The $\Delta T/\Delta T_0$–concentration curves were determined for tributylammonium picrate, tributylammonium iodide and tetrabutylammonium perchlorate in the concentration range of 0.001 to 0.02 N. All three electrolytes exhibit marked association. The results for tributylammonium picrate are in accord with a mass action equilibrium between dipoles and quadrupoles over the entire concentration range measured. At lower concentrations, the results for tributylammonium iodide are in accord with a dipole–quadrupole equilibrium, but, at higher concentration, more complex structures are formed. To account for the polarization curve of the iodide, two types of quadrupoles must be assumed to be formed. In the case of the perchlorate, highly complex structures are formed even at low concentrations.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Electrical Properties of Solids. I. Experimental Methods

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I. Introduction

Recent technical developments in the synthesis of high polymer plastics have opened a new field for investigation, that of the electrical properties of amorphous solids. At the present time, their behavior in a. c. and d. c. fields is not understood because very little reliable experimental work is available. One serious source of error is due to the obvious fact that the sample does not make molecular contact with the electrodes. In this paper it will be shown that the error due to series air film capacity between electrodes and sample may be eliminated by extrapolation to infinite thickness and results on two amorphous solids, fused quartz and Pyrex glass, will be given to illustrate the method.

II. Apparatus and Materials.—The Schering bridge[1] has unfortunately been neglected as a tool in physical chemical research. It furnishes a reliable means of obtaining accurate values for both dielectric constant and conductance, when at least half of the current is carried capacitatively.

The bridge is shown schematically in Fig. 1. S is a guarded air capacitor whose nominal value is 100 $\mu\mu$f. R_3 and R_4 are decade resistance boxes (0 to 10,000 in 0.1 Ω steps) whose quadrature terms are negligible in the frequency range used. C_3 is a fixed 1000 $\mu\mu$f condenser and C_4 is a decade capacity 0–1000 $\mu\mu$f plus a vernier capacity 0.3–2.0 mμf. When tan δ is so small that less than 0.3 mμf would be required in the 4-arm for balance, C_3 is thrown parallel to R_3 in order to increase the value of C_4 to a readable figure. F is a variable resistance in the guard line (to be described later) which may be substituted for R_3 by a selector switch to the amplifier as shown. The latter has three stages; the input is filtered. The bridge voltage is supplied by a set of alternators and transformers which cover the ranges 15–500 cycles at 10–25,000 volts and 500–2000 cycles at 10–10,000 volts.

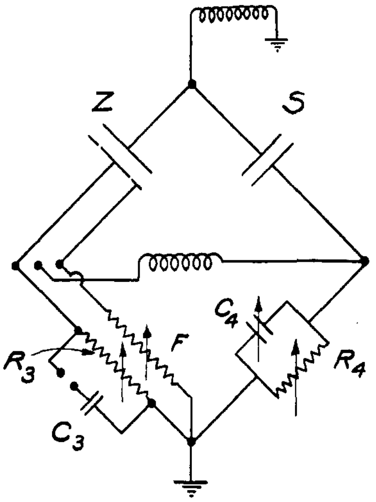

Fig. 1.—The Schering bridge.

The cells are shown in simplified cross section in Fig. 2. The test electrode T is 2.999_0 in. (7.617 cm.) in diameter and the guard ring G is 3.040 in. (7.722 cm.) inside and 4.000 in. (10.16 cm.) outside diameter. The two are mounted rigidly on a mycalex plate 0.5 in. (1.27 cm.) thick. The high potential electrode H and both T and G are hollow, to permit the circulation of oil pumped from a thermostat. In order to prevent temperature gradients in the oil line, due to dif-

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[1] Hague, "Alternating Current Bridge Methods," Pitman, London, 1932, pp. 241 ff.

ferences between ambient and oil temperature, the oil thermostat, pump and cells are mounted in an air thermostat held by independent control to the same temperature as the oil-bath. The electrodes are copper, silver plated; their surfaces are plane to about 0.002 cm.

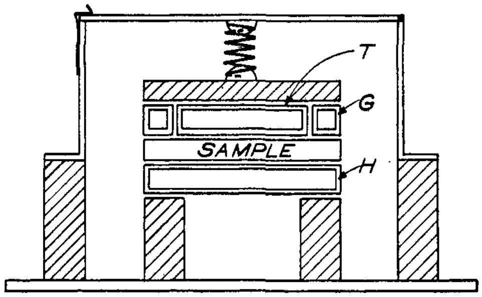

Fig. 2.—The measuring cell.

