DIELECTRIC RELAXATION OF CELLULOSE NITRATE AND CELLULOSE

A Thesis

by

Ralph W. Gordon, B.A.

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SYMBOLS

a - $(q-H')/(H'-1)$

a_i - distance between consecutive potential surfaces

$\bar{a}$ - $[(D''+D_o)(f/f') - c' (\Delta D/\Delta C)]$

b - r/q

C - capacitance

C_1 - capacitance of an element of dielectric contained in a flux tube between the base and first potential surfaces

C_2 - capacitance of an element of dielectric contained in a flux tube between the first and second potential surfaces

C' - capacitance reading of variable air condensers C_A, C_B on twin-T and Schering bridges respectively- with unknown disconnected and after correcting for error in drum scale reading of C_A, C_B

C'' - capacitance reading of variable air condensers C_A, C_B on twin-T and Schering bridges respectively- with unknown connected and after correcting for error in drum scale reading of C_A, C_B

C^* - apparent value of C_{XP} from twin-T bridge before corrections for L'

ΔC - value of $(C'-C'')$

C_A - variable standard air condenser in twin-T bridge

C_a - geometric capacitance across dielectric plates of a cell, which is identical to the true capacitance of the cell filled with vacuum, or, approximately so, with air

C_B - variable standard air condenser in Schering bridge

C_d - capacitance of leads and supporting tubes of cell

C_e - capacitance of an empty cell measured at its terminals

C_i	- capacitance of an element of dielectric contained in a flux tube between the (i-1)th and ith potential surfaces
C_{i+1}	- capacitance of an element of dielectric contained in a flux tube between the ith and (i+1)th potential surfaces
C_j	- capacitance of flux tube
C_k	- capacitance of imaginery condenser k in paper
C_K	- capacitance of a cell filled with pure benzene at 25°C as measured at its terminals
C_m	- capacitance of unknown dielectric in dielectric cell
C_n	- capacitance of an element of dielectric contained in the flux tube between the (n-1)th and nth potential surfaces
C_S	- variable condenser calibrated in units of dissipation factor--a condenser in the Schering bridge
C_{XP}	- equivalent parallel capacitance measured across the unknown terminals of the twin-T or Schering bridges
D	- Debye units of dipole moment, 10^{-18} e.s.u.
D	- dissipation factor
D'	- dissipation factor readings on Schering bridge with unknown disconnected--before being multiplied by frequency ratio f/f'
D"	- dissipation factor readings on Schering bridge with unknown connected--before being multiplied by frequency ratio f/f'
$\overline{D}$	- electric intensity of homogeneous electric field within dielectric
ΔD	- (D-D')(f/f')

D_a	dissipation factor across dielectric plates of cell filled with vacuum, or approximately so, with air--value of D_a is zero
D_d	dissipation factor of leads and supporting tubes of cell
D_e	dissipation factor of an empty cell measured at its terminals
D_K	dissipation factor of cell filled with pure benzene at 25°C as measured at its terminals
D_m	dissipation factor of unknown dielectric
D_o	dissipation factor corresponding to fixed capacitance across each ratio arm of Schering bridge--before being multiplied by frequency ratio f/f'
D_X	dissipation factor measured across unknown terminals of the twin-T or Schering bridges
d	differential
E	electric intensity
$\mathbf{E}$	electric intensity of that portion of D due to free surface charges on dielectric plate
E_i	average value of $\mathbf{E}$ at any point between the $(i-1)^{th}$ and i^{th} surfaces of potential
E_j	value of E at any point on an element dS_j of a potential surface
e	naperian base
e	$(H'-1)/H'$
e''	$\frac{\sqrt{(H'')^2 + (H')^2} - 1}{\sqrt{(H'')^2 + (H')^2}}$
Δe	increment in reading of torsion balance
$\mathbf{F}$	electric intensity of electric field acting on a molecule

ΔF^* - free energy of activation for dielectric relaxation

F_1, F_2, F_3 - components of $\bar{F}$

f - frequency of alternating current or of alternating field

f' - frequency of setting of range selector switch in Schering bridge

f_m - frequency of maximum in ϵ'', ϵ''_m - log f curves

f_o - nominal switch position frequency of twin-T bridge

G - conductance of unknown material in dielectric cell ($= R_{XP}^{-1}$)

G'' - $G_o\ (f/f_o)^2$ nominal conductance reading on twin-T bridge

G_o - reading of conductance dial on twin-T bridge before multiplying by frequency factor $(f/f_o)^2$

H - complex dielectric constant of fibre parallel to dielectric plates

H' - dielectric constant of fibre parallel to dielectric plates

H'' - dielectric loss of fibre parallel to dielectric plates

ΔH^* - enthalpy of activation for dielectric relaxation

H'_m - dielectric constant of composite material with all fibres parallel to dielectric plates

H''_m - dielectric loss of composite material with all fibres parallel to dielectric plates

h'_m - $1-(\bar{V}_2)^{1/2} + \epsilon' / \left\{\epsilon' \left[(\bar{V}_2)^{-\frac{1}{2}} - 1\right] + 1\right\}$

h''_m - defined by

$$\frac{1}{\sqrt{(H'')^2 + (H')^2}} = \frac{1}{\sqrt{(H'')^2 + (H')^2} + (\bar{V}_2)^{\frac{1}{2}} - 1} - \left[(\bar{V}_2)^{-\frac{1}{2}} - 1\right]$$

I - electric moment

i - $\sqrt{-1}$

k - Boltzman's constant

k - number assigned to an imaginary condenser in paper $k = 1, 2 \ldots\ldots n$

k_o - molecular rate of relaxation

L - length of composite dielectric

M - width of composite dielectric

$\overline{M}$ - molecular weight

$\overline{m}$ - moment induced in a molecule

N - depth of composite dielectric

$\overline{N}$ - Avogadro's number

n - number of divisions of an electric field by potential surfaces

n' - number of molecules per cc.

$\overline{n}$ - mean number of base units involved in a dipole relaxation

P - arbitrary value of $\overline{P}$

P' - molar polarization

$\overline{P}$ - electric potential of potential surface

P_o - value of $\overline{P}$ on dielectric plate side of binary interface

P'_o - value of $\overline{P}$ on opposite plate side of binary interface

P_1, P_2 - dielectric plates

$P'(\omega)$ - molar polarization in alternating field

$2q$ - dimension of imaginary condenser in paper

R - gas constant

R_{XP} - equivalent parallel resistance measured across the unknown terminals of the twin-T or Schering bridge.

r - radius of an imaginary cylindric fibre

$\bar{r}$ - mean number of alternative configurations possible

r_i - refractive index

S - projected surface on x, y plane of dielectric having dielectric constant ϵ_b

dS - element of surface

dS_i - area cut from surface of potential $\frac{iP}{n}$ by flux tube

dS_j - elements of surface on a potential surface

ΔS^* - entropy of activation for dielectric relaxation

S_1 - upper surface of dielectric of dielectric constant ϵ_b

S_2 - lower surface of dielectric of dielectric constant ϵ_b

T - temperature, °K

T_m - temperature, °K, of maximum in ϵ'', ϵ''_m - t curves

T_1, T_2, T_3 - routes followed by flux tubes

t - temperature, °C

t_m - temperature °C of maximum in ϵ'', ϵ''_m - t curves

V - complex dielectric constant of a fibre normal to dielectric plates

V' - dielectric constant of a fibre normal to dielectric plates

V'' - dielectric loss of fibre normal to dielectric plates

V'_m - dielectric constant of composite material with all fibres normal to dielectric plates

V''_m - dielectric loss of composite dielectric with all fibres normal to dielectric plates

V_2 - volume fraction of cellulose between dielectric plates

v'_m - $1 + (\epsilon' - 1)\,V_2$

v''_m - $\epsilon''\sqrt{V_2\ (V'_m/\epsilon')}$

Δw - increment in weight

X_j - constant value of flux passing up force tube

x - coordinate axis of a dielectric

y - coordinate axis of a dielectric

Z - impedance of a dielectric

z - coordinate axis of a dielectric

α - total polarizability

α_o - polarizability by distortion

δ - phase angle

∂ - partial differential

ϵ - complex dielectric constant $(\epsilon' + i\epsilon'')$

ϵ' - dielectric constant, ordinary

ϵ'' - dielectric loss

ϵ_a - dielectric constant in axial direction of fibre

ϵ_a, ϵ_b - dielectric constants of arbitrary materials

ϵ_K - dielectric constant of benzene of value 2.274 at 25°C

ϵ_o - steady value of ϵ as function of f, as $f \rightarrow 0$

ϵ_∞ - steady value of ϵ as function of f, as $f \rightarrow \infty$

ϵ'_m - dielectric constant of unknown material in dielectric cell, particularly of (i) solutions and (ii) composite dielectrics such as paper when the paper sheet is parallel to the dielectric plates

