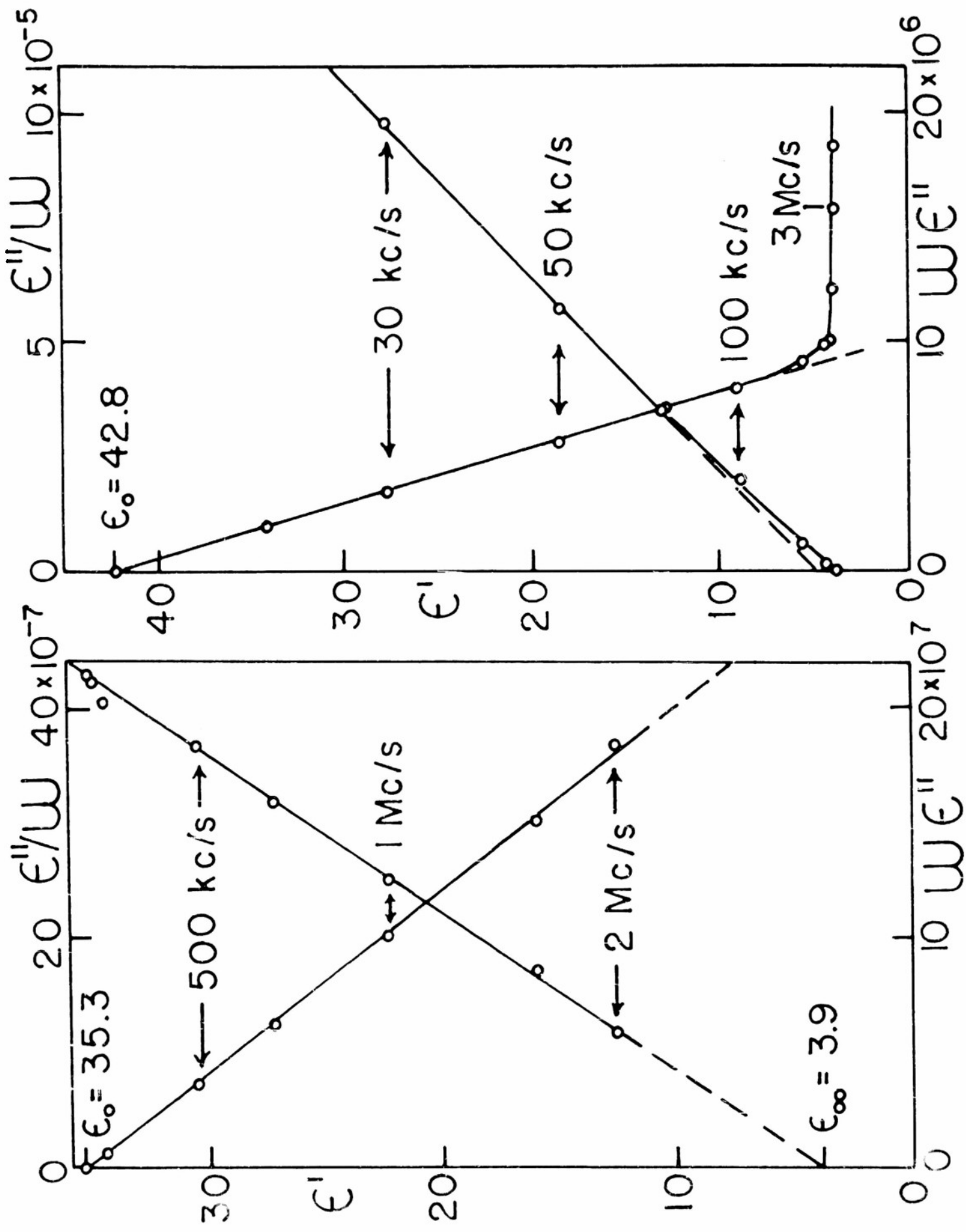
and since found in measurements of several other alcohols. Extrapolation of the straight line of ϵ' versus ϵ''/ω gives in these cases values of the high frequency limit ϵ_∞ for the lower frequency dispersion. Knowledge of this value, together with τ_0 , permits detailed analysis of the further dispersion, especially at lower temperatures for which the measurements give more complete information.

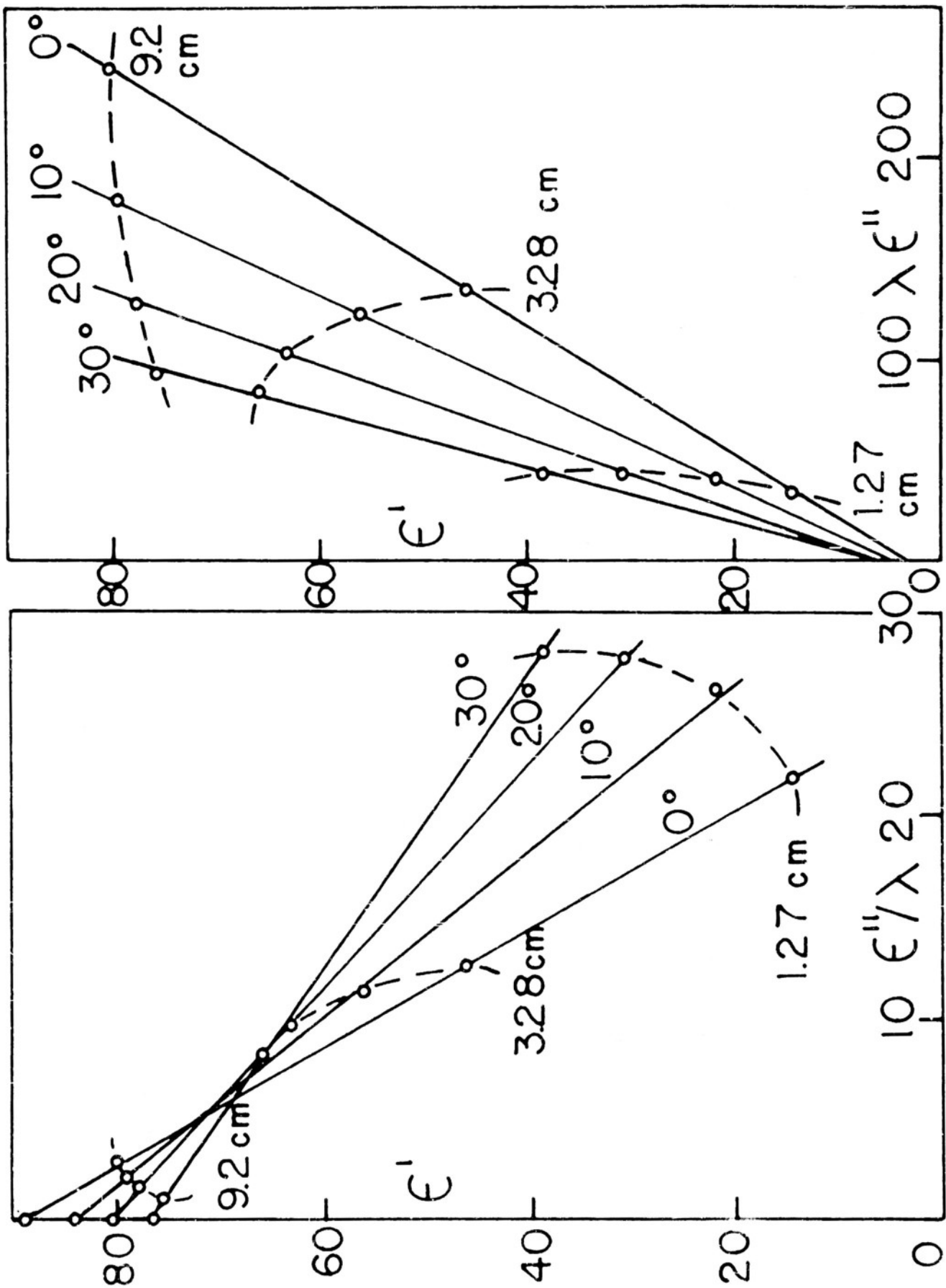
The data plotted in Fig. 3 are results of Hasted and El Sabeh⁴