The samples studied were disks 4 in. (10.2 cm.) in diameter and ranging from 0.050 to 0.270 in. (1.27–6.86 mm.) thick. The Pyrex disks were given to us by the Corning Glass Works, to whom grateful acknowledgement is made. The glass used is their type 774.

III. The Bridge Equations.—When the bridge is balanced,[2] the two components of the unknown admittance $1/Z$ are related to the other bridge elements through the equations

$$\mathrm{J}(1/Z) = \omega SR_4/R_3(1 + \mathrm{tn}^2\,\delta) \qquad (1)$$

$$\mathbf{R}(1/Z) = \mathrm{J}(1/Z)\cdot\mathrm{tn}\,\delta \qquad (2)$$

$$\mathrm{tn}\,\delta = \omega C_4R_4 \qquad (3)$$

where ω is 2π times the frequency and δ is the loss angle. If the unknown is simply a resistance R_x in parallel with a capacity C_x, we have of course

$$C_x = SR_4/R_3(1 + \mathrm{tn}^2\,\delta) \qquad (4)$$

$$1/R_x = (\omega SR_4\,\mathrm{tn}\,\delta)/R_3(1 + \mathrm{tn}^2\,\delta) \qquad (5)$$

Suppose the unknown is a disk of radius r and thickness d. If the flux is normal to the surface over the entire area, the equivalent geometrical capacitance C_v in farads is given by

$$C_v = \pi r^2/4\pi d \times 9 \times 10^{11} \qquad (6)$$

and if C is the capacity of the sample, also with normal flux, the dielectric constant ϵ' is defined as

$$\epsilon' = C/C_v \qquad (7)$$

For convenience in mathematical work, a complex constant ϵ defined as

$$\epsilon = \epsilon' - j\epsilon'' \qquad (8)$$

is often useful. Here ϵ'' is the loss factor, and if the unknown is equivalent to a resistance R parallel with C

$$\epsilon'' = 1/\omega RC_v \qquad (9)$$

The specific conductance κ in ordinary units is related to the loss factor and the frequency by the equation

$$\epsilon'' f = 18 \times 10^{11}\,\kappa \qquad (10)$$

The loss angle and the two components of ϵ are related by the equation

$$\mathrm{tn}\,\delta = \epsilon''/\epsilon' \qquad (11)$$

The primary purpose of the guard ring is to eliminate fringe effects and surface leakage at the edge of the sample and thus ensure normal flux under the area of the test electrode. A small correction must be made to allow for the finite separation of guard ring and test electrode. In balancing the bridge, T is first balanced against R, then G against F, and the process is repeated until a perfect balance is obtained. Then T and G are at the same potential, and except in the small annular space of width Δr, between T and G, the flux under T is normal to its surface. Since $\Delta r << r$, an approximation to the distribution of potential (solid line, Fig. 3) can be made easily. The dotted lines represent over and under estimates of the fringing in Δr, and their mean will be a good approximation when $\Delta r/r << 1$. In calculating the geometrical capacitance equivalent to the part of the sample under the test electrode, we shall accordingly use

$$C_v = C^0_v(1 + 3\Delta r/4r) \qquad (12)$$

where C^0_v is given by (6). For the cells used in the present work $\Delta r/r$ is 0.013.

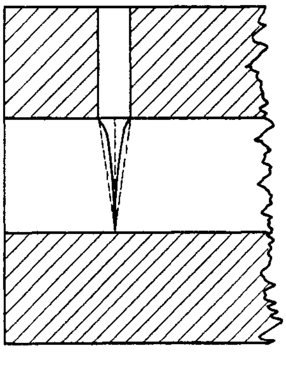

Fig. 3.—Fringing at the guard ring.

The determination of ϵ' and ϵ'' for an unknown material thus requires the evaluation of C, R, C_v and f. The experimental difficulty arises from the fact that C and R of equations (7) and (9) are in general not the $\mathrm{J}(1/Z)/\omega$ and $1/\mathbf{R}\ (1/Z)$ of (1) and (2). They will be, provided that surface effects are eliminated and also, of course, provided that leak resistance from T to H and stray capacitance are eliminated or negligible.