ϵ''_m	- dielectric loss of unknown material in dielectric cell, particularly of (i) solutions and (ii) composite dielectrics such as paper when the paper sheet is parallel to the dielectric plates
ϵ_n	- dielectric constant in radial direction of fibre
ϵ''_T	- peak values of dielectric loss from ϵ'', ϵ''_m - t curves
$(\epsilon'_m)_n$	- dielectric constant of such a composite dielectric as paper when the paper sheet is normal to the dielectric plates
$(\epsilon''_m)_n$	- dielectric loss of such a composite dielectric as paper when the paper sheet is normal to the dielectric plates
ϵ_{pl}	- steady value of ϵ' as function of f between regions of high and low temperature dispersions for cellulose paper
$\epsilon_1, \epsilon_2, \epsilon_3$	- dielectric constants in principal directions of anisotropic dielectric
η	- viscosity
θ	- angle of average orientation of fibres from the plane of the dielectric plates
κ	- constant in formula for dielectric constant from capacitance of parallel plate condenser
μ	- moment of a permanent dipole
ξ	- H'_m / h'_m, assumed to be constant
ρ	- density (gm./cc.)
σ	- density of surface charge
τ	- Debye relaxation time
τ^*	- $1/2\pi f$
χ	- V'_m /v'_m, assumed to be constant
ω	- $1/2\pi f$, angular frequency

TABLE OF CONTENTS

INTRODUCTION

THEORETICAL DEVELOPMENT

EXPERIMENTAL

RESULTS AND DISCUSSIONS

INTRODUCTION

1. General

The physical properties of cellulose nitrate (commonly known as nitrocellulose) and of the parent compound, cellulose, have been under investigation for nearly a century. Basic to their physical properties is the movement of the component molecules. Movement in polar molecules can be detected by perturbing the molecules with an electric field and by observing the electrical reaction as the molecules revert to a condition indistinguishable from their initial one. The latter process is known as dielectric relaxation. The molecules of cellulose and nitrocellulose are polar. Studies have been made on their dielectric relaxation but it was felt that these studies were by no means complete, and that further investigation was desirable.

The dielectric relaxation of cellulose nitrate is of particular interest, especially insofar as the nitrate is used as a component of smokeless propellants. The rigid specifications for the combustive and mechanical properties of propellants require a knowledge of the intrinsic characteristics of the individual and composite molecules of the compound, and their relation to its known physical and dynamic mechanical properties. Direct methods for dynamic measurement of mechanical properties have been advanced (1), but have not yet been systematically applied to cellulose or its derivatives. In the meantime, it is believed that for a polar molecule such as nitrocellulose, most of the dynamic mechanical properties will be reflected in its dielectric properties.

Investigation of properties by dielectric determinations has the advantage that the sample is not destroyed by the measurements, and that trends can be established without time consuming statistical sampling.

In the following parts of the Introduction, the properties of cellulose nitrate as a derivative of cellulose will be discussed. This will be followed by a resume of theories on dielectric relaxation and an account of previous dielectric investigations on cellulose nitrate, cellulose and other cellulose derivatives.

Previous workers have made dielectric measurements on cellulose paper but were hampered by inadequate formulae relating the dielectric constant and loss of paper to those of cellulose. In the present work, formulae were derived for this purpose and are presented in Theoretical Development. This necessitated the development of some theoretical techniques which are given in the same section. The results include considerations of the anisotropic nature of cellulose fibres. They are also applicable to sheets of cellulose nitrate or other fibrous materials.

Measurements of dielectric constant and loss were performed in the frequency and temperature ranges 50 c.p.s. to

18 Mc and -196 to 264°C. Immersion cells and other special equipment were designed for some of the experimental techniques.

Measurements were made on nitrocellulose: (a) in solution with acetone, (b) as plastic sheets plasticized with different concentrations of camphor, (c) as films cast from solutions with acetone and (d) in the form of fibrous handsheets. The last measurements were necessary in observing the effect of concentration of sorbed acetone. The effect was first studied using films but determinations for zero acetone content were not made because of the appreciable concentrations of acetone remaining in the films after drying. The difficulty was overcome by using the handsheets, although another problem was created--that of converting results for the handsheets to those for nitrocellulose. This was another reason for deriving the formulae in Theoretical Development.

Finally, previous measurements on dry cellulose paper were repeated and extended. They were compared to those on nitrocellulose for which four independent relaxation processes were detected. Two mechanisms of dielectric relaxation were believed to be common to both materials. These mechanisms and the known mechanical properties of cellulose and nitrocellulose were discussed.

2. Cellulose and Cellulose Nitrate

There is almost universal agreement today regarding the molecular structure of cellulose and its derivatives. The skeletal structure of all is considered to be essentially the same and is exemplified by cellulose. It consists of linear macromolecules built up from β-glucopyranose units as in the following scheme:

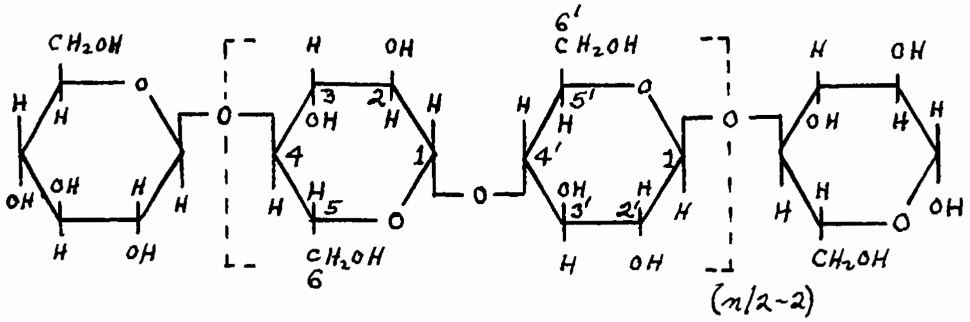

Figure 1

The pyranose rings are in the armchair form and are connected by 1-4 glucosidic units. In a straight portion of the macromolecule, the successive rings are in the same plane but are oriented at 180° to each other. The centres of gravity of the atoms of a ring are actually distributed over two parallel planes. The H atoms are above and below these planes, while the OH groups spread out between them. There is a high electrostatic energy of interaction between the hydrogen of one hydroxyl and the oxygen of a second hydroxyl, so that neighbouring chains of cellulose tend to associate to form ordered, or crystalline, regions.

In natural cellulose fibres there is a high degree of latticed order. It is especially pronounced in numerous regions which C. N. Nageli named "micellae" (2). They are also called crystalline regions although their crystallinity is imperfect. Nearly amorphous material lies between them. The lengths of micellae and of chains do not bear any known mutual relationship. The absence of any such relationship is indicated by the fact that some macromolecules extend from a crystalline into an amorphous region.

In the process of solvent sorption segments of these intraregional chains diffuse and permit the solvent, in its turn, to diffuse along the macromolecule, thus effecting penetration of the solvent into the finest amorphous regions and even into crystalline regions.

Materials of nearly the same cohesive energy density (C.E.D.) are generally good solvents for each other. The C.E.D. is the energy of vaporization per cubic centimeter of liquid and is a measure of the energy of separation of like molecules. However, even a perfect match of C.E.D. between a polymer and a solvent will not overcome the lattice energy of a crystalline polymer at temperatures well below its melting point. Some specific interaction between solvent and polymer is necessary.

In cellulose there is a specific interaction between its hydroxyl groups and solvents such as water, alcohols and amines which are capable of hydrogen bonding. In this way there is a stronger interaction between individual cellulose hydroxyls and solvent molecules than between neighbouring cellulose hydroxyls. However the lattice energy still prevents solvation of the most ordered regions, although the amorphous regions are readily soluble, and the sorption of water in these regions induces marked swelling of the cellulose specimen.

Hydroxyl ions have a stronger specific interaction with cellulose hydroxyls than have water molecules. However, when the hydroxyl concentration of an aqueous solution is increased by using an inorganic base such as NaOH, a new crystal structure is formed which is insoluble in the medium. On the other hand, the formation of a stable solvate lattice can be avoided by using a strong organic base with a bulky positive ion, such as tetraethyl ammonium hydroxide. Water has an appropriate C.E.D. to readily dissolve the solvate of such a base.

Some solvate formation occurs with water and cellulose but no independent structure has been obtained for it because dissolution occurs long before solvation is complete. The first molecules of water sorbed by cellulose are presumed to be solvated, since the limiting heat of swelling per mole of water was found to be 5.2 Kcals. per mole of water which is the same as the heat of formation of a hydrogen bond.

Sorption hysteresis can be explained by the above considerations. After a cycle of wetting and drying with a good swelling agent such as water the crystallinity of cellulose is generally (75) considered to be enhanced, although current measurements in this laboratory do not bear this out. The postulated mechanism of hysteresis is as follows. Water softens or plasticizes the amorphous regions and aids diffusion of chain segments. As drying proceeds, water is removed from some OH groups of the amorphous cellulose, and in their partially plasticized state, portions of neighbouring chains tend to associate. Their potential for association increases with dryness but the mobility of the chains diminishes. The net effect is that some but not all of the fibres arrange themselves into a more crystalline structure. When a sample is dried below a given relative humidity, the order of the cellulose is increased so that upon returning to the same relative humidity a portion of the new order is retained and less water will be absorbed than before.