4. J. B. Hasted and S. H. M. El Sabeh, Trans. Far Soc. 49, 1003 (1953).

Fig. 2. Plots of ϵ' versus $\omega\epsilon''$ and ϵ''/ω . Left, n-butyl alcohol at 197.2°K; right, n-butyl alcohol at 167.5°K.

Fig.3. Plots of ϵ' versus ϵ''/λ (left) and $\lambda\epsilon''$ (right) for water at 0°, 10°, 20°, 30°C. from data of Hasted and El Sabeh.





from microwave measurements of water at 0°, 10°, 20°, and 30°C and vacuum wave - lengths of 1.27, 3.3, and 9.2 cm. For convenience, the analogues of Eqs. (2)

in terms of wavelength λ have been used. In terms of the critical wavelength

$$\lambda_c = 2\pi C\tau_0, \text{ these are } \epsilon' = \epsilon_0 - \lambda_c (\epsilon''/\lambda) = \epsilon_\infty + (\lambda\epsilon'')/\lambda_c.$$

The measured values are satisfactorily fitted by straight lines with consistent values of λ_c from the slopes. The intercepts of the high frequency plots are not determinable with high accuracy because of the long extrapolation. It is significant, however, that the values of ϵ_∞ are of order 3.5 - 5.5 and so considerably larger than values of order 2.2 - 3.0 from visible and infrared measurements. It thus seems clear from the analysis that significant further dispersion in water must occur in the far infrared or millimeter wave region, and further study of this dispersion which Hasted and coworkers⁵

5. G. H. Haggis, J. B. Hasted, and T. J. Buchman, J. Chem. Phys. 20, 1452 (1952).

have discussed

is clearly important for an understanding of the dielectric behavior of water.

The two examples discussed are typical of the utility of Eqs. (2) and (3) for analysis of simple Debye dispersions. There are a number of advantages from their use which these examples may not make apparent. For example, Eq. (2) is particularly useful if bridge measurements of equivalent parallel capacitance $C'(\omega)$ and conductance $G(\omega)$ are made, as a plot of C' versus G is a straight line of slope $-\tau_0$. This is because C' and G for a dielectric with simple relaxation are proportional to ϵ' and $\omega\epsilon''$. (The determination of a time from the measurements without explicit use of frequency or time results from the ratio of consistent units of C and G having dimensions of time.) A second advantage is that neither (2) or (3) involves adjustment of parameters for testing

data, and systematic errors become evident which may be concealed in trial and error fitting of Eq. (1) to data. Although the difference of Eqs. (2) and (3) from Eq. (1) is trivial mathematically, the practical advantages of the former are real and considerable, and their use has on several occasions made evident otherwise unsupported implications or errors of experimental measurements.

III. SYMMETRICAL DISPERSIONS

As already mentioned, the experimental results for many dielectrics are not described by the time or frequency dependence of the form predicted by Eqs. (2) or their equivalent. Many such measurements have been found to exhibit deviations which preserve the symmetrical dependence on logarithmic frequency but with the differences that the frequency range of dispersion is greater and the absorption curve is broader and lower.

A number of empirical or semi-empirical expressions have been proposed to describe experimental results of this kind. The ones which have been most often used are the Wagner-Yager⁶

6. K. W. Wagner, Ann. Physik 40, 817 (1913).
 W. A. Yager, Physics 7, 434 (1936).

derivations of the consequences of an assumed logarithmic Gaussian distribution of relaxation times, the Fuoss-Kirkwood expression⁷

7. R. M. Fuoss and J. G. Kirkwood, J. Am. Chem. Soc. 63, 385 (1941).

for dielectric loss which is an approximation to their theoretical result for diffusion of polar polymer molecules in a non-polar solvent, and the empirical circular arc function originally proposed by K. S. Cole⁸

8. K. S. Cole, J. Gen. Physiol. 12, 29 (1928).

for
 electrical impedance of membranes in biological systems and later found by
 him and the writer¹ to represent a variety of dielectric data within their
 limitations of frequency range and internal consistency.

The similarities and differences of these functions in relation to
 available experimental data have been discussed by Kauzmann⁹.

9. W. Kauzmann, Revs. Modern Phys. 14, 12 (1942).

His con-
 clusion that the Wagner-Yager distribution leads to a dispersion function
 with too abrupt a frequency dependence in the limit of very low and high fre-
 quencies to describe a variety of data confirmed a previous analysis⁹, and is
 consistent with more recent results of which the writer is aware.

The other two dispersion expressions are more satisfactory and less
 obviously different in their functional form. Fuoss and Kirkwood originally
 gave an empirical expression for ϵ'' only; this expression is

$$\epsilon'' = \epsilon_m'' / \cosh \alpha' z, \quad z = \omega / \omega_m, \quad (5)$$

where ϵ_m'' is the absorption maximum at the radian frequency ω_m , and α'
 is an adjustable parameter varying from the value one for a Debye dispersion
 (for which $\epsilon_m'' = (\epsilon_0 - \epsilon_\infty)/2$) to zero for an infinitely broad dispersion.
 By solving the Kronig-Kramers¹⁰

10. R. deL. Kronig, J. Opt. Soc. Am. 12, 547 (1926),
 H. A. Kramers, Atti Congr. dei Fisici, Como, 545 (1927).

integral relations between the conjugate

quantities ϵ' and ϵ'' , Macdonald¹¹

11. J. R. Macdonald, J. Chem. Phys. 20, 1107 (1952).

has more recently obtained analytical expressions for ϵ' . These could be obtained only for particular values of α' permitting evaluation of the integral involved, but with their aid tables or graphs for interpolation of ϵ' versus z and α' can be constructed.