IV. Calibration of Cells.—The quantity C_v corresponds to the "cell constant" of conducti-

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(2) C_3 is used only when $\mathrm{tn}\,\delta << 1$, and for this case the bridge equations simplify to $C_x = SR_4/R_3$, $\mathrm{tn}\,\delta = \omega C_4R_4 - \omega C_3R_3$, $1/R_x = \omega C_x\,\mathrm{tn}\,\delta$.

metric work. It may be calculated by (12) but, as a check, an experimental determination seemed advisable. The method used also serves to locate several other sources of error. Quartz spacers of various thicknesses were placed at three points between the guard ring and the high potential electrode, thus giving a loss free air capacity as the unknown. Then

$$C_x = C' + \epsilon'_a k(A + \alpha)/(d - \delta) \qquad (14)$$
$$= (S + \sigma)\frac{R_4}{R_3}$$

where C' = stray capacity, ϵ'_a = 1.0006, the dielectric constant of air, $k = 36\pi \times 10^{11}$, A = area of T, α = correction to A for fringing, d = thickness of quartz spacer, δ = distance between planes of T and G, S = 100.00 $\mu\mu$f, σ = error in S, R_4/R_3 = bridge ratio. Define C_a, a calculated capacity, by

$$C_a = \epsilon'_a k(A + \alpha)/\mathrm{d} \qquad (15)$$

and ΔC by

$$\Delta C = C_x - C_a$$

Assuming that α/A and δ/d are small compared to unity

$$\Delta C = C' - C_a(\sigma/S) + C_a^2(\delta/kA) \qquad (16)$$

By using at least three different sets of spacers, the three constants of (16) may be evaluated, which determines C', σ and δ. Using this method, the values in Table I were obtained.

TABLE I

CELL CONSTANTS

Cell	C'	σ	δ	K_a
1	0.095 $\mu\mu f$	0.0 ± 0.05	0.0020 in.	16.00
2	.105	.0	.0012	16.01

The last column gives the experimentally determined values of the cell constant, defined here as

$$K_a = [R_4(d - \delta)/R_3\epsilon'_a]/[1 - C'R_3/SR_4] \qquad (17)$$

where d is in mils (0.001 in.), resistances in ohms and capacities in $\mu\mu f$. Each figure is the average of determinations with seven sets of spacers. The value of K_a calculated from (12) was 16.02. It should be pointed out that the agreement is in *absolute* value.

V. The Electrical Properties of Quartz and of Pyrex.—If a rigid solid is placed between the electrodes, perfect contact is never obtained on account of mechanical imperfections in both the electrode surfaces and those of the sample. This is equivalent to an air capacity in series with the unknown. If the average thickness of the air film is Δ, then at balance on the bridge, we have

$$C' + \left(\frac{d}{\epsilon' k(A + \alpha)} + \frac{2\Delta}{k(A + \alpha)}\right)^{-1} = \frac{SR_4}{R_3}\frac{1}{1 + \mathrm{tn}^2\,\delta} \qquad (18)$$

where d is the thickness of the material whose dielectric constant is ϵ'. Since $\Delta/d << 1$, (18) may be rewritten to a very close approximation

$$\epsilon' k(A + \alpha)/d = (SR_4/R_3)(1 + 2\epsilon'\Delta/d)(1 - C'R^3/SR_4)$$
$$\times (1 + \mathrm{tn}^2\,\delta)^{-1} \qquad (19)$$

By combining (19) with the corresponding equation for air as the unknown, we obtain

$$\epsilon'_x = \epsilon'_a \frac{R_3^a}{R_3^x}\frac{R_4^x}{R_4^a}\frac{d^x}{d^a}\frac{(1 - C'R_3^x/SR_4^x)(1 + 2\epsilon'_x\Delta/d)}{(1 - C'R_3^a/SR_4^a)(1 + \mathrm{tn}^2\,\delta)} \qquad (20)$$
$$= K_x(1 + 2\epsilon'_x\Delta/d)/K_a \qquad (21)$$

It will be noted that (20) gives an *absolute value for the dielectric constant* ϵ'_x, because the "standard" capacity S drops out of the equation except in the correction terms and the bridge resistances enter only as ratios.

From (21) we see that ϵ'_x is the value of K_x/K_a when $1/d = 0$. This fact is the basis of a method of eliminating the errors due to air film capacity: samples of several thicknesses are measured, and the experimental K_a/K_x values are plotted against $1/d$. The intercept at $1/d = 0$ gives $1/\epsilon'_x$.

As examples, values for fused quartz and Pyrex were determined. Within the limit of experimental error, the quartz was loss free ($\tan\delta \leqslant 0.00005$), and the dielectric constant was independent of temperature in the range 25–100° and of frequency in the range 60–500 cycles. Pyrex showed an appreciable loss, and, in this case, both ϵ' and ϵ'' were temperature and frequency sensitive.

For fused quartz, the value $\epsilon' = 3.810 \pm 0.005$ was found. This is in good agreement with Thornton's[3] value $\epsilon' = 3.78$ which was determined by an entirely different experimental method, that of the period of an ellipsoid swinging in an alternating field. The difference of 0.03 is due more probably to differences in our specimens of fused quartz rather than to errors in either method.