Cellulose can be nitrated to various degrees of substitution. The degree of substitution is defined as the average number of nitrate groups per anhydroglucose unit. It bears a simple relationship to the percentage nitrate-nitrogen content (93).

There are two main types of solvent for nitrocellulose. Tbe first contains nitrate and nitro groups; the second contains carbonyl groups or oxygens with free electrons. The best solvents for trinitrocellulose are those in the second group because they enter into specific interaction with the polymer, whereas the action of the first group is probably due only to good matching of cohesive energy densities (3)(4).

In cellulose derivatives as well as in the parent material there is interaction between solvent and polymer groups (3)(4). The derivatives can be divided into two functional groups-- those which act as acids, or as electron acceptors, and those which act as bases, or electron donors. Most small molecules which possess acceptor properties contain hydrogen attached to either oxygen or nitrogen, or are activated by a substituent group. Carbonyl groups have long been considered basic, but their interaction with functional groups of nitrocellulose remained a mystery for some time.

Chedin and Vandoni (5) attributed the acceptor properties of nitrocellulose to acidic hydrogens on the same carbon as the nitrate group.

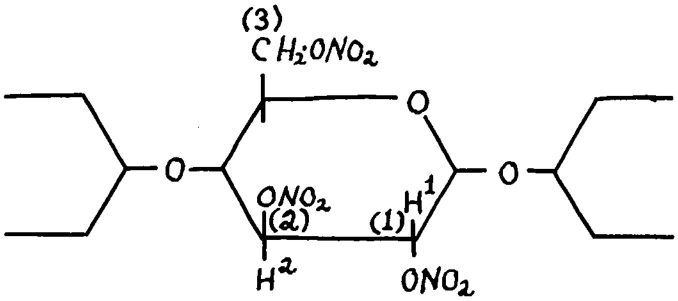

Figure 2

They recalled evidence that nitrocellulose is weakly acidic in character: (a) that nitrocellulose fixes basic dyes and (b) that in electro-osmosis its behaviour is acidic. This may not be very relevant as inspection of the literature reveals that practically all solids acquire a negative zeta-potential in contact with dilute neutral solutions. However, they pursued the nature of this acidity by comparing it with the interaction of acetone with small molecules having nitro or nitrate groups. This they did by observing the deviation in vapour pressure of their binary solutions from that forecast by Raoult's Law. They found that nitromethane, trinitrotoluene and methyl nitrate--and hence their groups NO_2 and ONO_2--did not interact strongly with acetone. Similarly they found that primary, secondary and tertiary hydrogens on the same carbon with a nitrate group were inactive, weakly active and moderately active respectively. This led them to conclude that the hydrogens on carbons C_1 C_2 and C_3 (Fig. 2) of trinitrocellulose were acidic and interacted with the carbonyl of acetone.

In support of this thesis, Chedin and Vandoni (5) pointed out that the limited heat of swelling of nitrocellulose with small amounts of acetone was found to be 4.5-5 Kcals. per mole of acetone, and that this corresponds to the heat of formation of a hydrogen bond. Spurlin (4), however, draws a subtle distinction between this interaction and that of compounds containing hydroxyl groups in which there is a great tendency for like groups to associate.

Due to the regularity of its cellulose substituents, trinitrocellulose has a more highly crystallized structure than cellulose or any of its less highly substituted derivatives. It follows that its higher lattice energy makes it more difficult to dissolve. Because of low order sorption, hysteresis does not occur with nitrocellulose whose nitrogen contents lie between 4.1% and 12.6% (6).

Solvents which have nitro or nitrate groups do not interact with chains in crystalline regions, but those with carboxyl groups have interaction which at equilibrium is almost equal in crystalline and amorphous regions. The interaction of esters is intermediate (7).

The case of camphor is particularly interesting. A solvate is formed with one mole of camphor per C_6 unit (8)(9). This is borne out by a study on the effect of camphor content on the rate of elongation of celluloid films under static stress. It showed that a discontinuity in the elongation-camphor content curve is obtained at 35% camphor content. These results as well as those obtained from double refraction and from X-ray measurements and from chemical examination of various mixtures of camphor and nitrocellulose indicate that a camphor-nitrocellulose compound is formed containing one mole of camphor or slightly more for each anhydroglucose unit in nitrocellulose.

However, camphor cannot penetrate nitrocellulose readily (94). Its vapours are ineffective. Penetration begins only at a 40% concentration in an inert solvent such as hexane, but thereafter proceeds smoothly with increased concentration, attacking both crystalline and amorphous regions simultaneously until the solvate is formed. A methanol-camphor solution penetrates the amorphous regions much more easily. Methanol dissolves the amorphous matter and permits its solvation by camphor. At higher concentrations of camphor the crystalline region is also solvated and the nitrocellulose begins to pass into solution.

3. Dielectric Theory

(a) General

The broad outlines of dielectric theory will be traced in this section. Firstly definitions for dielectric constant and loss factors of a material will be given. The factors influencing their values and methods of dielectric measurement will be reviewed. The former will be discussed on the basis of the Debye and the absolute rate theories, some consideration being given to the distribution of relaxation times.

(b) Definitions

The ordinary dielectric constant and dielectric loss of a dielectric material are defined as follows (11). Ordinary dielectric constant ϵ' is that property which determines the electrostatic energy stored in the material per unit volume per unit potential gradient. The dielectric loss factor ϵ'' is the product of its dielectric constant and its dissipation factor D, ($\epsilon'' = \epsilon' D$), where D is the cotangent of the dielectric phase angle. This latter is the angular difference in phase between the sinusoidal voltage applied to the dielectric and the component of the resulting current which has the same frequency as the applied voltage. The complex dielectric constant is defined by

$$\epsilon = \epsilon' + i\epsilon'' \qquad \ldots . \; \underline{1}$$

where $i = \sqrt{-1}$.

(c) Methods of Dielectric Measurement

The conditions which affect measurements of complex dielectric constant are frequency, temperature, pressure, voltage gradient, accuracy of measurement, and the shape of the specimen (10). Of these, frequency is the most important. Complex dielectric constant is not constant with frequency because one of its components ϵ' decreases with rising temperature, while ϵ'' peaks at every drop in ϵ'. The frequency at which this peak occurs is the relaxation frequency of the polarization causing it. There are four kinds of polarization with a relaxation frequency range corresponding to each; for interfacial polarization the relaxation frequency range is in the milli- and micro cycles; for dipole polarization it lies between a megacycle and a kilomegacycle; for electronic and atomic polarization it falls in the millimeter wave band, 30-300 Kmc, where electric measurements begin.

It is now possible to make dielectric measurements over a frequency range from one microcycle to 300 Kmc. With some materials it is considered possible to make static measurements at zero frequency. Bridges with null detectors are available for measuring from one cycle to 100 Mc, the Schering bridge being the most widely used of these. Below 1 cycle transient methods of measurement have been used; the complex dielectric constant is determined from the shape-magnitude of the discharge current of a charged capacitor (90)(91). Measurement between

1 and 100 Mc are made both by resonant circuit and bridge methods. The susceptance variation and frequency variation methods together with Hartshorn's micrometer-electrode sample holder eliminate most of the errors caused by series residual impedances.

Above 150 Mc it is necessary to use coaxial lines, wave guides and resonant cavities. The measuring technique most often adopted is that of measuring the change in the standing wave pattern and the standing wave ratio, usually by means of a moving probe on a slotted line, when the dielectric sample is suitably introduced into the line (12). The upper frequency limit is in the millimeter wave band, 30-300 Kmc, where the gases of the atmosphere have relaxation frequencies and absorption bands. The importance of measurements in the frequency range from 100 Mc to 1 MMc derives from the fact that the relaxation frequencies of most dipole and atomic polarizations lie in that band.

However, these methods of measurement are generally applicable only under special conditions, of which the most restrictive are the shape and size of the dielectric specimen. In general the sample must be either a disc or a cylinder with or without a central hole. All bridges are free from this limitation unless the Hartshorn sample holder is used. The admittance and impedance meters recently introduced in the frequency range from 100 Mc to 1 Kmc are also free from this limitation, but they cannot measure the losses in low-loss materials.

Formulae for many shapes of dielectric have been determined since the time of Faraday (11)(12).

Any temperature other than room temperature must be attained by placing the dielectric in a heating or cooling unit. This increases the length of the leads to the specimen and introduces errors at the higher frequencies. Above 10 Mc either a part or all of the measuring equipment should be heated or cooled with the specimen.

Of the three remaining conditions under which dielectrics are measured, pressure and voltage gradient produce little change except in gases and provided ionization does not occur. On the other hand, the effect of sorbed water is great. Although, strictly speaking, water is a contaminant, moisture is of such universal occurrence that it is usually treated as one of the important parameters. Measurements made under high humidity require a conditioned closed space so that interfacial polarization between the sample and water sorbed on its surface will not take place. Guard electrodes must be used below 10 Mc to remove the effects of surface conductivity and polarization.