The arc dispersion function has the form

$$\epsilon^* = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) / [1 + (i\omega T_0)^{1-\alpha}], \quad (6)$$

where the exponent $1-\alpha$ to which the operator $i\omega T_0$ is raised is an empirical parameter. The real and imaginary parts have the relatively simple analytical forms

$$\epsilon' - \epsilon_\infty = \frac{1}{2} (\epsilon_0 - \epsilon_\infty) \left[1 - \frac{\sinh(1-\alpha)z}{\cosh(1-\alpha)z + \sin \frac{1}{2}\alpha\pi} \right] \quad (7)$$

$$\epsilon'' = \frac{1}{2} (\epsilon_0 - \epsilon_\infty) \frac{\cos \frac{1}{2}\alpha\pi}{\cosh(1-\alpha)z + \sin \frac{1}{2}\alpha\pi} \quad (8)$$

where $z = \ln \omega / \omega_m$.

The differences between the Kirtwood-Fuess and arc functions are not great for the values of α and α' of the order ^{1.0 to 0.5 and} 0 to 0.5 required to fit many experimental data. The similarity of the results for ϵ'' has been pointed out by Böttcher¹²

12. C. J. F. Böttcher, Theory of Dielectric Polarisation (Elsevier Publishing Co., Amsterdam, 1952), p. 371.

in quoting a result of Poley. As they showed, Eqs. (6) and (8) when expanded in powers of z about $z=0$, i.e., around the central frequency $\omega = \omega_M$ agree to the second power in z if one takes $\alpha' = \cos \frac{1}{2} \alpha \pi / (1 + \sin \frac{1}{2} \alpha \pi)$ and normalizes both functions to the same value of ϵ_m'' . On the other hand, Macdonald points out that for $\omega \ll \omega_M$ or $\omega \gg \omega_M$ the Kirkwood-Fuoss result predicts a complex locus of ϵ'' vs. ϵ' which approaches the ϵ' axis at a smaller angle and more nearly as a straight line than the circular arc with depressed center predicted by Eq. (6). Neither of these discussions makes very clear the magnitude of the difference, and it is therefore appropriate to illustrate these by comparison with appropriate experimental data.

The data which have been examined from this point of view were obtained
 13
 by N. L. Brown

13. N. L. Brown and R. H. Cole, J. Chem. Phys. 21, 1920 (1953).

in this laboratory on solid hydrogen bromide below 89°K; these results for a considerable frequency range under very steady thermal conditions showed good internal consistency and reproducibility. The measurements were represented by Eq. (6) after a circular arc was found to be a good fit to the plot of ϵ'' vs. ϵ' . A comparison of the observed values at 73.1°K with values calculated from parameters of the arc function is given in Table I. The differences, of the order one percent of $(\epsilon_0 - \epsilon_\infty)$ or less, are within the combined errors of temperature drift and calibrations of frequency and other electrical quantities.

TABLE I. Observed and Calculated Dispersion and Loss of Solid Hydrogen Bromide at 73.1°K.

Calculated values from Eqs. (7) and (8) with $\epsilon_0 = 36.35$,
 $\epsilon_\infty = 4.35$, $\omega_m/2\pi = 290$ c/s, $\alpha = 0.322$.

f (kc/s)	ϵ'		ϵ''	
	obs.	calc.	obs.	calc.
.02	33.5	33.0	3.48	3.82
.05	30.5	30.1	6.18	6.30
.1	27.5	27.5	8.21	7.95
.2	23.0	23.1	9.25	9.21
.5	16.4	16.4	8.92	8.99
1.0	12.3	12.2	7.60	7.53
2	9.38	9.25	5.82	5.65
5	6.94	6.85	3.73	3.49
10	5.98	5.85	2.46	2.32
20	5.24	5.25	1.55	1.50
50	4.83	4.90	0.80	0.82
70	4.70	4.74	0.63	0.67

From the Kirkwood-Fuoss expression (5), one has

$$\cosh^{-1}(\epsilon_m''/\epsilon') = \alpha' \ln(\omega/\omega_m). \quad (9)$$

Hence the plot of $\cosh^{-1}(\epsilon_m''/\epsilon')$ versus $\ln \omega$ should be a straight line of slope α' , while from Eq. (8) one has the relation

$$\frac{\epsilon_m''}{\epsilon'} = \frac{\cosh(1-\alpha)z + \sin \frac{1}{2}\alpha\pi}{1 + \sin \frac{1}{2}\alpha\pi} \quad (10)$$

From this relation, the slope of $\cosh^{-1}(\epsilon_m''/\epsilon')$ vs. $\ln \omega$ is

$(1-\alpha)/[1 + \sin \frac{1}{2}\alpha\pi]^{\frac{1}{2}}$ near $\omega = \omega_m$ and changes for large values of $\ln \omega/\omega_m$ to $1-\alpha$. The comparison of Eqs. (9) and (10) with the

data of Table I is shown in Fig. 4. The experimental values appear to be slightly more consistent with the curve from Eq. (10), but it is apparent that the differences are small and not distinguishable with certainty even for the quite extensive and consistent data of the example.