The results for Pyrex glass are given in Table II.

TABLE II

PROPERTIES OF PYREX

	25°		100°	
	ϵ'/ϵ' (500~)	tan δ	ϵ'/ϵ' (500~)	tan δ
200	1.0055	0.010	1.0255	0.055
300	1.0029	.010	1.0135	.049
400	1.0012	.010	1.0060	.045
500	1.00005	.010	1.0000	.042

ϵ' (25°, 500~) = 4.810 ϵ' (100°, 500~) = 5.185

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(3) Thornton, *Proc. Roy. Soc.* (London), **82**, 422 (1909).

A direct experimental check on the method of extrapolation was obtained as follows: one surface of each sample was painted with diluted Aqua-Dag, a stabilized suspension of colloidal graphite in water. This gave a conducting film of carbon over one surface, which was placed in contact with the high potential electrode. The set of samples was then re-measured. The results are shown in Fig. 4. It will be seen that the painted samples extrapolate to the same value of ϵ', but with half the slope of the line for the unpainted samples, which is what one would expect if one air film were eliminated.

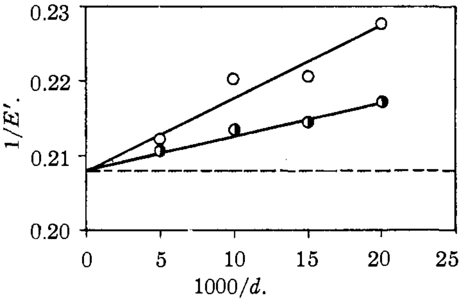

Fig. 4.—Extrapolation of dielectric constant for Pyrex: ○, uncoated sample; ◑, one side of sample coated with graphite.

If only one sample of material is available, a fairly accurate value of ϵ' and ϵ'' can still be obtained by measuring the sample uncoated and then with the high-potential side coated with carbon. When $\tan \delta < 1$, the correction to the constants obtained for the uncoated sample is twice the difference between the values for uncoated and one side coated samples. This method, of course, implicitly assumes that the two surfaces are identical, *i. e.*, that the film corrections for the two sides are equal.

Painting the side of the sample toward the test electrode leads to experimental difficulties. Granting that a sharply outlined area exactly equal to that of the test electrode could be obtained, the results are incorrect because the fringe effect is increased unless the area under the guard ring is covered by a paint film of exactly the same thickness. Even if a conducting film could be made with sharp outlines, there would remain the awkward task of centering the coated sample with respect to the electrodes, so with the present type of cell, the extrapolation method seems preferable.

It should be emphasized that the success of the method depends on the uniformity of the surfaces. The assumption is made that the average thickness of the air film is the same for different samples of the same material, if they are prepared in the same way. The scattering of the points in Fig. 4 indicates that the glass samples were not quite uniformly ground, because the deviations are beyond the experimental errors in bridge settings.

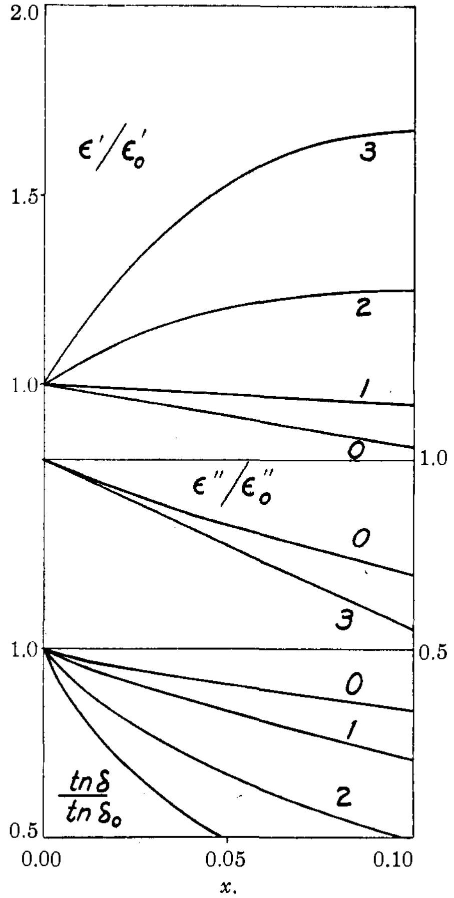

Fig. 5.—Dependence of apparent electrical properties on thickness.