The last condition to be discussed is accuracy. Null methods produce errors of ±0.1% in capacitance and ±1% or 0.0001 in dissipation factor. Errors 2 to 10 times greater may appear at the higher frequencies when resonance methods, slotted lines and waveguides are used. The analysis of current-time curves increases these errors to ± 10% and ± 50% respectively. Thickness measurements of disc samples limit the accuracy of the calculation of dielectric constant to ± 1%.

(d) Debye Theory

(i) Historical

Of the four types of dispersion mentioned in the preceding section the dipolar type is of major interest in the present work. In the late nineteenth century Drude (12) discovered a dispersion of the dielectric constant with electric fields of varying frequency. He was unable to offer any explanation of this phenomenon although as early as 1819 Berzelius (12) had assumed the existence of separated positive and negative charges in the molecules and had termed this state polarization in analogy to the polarity of magnets. Although this theory of electrochemical dualism was satisfactorily applied to salts, from 1840 onwards it was superceded by Dumas' unitary theory which provided a better explanation of the phenomena of substitution of organic compounds (12). From about 1900, following the discovery of the electron, interest in the polarity of molecules was revived, even in organic chemistry. In 1900 Fleming qualitatively anticipated some of Debye's ideas including that of a permanent electric dipole in some types of molecules. The quantitative theory for dipole moments of molecules was briefly presented in 1912 (13) and since the mid-twenties the singificance of dipole moments in the study of molecular structure has been realized and extensively utilized.

(ii) Polarizability and internal field

Debye accepted the prevailing theories on polarization which had been derived largely by Maxwell, Mossotti and Clausius (12)(14). They assumed that temporary dipoles due to electronic and atomic polarization could be induced in any dielectric by placing it between dielectric plates and charging the plates. With a uniform charge of surface density σ, a homogeneous field $\bar{D}$ is established within the dielectric and a field of electrical intensity $\bar{F}$ acts on a single molecule. There is induced in the molecule, a moment $\bar{m}$:

$$\bar{m} = \alpha_o \bar{F} \qquad \ldots 2$$

where α_o is the 'polarizability by distortion' of the molecule. It is a constant, characteristic of the substance in an isotropic condition, but, in anisotropic materials it may have different values in different directions so that the value in equation 2 may be a mean.

$\bar{F}$ was considered by supposing a unit charge in the medium to be enclosed by a small sphere. The sphere was large compared to molecular dimensions but small compared to the distance between the plates. The field acting on this unit charge was treated as consisting of three components

$$\bar{F} = F_1 + F_2 + F_3 \qquad \ldots 3$$

F_1 is the force due to the charges of surface density σ on the plates, so that

$$F_1 = 4 \pi \sigma$$

F_2 is due to polarization of the material outside the sphere supposing that the matter within it is removed. It is caused by the layers of induced charge on the material facing the plates plus the charge on the surface of the spherical cavity:

$$F_2 = -4\pi I + \frac{4}{3}\pi I$$

where I is the electric moment per unit volume such that every element of volume dS acts as though it possesses an electric moment IdS.

F_3 is due to the material within the spherical cavity. There is no general solution for its value although $F_3 = 0$ for cubical crystals and randomly oriented liquids and gases. A weakness of the Debye-Clausius-Mossotti expressions is that this force is assumed to be zero.

A fundamental law of electrostatics is that $\bar{D} = 4\pi\sigma$. Also

$$\bar{D} = \bar{E} + 4\pi I \qquad \ldots\ \underline{4}$$

where $\bar{E}$ is the electric intensity--that portion of $\bar{D}$ which is due to free surface charges on the plate, the other charges being bound by dipoles in the material. Therefore, from 1, $4\pi\sigma = \bar{E} + 4\pi I$ and furthermore from 3:

$$\bar{F} = \bar{E} + \frac{4\pi I}{3} \qquad \ldots\ \underline{5}$$

(iii) The Clausius Mossotti equation

By definition, the dielectric constant bears the simple relationship:

$$\epsilon = \bar{D} / \bar{E} \qquad \text{.... } \underline{6}$$

Also by definitions of I and $\bar{m}$ and where n' is the number of molecules per cc., then

$$I = n'\bar{m} = n' \alpha_o \bar{F}$$

$$= n' \alpha_o \left(E + \frac{4\pi I}{3}\right) \qquad \text{.... } \underline{7}$$

Whence from $\underline{4}$, $\underline{6}$, $\underline{7}$

$$\frac{\epsilon - 1}{\epsilon + 2} =, \frac{4\pi n'}{3} \alpha_o \qquad \text{.... } \underline{8}$$

It follows directly since $n' = \bar{N}\rho/\bar{M}$ where $\bar{N}$ is Avagadro's number, ρ is the density and $\bar{M}$ the molecular weight that:

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{\bar{M}}{\rho} = \frac{4\pi\bar{N}}{3}\alpha_o \qquad \text{.... } \underline{9}$$

which has been designated P', the molar polarization. This is an alternative form of the Clausius-Mossotti expression (15).

In his electromagnetic theory of light, Maxwell determined that

$$\epsilon = r_i^2 \qquad \text{.... } \underline{10}$$

where r_i is the index of refraction. Even when is determined for long electric waves and r_i for visible light, the relation is fairly close for many substances. It does not hold well, however, for those materials possessing permanent dipoles.

(iv) Contribution of a permanent electric moment

Debye considered that polar groups effected an unsymmetrical distribution of charges in a molecule. He treated the molecule as a rigid system of charges, which were resolvable into an electrical doublet and which give the molecule a permanent electric moment. Assuming the doublets to be randomly oriented with respect to an electric field, the mean 'orientation polarizability' due to the moment μ of a permanent dipole is

$$\frac{\mu^2}{3kT}$$

where k is Boltzman's constant and T is the absolute temperature. The total polarizability also includes the distortion polarization:

$$\alpha = \alpha_0 + \mu^2/3kT \qquad \ldots . \underline{11}$$

(v) Alternating electrical fields

Under normal experimental conditions the molecules are oriented slightly in the direction of the field, and on removal of the field Browian movement restores the random orientation. The latter process, designated dielectric relaxation, occurs over a definite period of time. Thus if an alternating electric field is applied, it is often varying so rapidly that orientation polarization lags behind it. When this occurs there is a limited contribution to the dielectric constant; at sufficiently high frequencies the contribution from orientation polarization is zero and the dielectric constant is termed ϵ_∞. When the frequency is sufficiently low the full contribution is effective and this limit of the dielectric constant is termed ϵ_0. At intermediate frequencies there is dispersion of the dielectric constant from ϵ_∞ to ϵ_0.

For a periodic sinusoidal field of angular frequency ω and for spherical molecules, Debye determined the mean moment m and the polarization $P'(\omega)$ to be complex functions (since they involve $i = \sqrt{-1}$).

$$\bar{m} = \left\{ \frac{\mu^2}{3kT} \cdot \frac{1}{1 + i\omega\tau} + \alpha_0 \right\} F \qquad \text{.... } \underline{12}$$

$$P'(\omega) = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{4\pi N}{3} \left\{ \alpha_0 + \frac{\mu^2}{3kT} \cdot \frac{1}{1 + i\omega\tau} \right\} \qquad \text{.... } \underline{13}$$

where τ is a relaxation time to be regarded as the time for the polarization to fall to 1/e of its initial value upon instantaneous removal of the field.

In equation <u>13</u> ϵ is a complex function separable into its real and imaginary parts:

$$\epsilon = \epsilon' + i\,\epsilon'' \qquad \text{.... } \underline{1}$$

where ϵ is the complex dielectric constant, ϵ' is the ordinary dielectric constant, which is the portion of which is in phase with the applied field, and ϵ'' is the dielectric loss, or the portion of ϵ which is out of phase with the applied field.

By the definitions of ϵ_0, ϵ_∞ and equations <u>1</u>, <u>13</u> the frequency dependence of ϵ', ϵ'' during dispersion was found to obey the following equations:

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1+\omega^2\tau^{*2}} \quad \ldots\ldots \underline{14}$$

$$\epsilon'' = \frac{\epsilon_0 - \epsilon_\infty}{1+\omega^2\tau^{*2}}\,\omega\tau^* \quad \ldots\ldots \underline{15}$$

where $$\tau^* = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2}\,\tau \quad \ldots\ldots \underline{16}$$

and $\omega = 2\pi f$ where f is the operating frequency.

Equation 14 yields a sinusoidal plot of ϵ' vs. log ω which is designated a dielectric dispersion curve; in it there occurs an inflection of maximal $d\epsilon'/d\omega$ when $\omega = 1/\tau^*$.