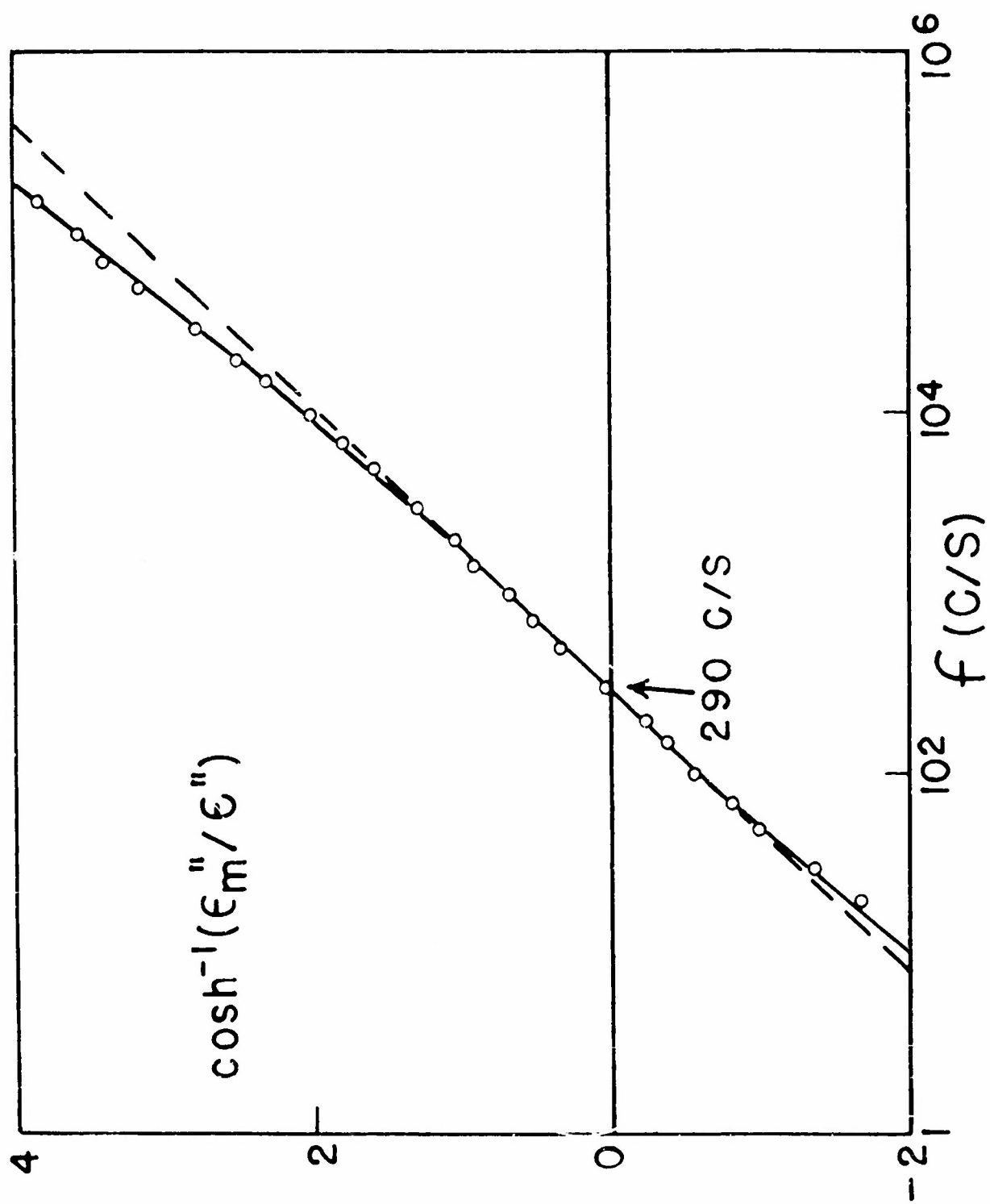
From this example, it can be seen that the differences between the two dispersion functions are not easily tested experimentally. At the present, there is no firm theoretical basis for preferring one over the other in general. The example, for a solid near an order-disorder transition, has no immediate relation to Fuoss and Kirkwood's model of a dilute polymer solution which led to their use of Eq. (9) as a semi-empirical function.

Macdonald (1) has pointed out that the linear relation (9) between $\cosh^{-1}(\epsilon_m''/\epsilon'')$ and $\ln\omega$ provides a convenient method of determining the central frequency ω_m of the dispersion, since ϵ_m'' is readily determinable. From Fig. 4 it is evident that this plot is, for data at frequencies not too far from ω_m , suitable in determining the value of ω_m for either functional dependence. In conjunction with the complex plane locus, one can then evaluate all the parameters of either empirical expression, by extrapolation if necessary. If there is no valid experimental distinction between the two functions for representing the data, then in the absence of independent grounds for choosing one of the other the more convenient one is preferable. This would seem to the writer to be the arc function, because of the simplicity graphically and in the complex form (6) and because of the relative simplicity of the corresponding expressions for both ϵ'' and ϵ' (Eqs. (7) and (8)) for any value of the parameter α expressing the breadth of the dispersion.

IV. ASYMMETRICAL DISPERSION FUNCTIONS

Data for a considerable variety of dielectrics are, over the range of

Fig. 4. Variation of dielectric loss with frequency for solid hydrogen bromide at 73°K. Circles are experimental values, the solid curve is calculated from the circular arc function by Eq. (10) with parameters listed in Table I, the dashed straight line corresponds to the Kirkwood-Fuoss expression (Eq. 9).



available measurements, consistent with the logarithmically symmetrical dispersion and absorption dependences on frequency discussed above. Recently, however, cases of asymmetrical frequency dependence have been found in dielectric and other relaxation processes. One form of departure investigated by D. W. Davidson and the writer¹⁴

14. D. W. Davidson and R. H. Cole, J. Chem. Phys. 19, 1484 (1951).

is in the dielectric behavior of glycerol and other liquid glycols with more than one hydroxyl group in the molecule. These results have been quoted and discussed by several other workers from various points of view, and with differing conclusions in regard to the original representation and its significance. Because of this, it is appropriate to consider in more detail the nature of the observed dispersion, its analytical description, and the conclusions to be drawn.

The complex plane loci for the dispersion in glycerol at temperatures from -40°C to -75°C were found to be asymmetrical of the form shown by the solid line in Fig. 5. It was found that these data could be represented analytically to within the probable accuracy of the data by a function of the form

$$\epsilon^* = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) / (1 + i\omega T_0)^\beta, \quad (11)$$

where β is an empirical parameter in the range $0 < \beta < 1$, and the other quantities have their previous significance. The accuracy of this representation is illustrated in Table II, where experimental values of ϵ' and ϵ'' are compared with those calculated using the parameters ϵ_0 , ϵ_∞ , T_0 , and β determined from the arc locus and the dependence of $\epsilon''/(\epsilon' - \epsilon_\infty)$ on ω (see Ref. 14). Except at frequencies above 100 kc ($\omega > 80 \omega_m$) the agreement is within experimental error.

Table II. Observed and Calculated Dispersion and Loss of Glycerol at -50°C .

Calculated values from Eq. (11) with $\epsilon_0 = 64.1$,
 $\epsilon_{\infty} = 4.10$, $\omega_m/2\pi = 1.26 \text{ kc/s}$, $\beta = 0.603$.

f (kc/s)	ϵ'		ϵ''	
	obs.	calc.	obs.	calc.
0.1	63.9	63.9	2.82	2.69
0.2	63.4	63.4	5.71	5.70
0.5	59.5	60.1	13.3	13.0
1	50.8	51.6	20.1	20.4
2	37.6	37.8	23.1	23.5
5	22.0	22.0	13.5	18.5
10	15.2	15.1	13.3	13.1
20	10.8	11.1	8.97	8.95
50	7.84	7.70	5.15	5.27
100	6.68	6.68	3.37	3.43
200	5.83	5.78	2.26	2.28