VI. Theory of Series Capacity.—When the unknown has an appreciable conductance, extrapolation becomes difficult because the curves are no longer linear. Suppose we have an unknown whose equivalent parallel components are C and R, between two air film capacities C_a. Then if

$$C/C_a = x \tag{22}$$

$$1 + \text{tn}^2\,\delta_0 = y \tag{23}$$

we have

$$\epsilon'/\epsilon'_0 = (1 + 2xy)/(1 + 4x + 4x^2y) \tag{24}$$

$$\epsilon''/\epsilon''_0 = 1/(1 + 4x + 4x^2y) \tag{25}$$

$$\text{tn}\,\delta/\text{tn}\,\delta_0 = 1/(1 + 2xy) \tag{26}$$

Here ϵ', ϵ'' and $\tan \delta$ are fictitious values, calculated from bridge readings. They are equal to the corresponding quantities for the unknown only in the limit $x = 0$.

In Fig. 5 are plotted values for ϵ'/ϵ'_0, etc., as functions of x for different values of $\tan \delta_0$. For example, suppose we measure a sample whose actual dielectric constant ϵ'_0 is 10 and for which $\tan \delta_0 = 2.00$. If the sample is 0.050 in. (1.27 mm.) thick and there is present an average air film only 0.0005 in. (0.0127 mm.) thick, then the uncorrected dielectric constant found will be 12.5, $\tan \delta$ will be 1.00 and ϵ'' will be 12.5 instead of 20. Obviously, the errors are more serious the thinner the sample and, for this reason, much of the work in the technical literature on insulation materials becomes of very doubtful scientific value.

For the method of obtaining ϵ'_0 and ϵ''_0 from measurements on a single sample, the following equations are useful. Let ϵ'_1 be the apparent dielectric constant of the uncoated sample and t_1 its $\tan \delta$, and let ϵ'_2 and t_2 be the corresponding quantities for the sample with the high potential side coated with carbon. Then

$$t_1(1 + 2xy) = t_2(1 + xy) \tag{27}$$

evaluates xy and

$$\text{tn}\,\delta_0 = t_1(1 + 2xy) = t_2(1 + xy) \tag{28}$$

This equation in turn evaluates y. From (27) and (28), x could be obtained, but a more accurate value can be obtained from the ratio ϵ'_2/ϵ'_1 as follows. We have

$$(1 + xy)(1 + 4x + 4x{\cdot}xy)/(1 + 2xy)(1 + 2x + x{\cdot}xy) = \epsilon'_2/\epsilon'_1 \tag{29}$$

In the first and third terms, the value of y from (28) is used; in the second and fourth, the value of xy from (27) is inserted, which gives a linear equation to determine x. Having x and y, it is simple to compute ϵ'_0 from ϵ'_1 or ϵ'_2.

Another convenient method is as follows. Let

$$\Delta = (\epsilon'_2/\epsilon'_1) - 1 \tag{30}$$

Substituting the above equations in (24) and rearranging, we find

$$x = \frac{(1 + 2xy)(1 + 2x + x^2y)}{2 - y(1 - 3x - 2x^2y)} \times \Delta = f(x,y) \times \Delta \tag{31}$$

Equation (27) evaluates xy and (28) gives y. Then in zeroth approximation

$$x_0 = f(\Delta,y)\cdot\Delta \tag{32}$$

and in first approximation

$$x_1 = f(x_0,y)\,\Delta \tag{33}$$

The scheme

$$x_n = f(x_{n-1},y)\,\Delta \tag{34}$$

converges very rapidly; in fact, when $\tan \delta < 1$, (32) is already a very good approximation.

VII. Other Surface Effects.—At least two other electrical surface effects might be expected in certain cases: surface resistance and polarization. For most work with solids, the volume resistance of the sample is large compared to surface resistance, but in cases where it would appear experimentally, it is obvious that an analogous extrapolation method can be obtained. Polarization is likely to appear when electrolytes are present in the solid. Since polarization behaves like a frequency sensitive *series* capacity, the above method will again eliminate it as a source of error. The criterion for the presence of polarization is, of course, a variation with frequency of the apparent thickness of the air film calculated on the assumption that all of the series capacity was air film capacity.

Summary

1. A method of determining absolute values of dielectric constants of solids is described.
2. Errors due to imperfect contact between sample and electrodes are discussed, and a method of eliminating them is explained.
3. The dielectric constant of fused quartz is 3.810.
4. Pyrex glass at 500~ has the following constants: $\epsilon' = 4.810$, $\tan \delta = 0.010$ at 25° and $\epsilon' = 5.185$, $\tan \delta = 0.042$ at 100°.

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