Equation 15 yields a bell-shaped curve of ϵ'' vs. ω which is designated a dielectric absorption curve. ϵ'' is zero for $\omega \ll 1/\tau^*$ or $\omega \gg 1/\tau^*$ and is a maximum for $\omega = 1/\tau^*$.

The frequencies of inflection in ϵ' vs. log a coincide with the frequencies f_m of maxima in ϵ'' vs. log ω. The latter plot is generally more sensitive in experimentally determining $\tau^* = 1/2\pi f_m$.

The factor $(\epsilon_0 + 2)/(\epsilon_\infty + 2)$ in equation 16 has been criticized. Onsager (16) based his criticism on evidence that the Clausius-Mossotti relation is invalid for the internal field in polar liquids. He and others (17)(18) have suggested that this factor be replaced by unity. In the present work this suggestion has been heeded and $1/2\pi f_m$ is utilized as the relaxation time.

Dispersion and absorption curves similar to ϵ', ϵ'' vs log ω can be obtained at constant frequency if τ is systematically changed. Debye presumed that this could be done by altering the viscosity by changing the solvent or temperature. Thus he found on applying Stoke's law to a dipole of radius a rotating in a medium of viscosity η.

$$\tau = \frac{4\pi\eta a^3}{kT} \qquad \ldots\ \underline{17}$$

From equations 15 to 17 curves of ϵ', ϵ'' vs. -T or vs. -t (t in °C being equal to T in °K) will have the same shape as those of ϵ', ϵ'' vs. log ω. The temperature dependence of a relaxation time can thus be found (a) by measuring values of f_m from a family of curves ϵ'' vs. log f_m at constant temperatures t, or (b) by measuring values of t_m from a family of curves ϵ'' vs. t at constant frequencies f (where t_m is the temperature of peaking of ϵ'').

To a first approximation (a) and (b) give the same result even though equations 16 and 17 may not be valid. The introduction of Stoke's law and macro viscosity in equation 17 leads to serious discrepancies in values of (a)(19)(20). To overcome this for solids the concept of internal viscosity was introduced, but it was of limited usefulness. The concept of relaxation as a rate process is more useful and will be treated later in this section. It also leads to equivalence of (a) and (b)(22).

Objections to this have been raised on the grounds that there is a characteristic dipolar structure corresponding to each temperature (21), presumably due to such properties as intermolecular distances and cohesion. Nevertheless, method (b) will largely be used in this work since experimental errors in ϵ'' are smaller for an increment of temperature than they are for an equivalent dispersion-spanning increment of frequency. These errors will be considered in Experimental and also in Results and Discussions.

(e) Dielectric Relaxation as a Chemical Rate Process

(i) Kinetic theory

Dielectric relaxation was treated from the point of view of chemical kinetics by Frank (22), Eyring (23)(24) and Kausman (20). It was assumed that during relaxation the dipoles change their orientation in a series of sudden jumps and that the rate of jumping was equal to the molecular rate of relaxation k_o, where

$$k_o = 1/\tau \qquad \text{.... } \underline{18}$$

k_o being analogous to the specific rate constant of chemical reactions.

In the theory of absolute reaction rates (24) it is assumed that, in any atomic or molecular process whose rate is temperature dependent, the atoms or molecules must first be energized to the state of an activated complex before the reaction can go to completion. The free energy of activation ΔF^* for dielectric relaxation is given by

$$\frac{1}{\tau^*} = \frac{kT}{h} e^{-\frac{\Delta F^*}{RT}} \qquad \text{.... } \underline{19}$$

where k and h are the Boltzman and Planck constants. This equation can be expanded in terms of the enthalpy ΔH^* and entropy ΔS^* of activation.

$$\frac{1}{\tau^*} = \frac{kT}{h} e^{-\frac{\Delta S^*}{R}} e^{-\frac{\Delta H^*}{RT}} \quad \ldots. \ \underline{20}$$

These lead to the equations

$$\begin{aligned} \Delta F^* &= 2.303 \ RT \log (kT \tau^*/h) \\ \Delta H^* &= 2.303 \ R \left[\partial \log \tau^*/\partial (1/T)\right] - RT \quad \ldots. \ \underline{21} \\ \Delta S^* &= (1/T)(\Delta H^* - \Delta F^*) \end{aligned}$$

whereby ΔF^*, ΔH^*, ΔS^* can be determined provided there is a linear plot of log $(1/2\pi f_m)$ vs. $1/T$ or of log $(1/2\pi f)$ vs. $1/T_m$.

Similar equations can be written for the process of viscous flow. It is found that better correlation between the processes of dielectric relaxation and viscous flow can be obtained in this way than by application of the Debye theory (37). When the free energies are nearly equal it is now generally assumed that there is a close correlation between the two processes (25).

(ii) Thermodynamic parameters and mechanisms of dielectric relaxation

Implications from values of ΔF^*, ΔH^*, ΔS^* are of prime importance in determining the mechanism of a dielectric relaxation. Debye (14) considered that an applied field caused (1) orientation perturbation of small molecules in the liquid state and (2) rotation through 180 degress of

HOH molecules in ice, the dipoles relaxing from and to the positive and negative directions parallel to the electric field of force. Relaxation in macromolecules involves other mechanisms.

According to current ideas about liquid and solid structure (20) a molecule is surrounded by an approximately crystalline state. Orientation of a molecule is accompanied by a change in order of the neighbouring molecules by a process involving the loosening of bonds holding the molecules together. Then the activated state approximates to that of a gas as far as intermolecular forces are concerned. This requires an entropy increase comprised of the contributions of the members of the "crystal." From this activated state the molecules can go back to their original configuration or proceed to another stable one.

If a molecule is asymmetric and the degree of order about the molecule is high, a large entropy increase will be involved and the process of activation is regarded as essentially a vaporization. From Trouton's rule the entropy of vaporization of a molecule of molecular weight 100 is 10 to 15 e.u. Thus the number of molecules involved in a dielectric relaxation can be estimated.

When relaxation occurs in macromolecules it may involve rotation of segments of the polymer chain. A method (26) to determine the numbers of monomers in the segment and the number of possible configurations of the segment is described in Results and Discussions, Part 6.

Values of zero or slightly negative values of entropy have been found for several substances. This is interpreted by Eyring and others as an indication that the molecules are rotating freely in the normal state (28).

(f) Distribution of Relaxation Times

The Debye theory of dielectric dispersion is based on a dipole rotor having a single relaxation time τ. This postulate holds for some small molecules (74), but breaks down for highly polar liquids, large molecules and solids.

The effect of having a distribution of relaxation times is most readily seen from Cole-Cole plots which are of ϵ'' vs. ϵ' (74). For Debye materials they are semicircular arcs cutting the ϵ' - axis at ϵ_∞ and ϵ_0, the centres of the arcs being at $\epsilon'' = 0$, $\epsilon' = \frac{1}{2}(\epsilon_0 + \epsilon_\infty)$. Cole and Cole pointed out that Debye materials are exceptional and that for most materials, plots of ϵ'' vs. ϵ' will be circular arcs but that the centres of the arcs lie below the ϵ' - axis.

Fuoss and Kirkwood (73) considered in detail the polyvinyl chloride-diphenyl systems. They determined theoretically that a distribution of relaxation times would have somewhat similar effects to that noted by Cole and Cole, and that the distribution could be calculated from the observed loss factor-frequency curves. A formula between ϵ'' and f for their materials was presented which included a new constant, the distribution parameter. Its value could vary from 0 to 1 for infinite to unit times of relaxation,

4. Dielectrics of Cellulose and Cellulose Nitrate

Investigators in this field claim to have detected the dielectric dispersion of nitrocellulose in both its solid and dissolved states. Three papers have appeared on the dielectric behaviour of cellulose hitrate in the solid state, all of them reporting observations of dielectric loss made at constant temperatures and variable frequencies:

(1) Burke (1942) claimed to have found a maximum in dielectric loss at 30 Mc, with a secondary one near 1 Mc. These were attributed respectively to ionic polarization within the micellae and to "rotation of the polar groups." She presumably took her measurements at room temperature (29).

(2) Girard and Abadie (1944) found an absorption peak at about 10 Mc and 20°C, while at 45°C there was no peak for frequencies up to 30 Mc (30).

(3) Deiser and coworkers (1948) found that dielectric loss increased with frequency without any sign of an absorption peak up to 100 Mc at 25°C (31). They detected a minor peak in each of cellulose acetate and propionate. However, a general increase in dielectric losses persisted with increasing frequency.

These publications did not reveal much about nitrocellulose. The materials used were not defined and the results of the different workers are contradictory and incomplete.

Lee and Sakurada measured the dielectric constants of solutions of nitrocellulose (32). They found a slight decrease in the dielectric constant with frequencies from 2 to 7 Mc, but did not investigate the dispersion further. However, they did determine the apparent specific polarization of nitrocellulose and, using the Debye-Clausius-Mossotti formula, calculated that its apparent dipole moment lay between 1.666 and 1.791. They found that the specific polarization was only slightly dependent on viscosity or nitrogen content; that it was practically independent of concentration in acetone and ethyl acetate solutions, but varied with nitrocellulose concentration in acetone-hexane. Their conclusions were (a) that nitrocellulose is so strongly solvated in acetone and in ethyl acetate that dipole association and change in solvation do not take place within a wide range of nitrocellulose concentrations and (b) that degree of polymerization has little effect on dielectric properties.