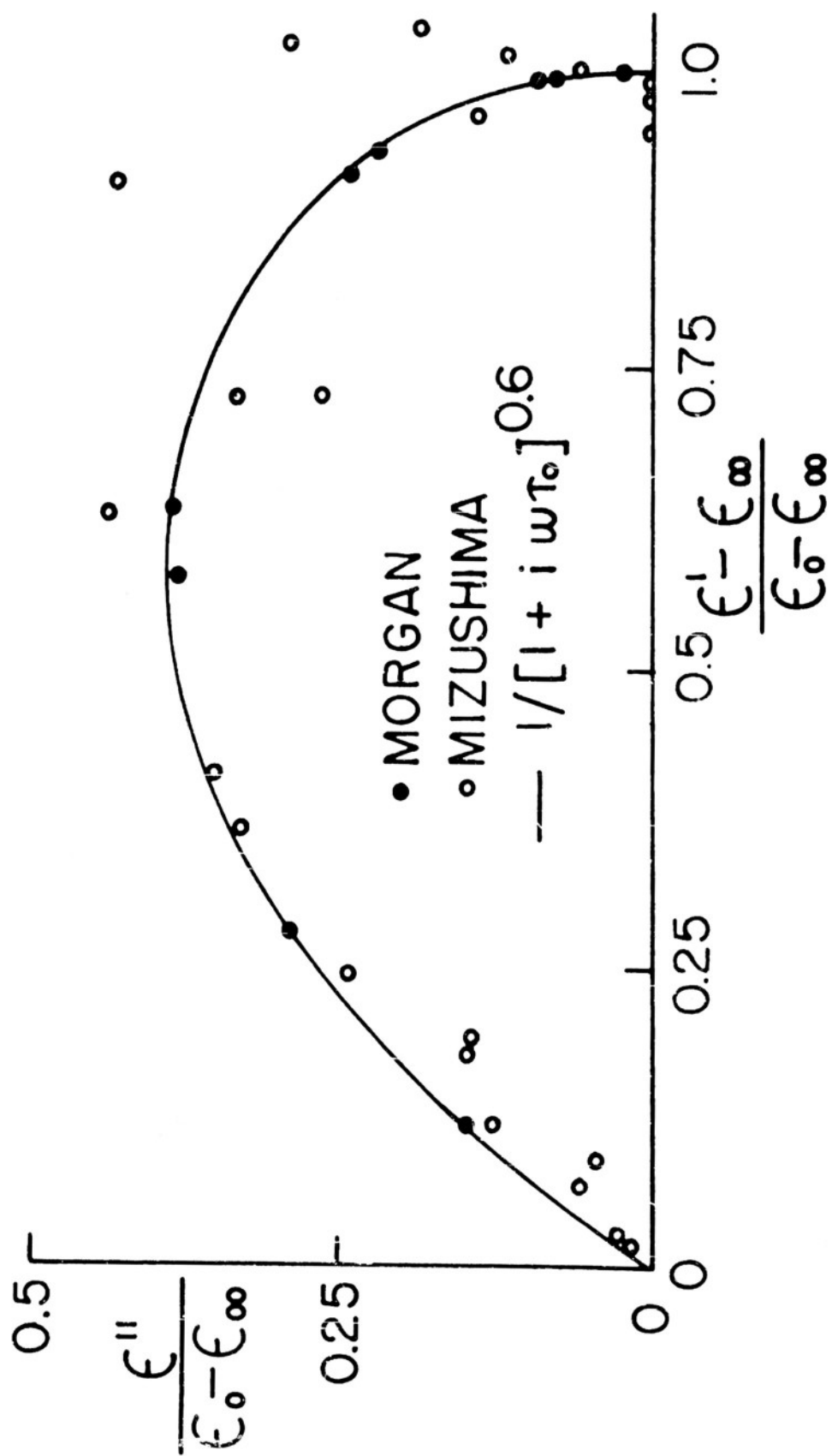
The deviations from Eq. (11) first become evident for frequencies much above the principal part of the dispersion range which the equation describes, and are in the sense expected of a second distinct dispersion; namely, the values of ϵ' are smaller and of ϵ'' larger. In the original paper, therefore, the observed relaxation in glycerol and propylene glycol was described as the sum of two processes; the first satisfying Eq. (11) and the second making much smaller contribution at much higher frequencies.

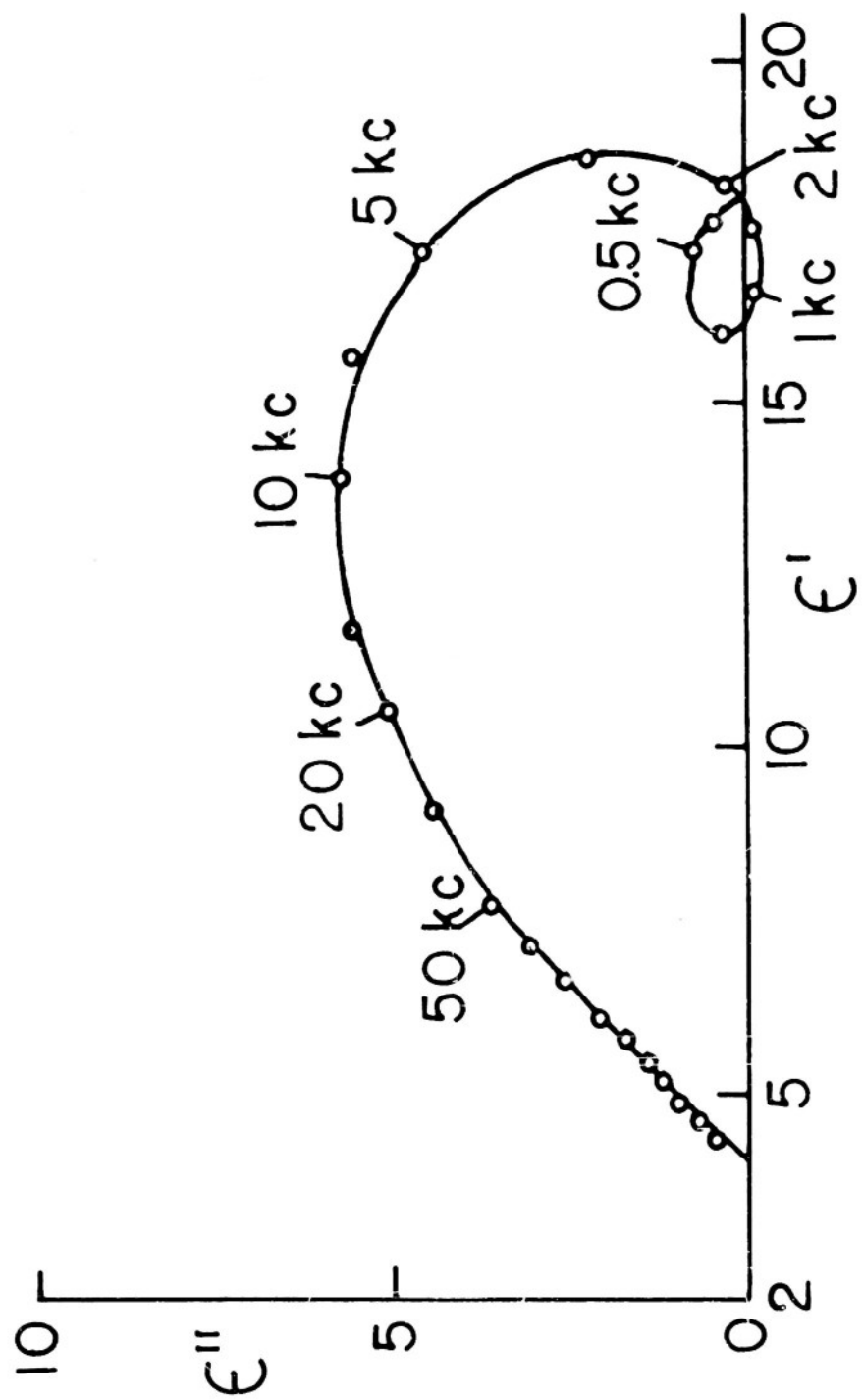
Other interpretations as to the significance of the observed behavior have been proposed. Böttcher¹⁵

15. Ref. 12, p. 374.

Fig. 5. Reduced complex dielectric constant locus for glycerol. Filled circles from data of Morgan, open circles from data of Mizushima, solid curve calculated from reduced form of Eq. (11) with $\beta = 0.6$.

Fig. 6. Residual dielectric constant locus for glycerol at -50°C after subtraction of Debye-type dispersion as proposed by Poley.





suggested that the broader dispersion for frequencies $\omega > \omega_M$ than for a simple relaxation process was better to be explained wholly in terms of a different process or processes. Poley

16. J. Ph. Poley, *Physica* 19, 300 (1953).

has

proposed more explicitly that the experimental data for glycerol can be represented by a Debye function of long relaxation time, plus a second symmetrical dispersion function (such as the empirical arc function), plus a further function for the behavior at the highest frequencies. Magat and coworkers

17. M. Magat, in discussion of paper by R. Feldtheller, *Kolloid Zeits.* 134, 46 (1953).

have cited the behavior in glycerol as analogous to the distinct secondary high frequency dispersions found in a number of aliphatic alcohols

18. For higher alcohols, see: M. K. Bruma, R. Dalbert, L. Reinisch, and M. Magat, *Comptes Rendus* 1952, 373-378 (Paper in symposium volume "Changements de Phases"). For n-propyl alcohol, Reference 3, for ethyl alcohol, F. X. Hassian and R. H. Cole, *Nature* 172, 212 (1953). Similar unpublished results have been obtained in this laboratory for methyl alcohol by D. J. Denney, and for n-butyl and isobutyl alcohols by W. Dannhauser.

In a critical consideration of these various conjectures, it is important to keep in mind the fact that Eq. (11) as it stands first fails to represent the experimental results at frequencies much greater than $1/\tau_0$, and gives an excellent fit over most of the dispersion range, as shown by the comparison in Table II. Poley's proposal that the dispersion should instead be represented as the sum of a simple Debye dispersion as in Eq. (1), using $\epsilon_0 = 64$, $\epsilon_\infty \cong 18$, $\omega_M/2\pi = 1.7$ kc/s, and a second symmetrical dispersion does not lead to a satisfactory fit of the data. This can be shown from

calculation of the residual dispersion and loss by subtracting the values for the proposed principal dispersion from the observed total dispersion and loss. The residual values are plotted in Fig. 6, and the curious locus which results evidently does not correspond to a further symmetrical dispersion as proposed by Peley. His further objection to Eq. (11) as a description of the principal dispersion behavior on the grounds that it does not have the symmetry with frequency so often found in dielectric relaxation seems to have no fundamental basis, and the experimental fact is that the observed variations of dielectric constant and loss of polyhydric alcohols are asymmetrical.

Another approach to the question of suitable representation is in a consideration of the nature of an assumed distribution of relaxation times which will describe the data. Peley has cited the asymmetrical form of the distribution corresponding to the dispersion equation (11) as evidence against this equation. Here the question is really one of how well Eq. (11) fits the data, because the necessary distribution function is determined by the data and hence by the adequacy of a function for the experimental results from which the function can be determined analytically. This is because the distribution function $F(\tau)$ of relaxation times in the logarithmic intervals $d \ln \tau$ is expressed by assumption as

$$\epsilon^* - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty) \int_{-\infty}^{\infty} \frac{F(\tau) d(\ln \tau)}{1 + i\omega\tau} \quad (12)$$

Inversion of this integral equation can be accomplished as a Stieltje transform, or by the convolution theorem for Fourier integrals (see E. C. Titchmarsh, Theory of Fourier Integrals (Oxford 1949), p. 92). The result is

$$F(\tau/\tau_0) = \frac{1}{\epsilon_0 - \epsilon_\infty} \cdot \frac{1}{2\pi i} \left[\epsilon^*(\tau/\tau_0 e^{i\pi}) - \epsilon^*(\tau/\tau_0 e^{-i\pi}) \right] \quad (13)$$

This

expression for F in terms of ϵ^* is the analogue of Kirkwood and Fuoss' result for F in terms of ϵ'' .

To the extent that an analytical expression for ϵ^* fits the data, the resultant $F(\tau/\tau_0)$ describes the form of the distribution which must be assumed. The function (13) leads to the expression

$$F(\tau/\tau_0) = \frac{\sin \beta \pi}{\pi} \left(\frac{\tau}{\tau_0 - \tau} \right)^\beta, \quad \tau < \tau_0, \quad (14)$$

$$= 0, \quad \tau > \tau_0.$$

Although Eq. (12) is an integral expression for ϵ^* and hence not overly sensitive to details of a spectrum for $F(\tau)$, various trial calculations for different forms of $F(\tau)$ than (14) have not given satisfactory agreement with measured values of ϵ^* unless continuous distributions for $\tau < \tau_0$ similar to that of Eq. (14) are assumed.

17

The comparison of Magat¹⁷ of the behavior of glycerol at high frequencies to that of monohydric alcohols is not in our opinion a proper analogy. The difference is that for glycerol and other polyhydric alcohols so far studied (propylene glycol¹⁴ and trimethylene glycol¹⁹)

19. Unpublished results by D. W. Davidson in this laboratory

the deviations from simple Debye behavior set in continuously at frequencies greater than $1/\tau_0$, while for monohydric alcohols departures occur only for $\omega \gg 1/\tau_0$ and are more analogous to the higher frequency "tail" of the glycerol data. The definite distinction seems clearly associated with the presence of two or more hydroxyl groups on the carbon skeleton.

V. REDUCED REPRESENTATIONS OF DIELECTRIC DATA

An accurate test of the dispersion equations so far discussed requires

experimental data over at least two decades of frequency at any temperature. A study of their significance is facilitated enormously if the temperature dependences of the various parameters can be determined over a wide range. Because of the exponential dependence of relaxation rates on inverse temperature characteristic of rate processes, such studies require a considerably wider range of frequencies. A still further need for wider range of measurements occurs if more than one dispersion process occurs.

The technical problems of adequate measurements over the many decades of frequency necessary for really complete studies are often considerable. These difficulties have led various workers to examine the possibilities of comparing measurements at one frequency or in a less wide range, these measurements being, however, made over a sufficient range of temperature to follow the change from equilibrium polarization to vanishingly small orientation polarization.