Continuing their investigation, Lee and Sakurada found that the dipole moments of other cellulose derivatives, notably cellulose triacetate and of starch triacetate were nearly identical when based on the C_6 group. Anomalous increases with increasing temperature were noted in the specific polarization of cellulose acetate. This was explained by hindrance to free rotation of the acetate groups (33).

Jatkar and coworkers (34) contended that Lee and Sakurada's results were inconsistent with glucose being the monomer of cellulose and derivatives. They recalled that there was little difference in the dielectric properties of disubstituted and of trisubstituted cellulose acetate. The polar asymmetry of the glucose unit should have been appreciably different and so should the dipole moments. This discrepancy vanishes, Jatkar reasoned, if the cellobiose unit is the base unit, and if the substituents were affixed symmetrically to the cellobiose unit.

Jatkar et al combined their results for nitrocellulose in solution with those of Lee and Sakurada (32) and with the value of 6.1 for the dielectric constant of cellulose found by Argue and Maass (35). Using their own equation in place of the Debye-Clausius-Mossotti equation, they found the dipole moment of unsubstituted, tetrasubstituted and hexasubstituted cellobiose units to be identical and equal to 2.0 D, whereas in trisubstituted and pentasubstituted cellobiose units, the dipole moment was three to four times as large. Discrepancies with the tetrasubstituted material were attributed to a lack of homogeniety in degree of nitration.

Jatkar has further shown that the dipole moment of 2.0 D which was found for an even number of substituent groups corresponds to the resultant of two CO links at each end of a cellobiose unit, or to the moment of a COC link.

Scherer and Testerman (36) observed two centres of dielectric dispersion in nitrocellulose in acetone. These occurred so sharply at 125 and 250 Kc that they were assumed to be resonant dispersions. These workers rightly considered that the nitrocellulose molecule in acetone is convoluted but possessing a certain degree of rigidity; Badger and Blaker (37) calculated that about 10 monomer units are needed to obtain the equivalent of one bond with complete rotational freedom. On the basis that the contour of such a randomly coiled molecule is that of an ellipsoid of revolution, Scherer and Testerman attributed the dispersions to two modes of oscillation: (1) about an axis normal to the total dipole moment vector of the molecule (at 125 Kc) and (2) about the major axis (at 250 Kc). From this concept they made interesting speculations on the relation between molecular weight and the nature of coiling, and also worked out a correlation between their data on dielectric dispersion and the distribution of molecular weights in their samples.

There were weaknesses in their work which will be described in more detail in Results and Discussions. The most obvious one can be seen from their own results on dispersion. The frequency centre of dispersion (f_m) was not temperature dependent, but the temperature centre of dispersion (t_m) was frequency dependent. They used chemically pure acetone that was not further purified and nitrocellulose which probably contained some impurities. The two dispersions they observed were very small in magnitude, but may have existed. If so, they were probably produced by ionic impurities. Cole (69), using acetone, noted one or two dispersions in this frequency region which were certainly due to impurities. In any event there were sufficient possible sources of error in their work to throw considerable doubt on their findings.

The dielectric investigation of cellulose itself began in 1906 with the determination of its dielectric constant (39) by Campbell. Stoops (40), using dry cellophane, was the first to discover dielectric dispersion of cellulose. A review of his results showed that no significant difference was detectable in the temperature-frequency characteristics of dispersion whether measurements were made at constant temperature or constant frequency (41). Stoops considered it unreasonable to attribute the dispersion to hydroxyl groups since their resonant frequency should be in the Raman spectral region. With the additional evidence of a similar though less marked dispersion in cellulose triacetate, he concluded that the dispersion was due to a rotation of glucose anhydride rings of the cellulose chain.

Brown (42), however, discovered that cellulose fibres which were known to be optically anisotropic were also dielectrically anisotropic. The dielectric constant in the direction of the fibre axis was 7.19, but only 5.27 in the direction normal to the fibre axis. He considered his results incompatable with rotation of anhydroglucose units, claiming such rotation to be virtually impossible in the chain direction. Instead, he suggested that his results indicated that the hydroxyl groups are restrained either weakly by entering into secondary valence bonds, or more strongly by coordination to neighbouring chains through hydrogen bonds. Reddish (43) independently conceived this idea of the rearrangement of hydroxyl groups in the amorphous and crystalline parts of Terylene. He also assumed that further hydrogen bonds were formed between Terylene and sorbed water which contributed to the dispersion.

Like Reddish, Seidman and Mason (44) studied the effects on dispersion of materials sorbed onto cellulose. They used water, methanol and ethanol which were believed to increase the number of hydrogen bonds in the cellulose-sorbate system and thereby to augment the dispersion. They too attributed the dispersion to hydroxyl groups of the cellulose.

Muus (45) detected two dispersion regions in dry cellophane. These he attributed to rearrangement of hydroxyl groups which were restricted in amorphous regions and more so in crystalline regions. According to measurements made at constant temperatures over a range from 20 to 70°C, the dispersions corresponding to the amorphous and crystalline regions centred at frequencies above 100 Kc and below 0.1 Kc respectively. He claimed to have found a third dispersion with the cellulose-water system in the region of 1 Kc at 60°C. This displayed negative entropies of activation which were different for each of four samples. The phenomenon was attributed to transfer of molecules of water from one sorption site to another. It was more probably caused by an overlapping of the two other dispersions, for they approach each other in this region. If they were independent, their losses would be additive (46) and in this way such an apparent dispersion could be effected.

The higher frequency dispersion was the same as that investigated by Stoops (40) and later by Dakin and Auxier (47), Veith (48), Henniger (49), and most thoroughly by Seidman and Mason (44).

In summary, Stoops believed that a high frequency dispersion of cellulose and derivatives is due to rotation of anhydroglucose units. Jatkar and coworkers said that rotation of cellobiose units is responsible. Both these theories are supported by the known flexibility of molecules of cellulose derivatives in solution. On the other hand , recent workers (44)(45) who have studied dispersion of solid state cellulose seem to be in unanimous agreement that restricted hydroxyl groups are the effective dipoles.

Thus three different mechanisms have been postulated for the same dielectric relaxation in cellulose, two of them being applicable to derivatives. Dispersion measurements which have been made on cellulose are reliable but those on cellulose derivatives --both in solution and solid state--are contradictory and inconclusive. It was therefore deemed expedient to attempt to find and to characterize dispersions for the nitrate ester.

THEORETICAL DEVELOPMENT

1. Introduction

This section deals with the theoretical evaluation of dielectric constant and loss of fibrous materials and with some theoretical techniques developed for that purpose. This was necessary for the reasons given in the General Introduction. The dielectric values for sheets or other forms of fibre-containing dielectrics can be evaluated by the methods sketched in the Introduction and elaborated in the Experimental section. To convert these values into those for the fibre itself has previously been found to be virtually impossible.

Attempts to do this have been made for cellulose and regenerated cellulose (35), (50) but not for nitrocellulose. The discussion will therefore be restricted to cellulose fibres although the treatments are general to all fibres.

Firstly, from Maxwellian concepts, the capacitance of a tube of force between two potential surfaces will be determined with respect to the difference in the surface potentials, the flux in the tube and the dielectric constant of the material in the tube. From this it will be shown how the capacitance of a composite dielectric can be determined by integrations along real and imaginary tubes of force.

The contributions of previous workers to this problem for fibrous cellulose will then be restated and will include considerations of anisotropy. An equation for the dielectric constant of fibres lying parallel to the dielectric plates of a parallel plate cell will be developed. This will be used with a previous formula for fibres aligned perpendicular to the plates. These formulae represent extremes of fibre orientation to the dielectric plates. The relations will be combined with previous findings on the dielectric anisotropy of crystals to give equations for any average fibre orientation.

Corresponding to these new formulae for dielectric constants, it was necessary to derive formulae between the dielectric loss of paper and of fibres. For this purpose a substitution method was developed whereby formulae for dielectric losses were derived from those for dielectric constants.

From these equations, dielectric values for the axial and radial directions of fibres can be determined. As will be seen, this requires that dielectric measurements of fibrous sheets be made in two ways: (a) with the sheets directed parallel to the dielectric plates, and (b) with the sheets perpendicular to the plates.

As experimental measurements in this work preceded the Theoretical Development, it was not realized that type (b) measurements were necessary, and they were not made. To analyze the type (a) measurements which were made, semi-empirical equations were derived and are presented in Results and Discussions.