²⁰
Stark

20. K. H. Stark, Nature 166, 436 (1950).

has proposed simply plotting the measured values of ϵ' and ϵ'' at one fixed frequency and different temperatures on the complex plane and using the resultant locus as a characterization of the dispersion process and dispersion function.

²¹
As Powles

21. J. G. Powles, Proc. Phys. Soc. B, 64, 81 (1951).

pointed out, this procedure cannot lead in general to a satisfactory representation of the dispersion function (i.e., the functional dependence of ϵ^* on ω and T), because the parameters ϵ_0 and ϵ_∞ also have a temperature dependence for which no allowance is made, and because the

character of the dispersion function may well depend on temperature. Starks' example of solid hydrogen bromide was particularly unfortunate in these respects so this substance undergoes a phase transition in the temperature range from which he took his data and also exhibits two distinct dispersions at any one temperature in the range 63°-90°K below this phase transition¹³.

Despite these inherent limitations of such a substitute for complete frequency spectra at each of a series of temperatures, one can obtain useful information in this way in some cases. The objection on the basis of temperature dependence of ϵ_0 and η can be met in part at least if reduced or normalized variables $(\epsilon' - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty)$ and $\epsilon''/(\epsilon_0 - \epsilon_\infty)$ are calculated and used for a complex plane locus or for plotting separately against a suitable reduced frequency (e.g., $\omega\eta/T$ where η is the static viscosity, and T the temperature, would be possible for a polar liquid on the basis of Debye's theory²).

If the procedure of using reduced variables is followed one can obtain a synthesis of results at a few frequencies and a range of temperatures which is very similar to those from much more complete measurements at one temperature. An example is the comparison in Fig. 5 of data for glycerol obtained by earlier workers with the reduced form of Eq. (11):

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

In making this comparison, the value of ϵ_0 was taken to be 3.5, the values of ϵ_0 were for internal consistency taken from estimates or values given in the original papers²², and an average value $\beta = 0.60$ was used to calculate the solid curve.

22. S. O. Morgan, Trans. Electrochem Soc. 65, 109 (1934).
S. Mizushima, Bull. Chem. Soc. Japan 1, 47 (1926).

The example of Fig. 5 suggests both the possibilities and limitations of the reduced representation. It is clear that the asymmetric frequency dependence of the dispersion process can be deduced from the less complete data. At the same time, finer details are missing or obscured: for example, the small but definite dependence of the dispersion parameter β on temperature and the existence of a distinct secondary high frequency dispersion. Thus useful information can be gained from incomplete data, but at the risk of overlooking significant features. In view of this, it is important to emphasize, as a number of writers have done, that the only completely satisfactory description is by measurements over the entire frequency range of significant changes in properties and over a sufficient temperature range to establish clearly the temperature dependence.

VI. CONCLUSION

The discussion in this paper has been purposely confined to the mechanics of representation of dielectric relaxation measurements, but the questions considered are relevant to the more fundamental significance of the experimental results in relation to other physical properties and to intermolecular forces and molecular constitution. Many of these questions will probably be resolved only by correlation of a variety of evidence from structure and equilibrium properties, from differences of chemically related substances, and from similarities and differences of such other irreversible processes as viscosity, diffusion, and viscoelastic relaxation. From available evidence, comparisons of dielectric and other relaxation effects have significant possibilities, and it is hoped that the present discussion may prove useful in their analysis.

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DIELECTRIC CONSTANTS OF LIQUID AND SOLID HYDROGEN SULFIDE

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ABSTRACT

The equilibrium dielectric constants of the disordered highest temperature solid phase show a regular increase with decreasing temperature which is in moderate agreement with Onsager's equation. Larger values than would be expected on this basis are found in the intermediate solid phase, while the values in the ordered phase below 103°K are a little larger than the square of the estimated refractive index. No evidence of relaxation effects or of electrode polarization was found in the frequency range from 15 c/s to 500 kc/s studied.

I. INTRODUCTION

The relatively large dielectric constants reported for the higher temperature solid phases of hydrogen sulfide indicate that, as in solid hydrogen bromide⁽¹⁾

(1) W. L. Brown and R. H. Cole, J. Chem. Phys. 21, 1920 (1953).

(2)
and chloride ,

(2) R. W. Swenson and R. H. Cole, J. Chem. Phys. 22, 284 (1954).

there is considerable freedom for reorientation of the molecules in the structures. For the hydrogen halides it has been found

that the equilibrium dielectric constants have a simple temperature dependence in the face centered cubic phases stable just below the melting point, and that the values were in fair quantitative agreement with Onsager's equation⁽³⁾

(3) L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936).

for

polar liquids. Since hydrogen sulfide also crystallizes in cubic close packing, it is of interest to make a similar examination of the dielectric data in this case.

(4)

Measurements have been reported by Kemp and Denison

(4) J. D. Kemp and G. H. Dennison, J. Am. Chem. Soc., 55, 251 (1933).

and by Smyth and

(5)

Hitchcock .

(5) C. P. Smyth and C. S. Hitchcock, J. Am. Chem. Soc., 56, 1084 (1934).

The former included no tabular data, but their graph shows an erratic temperature dependence for the solid. The more complete results of Smyth and Hitchcock were more consistent, but they found somewhat irregular increases of dielectric constant in the two solid phases stable between the melting point (187.6°K) and 126.2°K, and between 126.2°K and the second solid transition at 103.5°K. Behavior of this kind in solid hydrogen halides has been found to result from sample voids and inhomogeneities unless special measures are employed in freezing and cooling of samples. The measurements reported here were undertaken using similar measures, and were extended over the frequency range 15 c/s to 500 kc/s to find whether dispersion effects

occurred in this range.

II. EXPERIMENTAL

Commercial gaseous hydrogen sulfide (Matheson) was condensed in a dry ice trap and slowly distilled into the experimental cell. The melting point (187.6°K) and specific conductance (9.2×10^{-10} mho/cm) were in good agreement with previously reported values after one distillation. The cell employed was one built by R. W. Swenson⁽²⁾ for measurements of solid HCl; the conductance-capacitance bridge has been described elsewhere⁽⁶⁾.

(6) R. H. Cole and P. M. Gross, Jr., Rev. Sci. Inst. 20, 252 (1949)

Measurements were made from temperatures of the liquid to 65°K, with reproducibility for different samples within 0.5 percent and precision of order 0.1 percent.

III. RESULTS

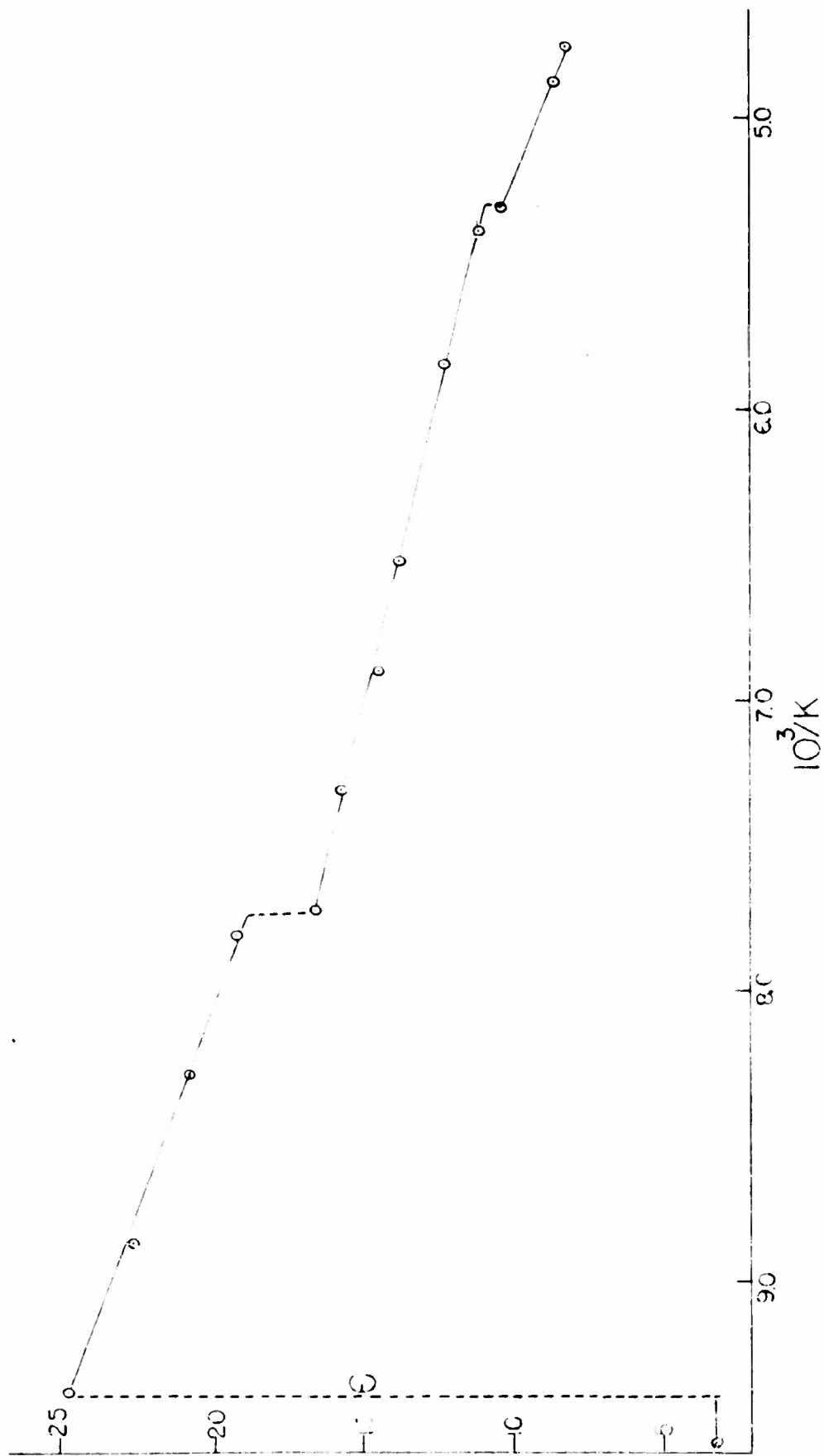
No evidence of frequency dependence of the dielectric constant or of significant dielectric loss was found either in the liquid or the three solid phases. It is concluded therefore that the measured values are of the equilibrium dielectric constant without effects either of dispersion or of electrode polarization. Representative values from data for two samples are listed in Table I and the results are plotted against reciprocal of absolute temperature in Fig. 1.

IV. DISCUSSION

The behavior of hydrogen sulfide in the liquid and the two higher temperature solid phases is in fair agreement with the Onsager theory⁽³⁾. The comparison is conveniently made by using Onsager's equation to calculate the dipole moment μ_0 from measured dielectric constant and refractive index

Fig. 1. Dielectric constants of the liquid and solid phases of hydrogen sulfide as a function of reciprocal absolute temperature.

Dielectric Properties of Hydrogen Sulfide



n and comparing this value with the experimental dipole moment from gas phase measurements. Results of these calculations, given in Table I, are obtained using $n^2 = 2.44$ as evaluated from the refractive index of the liquid by the Clausius-Mossotti equation, liquid densities of 0.967 at 212°K⁽⁷⁾

(7) B. D. Steele, D. McIntosh, and E. H. Archibald, Phil. Trans. Roy. Soc. (London) 205, 99 (1905)

and 1.004 at 190°K, and solid density of 1.17 at 103°K⁽⁸⁾.

(8) G. Natta, Atti Accad. Lincei 11, 749 (1930).

The variations in calculated dipole moments and differences from the gas value are not significantly greater than the uncertainties in refractive index and density.

The values of dielectric constant in the lowest temperature phases decreases from 3.7 to 103°K to about 3.5° at 65°K. These values are thus definitely but not greatly in excess of the figure 2.4 calculated for n^2 , and the difference is presumably to be attributed to molecular vibrations in the ordered structure.

The equilibrium behavior is thus quite simple and in part quite well accounted for by simple theory. The fair agreement of the results for the liquid and high temperature isotropic phase with Onsager's theory are reasonable consequences of disordered structures without significant hydrogen bonding. The increase of the dielectric constant in the intermediate solid phase is not surprising in view of the presumably greater coordination of neighbors but not enough is known of the structure to permit more quantitative

discussion. The low value of the dielectric constant below 103.5°K indicates a high degree of order in dipole orientation.

Acknowledgments. One of us (R.W.S.) is indebted to the Union Carbide and Carbon Corporation for a predoctoral fellowship in 1952-53. The work was supported in part by ONR.

TABLE I. DIELECTRIC CONSTANTS OF LIQUID AND SOLID HYDROGEN SULFIDE,
AND DIPOLE MOMENTS CALCULATED FROM ONSAGER'S EQUATION.

$T^{\circ}K$	ϵ	μ_0 (debye)	$T^{\circ}K$	ϵ	μ_0 (debye)
	<u>Liquid</u>			<u>Intermediate Solid</u>	
212.0	8.04	0.78	124.2	19.4	1.04
194.6	8.99	0.88	110.9	22.7	1.07
			103.4	24.7	1.08
	High Temp. Solid			Low Temp. Solid	
186.1	10.9	0.92	101.0	3.70	-
170.9	12.1	0.94	95.8	3.64	-
157.9	13.7	0.95	90.0	3.59	-
133.0	15.8	0.96	77.7	3.56	-
125.9	16.6	0.96	63.0	3.52	-

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