2. Determination of the Capacitance of a Tube of Force Between Two Potential Surfaces

This determination is developed from Maxwellian concepts of tubes of force and potential surfaces in an electric field of force following the method of Mascart and Joubert (51). Suppose that the field is bounded by two surfaces of electrostatic potential, $\bar{P}$, such that for one $\bar{P} = P$ and for the other $\bar{P} = 0$. The state of an electric field between these surfaces can be defined at every point by the direction and magnitude of the field strength, i.e. the electric intensity E. This can be done either by representing it by potential surfaces or by lines of force.

Firstly, n + 1 potential surfaces can be mapped out corresponding to values of potential 0, $\frac{1P}{n}$, $\frac{2P}{n}$, $\frac{3P}{n}$, ... $\frac{(n-1)P}{n}$, P, which are consequently of such a nature that moving unit electric charge from one surface to the next corresponds to unit work. At each point the intensity is normal to the potential surface; its mean value E_i between two consecutive surfaces of potentials $\frac{(i-1)P}{n}$, $\frac{iP}{n}$ separated by a distance a_i is given by the equation

$$E_i a_i = \frac{iP}{n} - \frac{(i+1)P}{n} = \frac{P}{n} \qquad \ldots\ldots \underline{22}$$

Secondly, lines of force can give an equivalent portrayal of the field. These are a system of lines orthogonal to the potential surfaces, so representing the direction of force. The intensity of the field is indicated by dividing the field into tubes of force, which are composed of a continuum of lines of force and are such that the flux of intensity passing along each one has a constant value X_j.

A potential surface can be divided into elements of surface dS_j such that

$$E_j\, dS_j = X_j, \qquad \ldots\ldots \underline{23}$$

where E_j is the intensity of the field emanating from any point on dS_j, in the direction normal to the surface. Each of these elements can be taken as the base of an orthogonal tube of force.

In this thesis such a tube of force is considered to join a dielectric plate of $\overline{P} = P$ and a potential surface of $\overline{P} = 0$. This surface is very near, but does not touch the surface of the sample, so that the force tube lies entirely in one dielectric medium with a dielectric constant termed ϵ_a (Fig. 3a). Now the tube is divided into n segments by potential surfaces which satisfy the foregoing principles (Fig. 3b). Then, as will be shown, the capacitances C_i, C_{i+1}, etc., taken between successive potential surfaces and contained in the flux tube, have equal values as $n \to \infty$ and $dS \to 0$.

In these limits successive potential surfaces will be parallel to each other and the portion of the tubes of force which join them will be orthogonal to them and straight. Thus the formula (11) for a parallel plate condenser will hold, i.e.

$$C_i = K \frac{dS_i}{a_i} \epsilon_a, \qquad \ldots\ldots \underline{24}$$

where κ is a constant whose value depends on the units used, dS_i is the area cut from a surface of potential iP/n by the flux tube, and a_i is again the distance separating the surfaces of potentials $(i-1)P/n$ and iP/n. Similarly

$$C_{i+1} = \kappa \frac{dS_{i+1}}{a_{i+1}} \epsilon_a . \qquad \ldots\ldots \underline{24a}$$

In a tube of force, the flux traversing any cross section of the tube is the same. In the case of this tube consider that the flux is X_j. Where the tube is cut by the element dS_i of the surface of potential iP/n, then equation $\underline{23}$ becomes

$$E_i \, dS_i = X_j .$$

Similarly $E_1 \, dS_1 = E_i \, dS_i = E_{i+1} \, dS_{i+1} = \ldots\ldots = X_j$

But from $\underline{22}$

$$E_1 \, a_1 = E_i a_i = E_{i+1} \, a_{i+1} = \ldots\ldots = P/m.$$

Whence $\quad dS_i/a_i = dS_{i+1}/a_{i+1}$

and $\quad C_i = C_{i+1}$

Similarly $C_1 = C_2 = \ldots\ldots = C_i = C_{i+1} = \ldots\ldots = C_n$, as required.

From the law of summation of capacitances in series it also follows that the capacitance C_j of the flux tube is

$$C_j = \left[\sum_{i=1}^{n} (C_i)^{-1} \right]^{-1} = \frac{C_i}{n} = \frac{\kappa}{n} \cdot \frac{dS_i}{a_i} \cdot \epsilon_a$$

$$= \frac{\kappa}{n} \cdot \frac{X_j \cdot \epsilon_a}{P/n} = \kappa \, \epsilon_a \frac{X_j}{P} \qquad \ldots\ldots \underline{25}$$

Hence in a given uniform dielectric, the capacitance of an infinitely harrow force tube between its terminal surfaces is proportional to the flux of intensity passing along it divided by the difference in potential between the surfaces.

One terminal surface is the dielectric plate, where $\bar{P} = P$ in Fig. 3, 4. The other can be extended so close to a segment of dielectric interface of two dielectrics that there is, as $dS_0 \to 0$, no difference in its potential from that of the plate-side surface of this segment. Thus the conclusions from equation 25 apply to a tube of force joining such a segment and a dielectric plate. The capacitance of the tube is thus a potential function. That is, if a given flux of intensity crosses a given segment of dielectric interface the capacitance of the tube of force cutting out this segment does not depend on the path by which it reaches a dielectric plate of potential $\bar{P} = P$.

3. Determination of Capacitance for a Composite Dielectric

The results reached in the preceding section can now be used to evaluate the dielectric constant of a parallel plate condenser (Fig. 4) containing two dielectric media if they are symmetrically distributed about a central plate between its plates. Since tubes of force must necessarily map out the entire volume between two dielectric plates, the capacitance of the contained dielectric must be integrated by a coordinate system which also maps out this entire volume. The cartesian coordinate system is generally the most convenient to use. In such a case the flux lines will also be symmetric about the central plate whether the field is static or whether there is an alternating field subject to dielectric dispersion. The distribution of potential over the dielectric interface will likewise be symmetric. Whether the flux tubes follow routes T_1, T_2, or T_3 of Fig. 4, T_3 being linear and orthogonal to both plates, and as long as they each map out the identical surfaces at P_o, P_o', they will map out identical surfaces at $-P_o$, $-P_o'$. Then the capacitance of the three tubes will be identical between the surface elements of potentials P and P_o, P_o' and $-P_o'$, and between $-P_o$ and $-P$, so that the capacitance found by integrating along T_3 is, in fact, the true capacitance of the force tube passing through this element of surface. Whence the capacitance of such a dielectric, for example (Fig. 5) without folds in any of the principal coordinate directions x, y, z, is found by the laws of summation of capacitances in series and parallel to be

$$\sum_{x=0}^{X} \sum_{y=0}^{Y} \left[\sum_{z=0}^{Z} \left[\frac{\kappa \epsilon_a dxdy}{dz} \right]^{-1} \right]^{-1} - \sum\sum_{S} \left[\sum_{z=0}^{Z} \left[\frac{\kappa \epsilon_a dxdy}{dz} \right]^{-1} \right]^{-1}$$

$$+ \sum\sum_{S} \left[\sum_{z=0}^{S_1} \left[\frac{\kappa \epsilon_a dxdy}{dz} \right]^{-1} + \sum_{z=S_1}^{S_2} \left[\frac{\kappa \epsilon_b dxdy}{dz} \right]^{-1} + \sum_{z=S_2}^{Z} \left[\frac{\kappa \epsilon_a dxdy}{dz} \right]^{-1} \right]^{-1}$$

where, of course,

$$\sum_{z=0}^{S_1}\left[\frac{\kappa\epsilon_a dxdy}{dz}^{-1}\right] = \sum_{z=S_2}^{Z}\left[\frac{\kappa\epsilon_a dxdy}{dz}\right]^{-1}$$

In the limit as dx, dy, dz → 0, this becomes:

$$\kappa\epsilon_a \int_{x=0}^{X}\int_{y=0}^{Y}\left[\int_{z=0}^{Z} dz\right]^{-1} dx\,dy = \kappa\epsilon_a \iint_{S}\left[\int_{z=0}^{Z} dz\right]^{-1} dx\,dy$$

$$+\ \kappa \iint_{S}\left[\frac{2}{\epsilon_a}\int_{z=0}^{S_1} dz + \frac{1}{\epsilon_b}\int_{z=S_1}^{S_2} dz\right]^{-1} dx\,dy \qquad \ldots\ldots \underline{26}$$

It also follows that these findings hold for plates P_2, P_1 which are symmetrically distributed about the same central plane as that of such composite dielectrics.

The principles discussed pave the way for straightforward evaluation of many systems of composite dielectrics.

4. Dielectric Constant of Cellulose from That of Paper

(a) Geometry of Paper Samples

It is of immediate interest to establish a relationship between the dielectric constant of cellulose and that of cellulose paper. Argue and Maass (35) considered three models for cellulose fibres packed between dielectric plates. Assuming air to have unit dielectric constant, the formulae were presented in terms of the dielectric constant of cellulose ϵ', the dielectric constant of the composite material ϵ'_m, and the volume fraction of the cellulose V_2 between the dielectric plates. The models were (a) alternate and uniformly distributed layers of cellulose and air (b) cylindrical pillars uniformly distributed normal to the dielectric plates, and (c) a powdered material for which Lichtenecker (52) used an empirical formula. The formulae for the first and third models were shown to be completely unsuitable whereas the second yielded values for cellulose which were 55% low (42). This formula was used by Argue and Maass, by DeLuca, and by Brown (35), (53), (42) to determine the dielectric constant of water sorbed on cellulose, and to see how it differed from bulk water in the liquid state. Brown noted that the formula was unsatisfactory for this purpose.

All these workers used formulae which were based on the assumption that the fibres of the sample lay normal to the dielectric plates. However, when paper is placed flat between dielectric plates the average orientation of the fibres is closer to being parallel than perpendicular to the plates. Brown assumed that in his samples of flax paper the fibres and fibrils were all lined up parallel to the plates (42). For such a case two models are suggested. Model (a) is shown in Fig. 6a. Right circular cylinders of cellulose are considered to be uniformly positioned parallel to each other and to the plates in such a way that they be equidistantly spaced side by side and one above the other. In model (b) bars of square cross-section are substituted for the cylinders; in every other respect it is identical with model (a).

(b) Formula for Dielectric Constant of Fibres Lying Parallel to the Dielectric Plates

Relations for model (a) are established as follows. Suppose that equal rectangular volumes are taken symmetrically about each cylinder and that the upper and lower faces of these volumes are considered as imaginary dielectric plates. The cross sections of the resultant imaginary condensers will then be squares of sides 2q say, and their capacitances C_k will be equal. These form a series-parallel network as shown in Fig. 6b. If the length, width, and depth of the composite dielectric are L, M and N respectively, then there are N/2q and M/2q rows and columns of the imaginary condensers. The capacitance C_m of the composite dielectric may be found from C_k by the series and parallel formula:

$$C_m = \sum_{k=1}^{M/2q} \left[\sum_{k=1}^{N/2q} (C_k)^{-1} \right]^{-1} = \left[\sum_{k=1}^{N/2q} \left[\sum_{k=1}^{M/2q} C_k \right]^{-1} \right]^{-1} = \frac{M}{N}.C_k \quad \ldots \quad \underline{27}$$

Whence the composite dielectric constant H_m' is seen to be:

$$H_m' = \frac{N}{\kappa\, L\, M} \cdot C_m = \frac{C_k}{\kappa\, L} \quad \ldots. \quad \underline{28}$$

The next step is to find the value of C_k in terms of the dielectric constant H' of the cellulose cylinder. The end view of one of the imaginary condensers is shown in Fig. 7 and the value of its capacitance is seen by equation 5 to be:

$$C_k = \kappa L \int_{x=r}^{q} \left[\int_{z=0}^{q} dz \right]^{-1} dx + \kappa L \int_{x=0}^{r} \left[\int_{z=\sqrt{r^2-x^2}}^{q} dz + (H')^{-1} \int_{z=0}^{\sqrt{r^2-x^2}} dz \right]^{-1} dx \qquad \ldots\ldots \underline{29}$$

where r is the radius of the circular cross section of the cylinder and the dielectric constant of air is assumed to be unity.

Then on substituting 29 in 28 and integrating

$$H'_m = \frac{C_k}{\kappa L} = \frac{q-r}{q} + \int_{x=0}^{r} \left[(q - \sqrt{r^2-x^2}) + (H')^{-1}\sqrt{r^2-x^2} \right]^{-1} dx$$

$$= 1 - \frac{r}{q} + \frac{H'}{H'-1} \int_{x=0}^{r} \frac{dx}{a - \sqrt{r^2-x^2}}$$

where $a = \frac{q\,H'}{H'-1}$

Whence $H'_m = 1 - \frac{r}{d} - \frac{\pi}{2}\frac{H'}{H'-1} - \frac{H'}{H'-1} \cdot \frac{2a}{\sqrt{a^2-r^2}} \tan^{-1}\left[\frac{-r}{\sqrt{a^2-r^2}} - \tan^{-1}\frac{a-r}{\sqrt{a^2-r^2}} \right]$

for $r/a < 1$ which is always the case.

By simplifying:

$$H'_m = 1 - \frac{H'}{H'-1}\left[\frac{\pi}{2} + eb - \frac{2}{\sqrt{1- e^2b^2}}\left(\sin^{-1}eb + \sin^{-1}\sqrt{\frac{1-eb}{2}}\right)\right]$$

$$\therefore H'_m = 1 + e^{-1}\left[\frac{\pi/2 + \sin^{-1} eb}{\cos \sin^{-1} eb} - \pi/2 - eb\right] \qquad \ldots\ldots \underline{30}$$

$$\text{where} \quad e = \frac{H'-1}{H'}, \qquad b = \frac{r}{q} = 2\sqrt{\frac{V_2}{\pi}} = 1.128\sqrt{V_2}$$

and V_2 is the volume fraction of cellulose in the composite dielectric.

The formula for model (b) is easily derived by the above method to be:

$$H'_m = 1 - (V_2)^{\frac{1}{2}} + \frac{H'}{H'\,[(V_2)^{\frac{1}{2}}-1] + 1} \qquad \ldots\ldots \underline{31}$$

This can also be expressed

$$1/H' = \frac{1}{[\,H'_m + (\overline{V}_2)^{\frac{1}{2}}-1]} - [(\overline{V}_2)^{\frac{1}{2}} - 1] \qquad \ldots\ldots \underline{32}$$

(c) Formula for Dielectric Constant of Fibres of Average Orientation

It is now necessary to make allowance for the fact that the fibres and fibrils in paper have in general an average orientation θ from the plane of the dielectric plates which is different from zero. The general model herein presented for paper will be represented partly by formula 30 or 31 and partly by a second formula. The latter formula is for either cylindrical or square-sectioned pillars which are uniformly distributed normal to the dielectric plates:

$$V'_m = 1 + (V'-1)\,V_2 \qquad \ldots\ldots\ \underline{33}$$

where V'_m is the dielectric constant of the composite material and V' is the dielectric constant of the cellulose in the axial direction (54).

(d) Anisotropy of Cellulose Fibres re Dielectric Constant

The asymmetric nature of the dielectric constant of cellulose was neatly demonstrated by Brown (42) using the method of mixtures (12). Dielectric constants of solutions of benzene and ethylene dichloride were varied.

When the addition of cellulose to the solution caused no alteration in its dielectric constant, the dielectric constant of cellulose was assumed to be the same as that of the solution. Brown noted that Schmidt had used this method in 1903 to evaluate the dielectric constants of crystalline substances in powder form. Schmidt found that dielectric constants ϵ' were the mean of dielectric constants in the three major directions ϵ'_1, ϵ'_2, ϵ'_3 in the crystal:

$$3\,\epsilon' = \epsilon'_1 + \epsilon'_2 + \epsilon'_3 \qquad \ldots\ldots\ \underline{34}$$

X-ray studies have shown that cellulose has a monoclinic structure (55). However, since orientation in fibres occurs only in the structural chain direction, only two refractive indices and therefore only two dielectric constants may be distinguished. The equation thus becomes similar to that for uniaxial powders (42):

$$3\,\epsilon' = V' + 2H' \qquad \dots\dots\ \underline{35}$$

where V' is the dielectric constant in the direction of the ortho (b) axis and H' is the dielectric constant in the radial direction perpendicular to the ortho axis. Brown noted that, when cellulose fibres lie flat, as was assumed to be the case in linen paper, then

$$\epsilon' = H' \qquad \dots\dots\ \underline{36}$$

Also, if fibre directions are randomly distributed in the plane of the paper, and if paper sheets are stacked in a direction normal to the dielectric plates, then

$$2\,\epsilon' = V' + H' \qquad \dots\dots\ \underline{37}$$

From his results, Brown found $H' = 5.27$, $V' = 7.19$ at 300 Kc and 25°C for cellulose dried under vacuum at 25°C.

A solution of equations <u>35</u>, <u>36</u>, and <u>37</u> for a single fibre is

$$\epsilon' = V' \sin^2 \theta + H' \cos^2 \theta \qquad \dots\dots\ \underline{38}$$

From equations <u>30</u> or <u>31</u> and <u>33</u>, <u>38</u> it can be seen that when H'_m, V'_m, V_2 and θ are known, then H', V', and ϵ' can be established. By analogy to <u>38</u> it is suggested that the composite dielectric constant ϵ'_m of a sheet of paper, when measured in the ordinary manner with the sheet parallel to the dielectric plates, could be described by

$$\epsilon'_m = V'_m \sin^2 \theta + H'_m \cos^2 \theta \qquad \dots\dots\ \underline{39}$$

Similarly, the composite dielectric constant $(\ '_m)_n$ measured by Brown's method with the sheeting normal to the plates would be given by

$$\begin{aligned}(\epsilon'_m)_n &= V'_m \sin^2 \frac{\pi}{4} \cos^2 \theta + H'_m \left(1 - \sin^2 \frac{\pi}{4} \cos^2 \theta\right) \\ &= \frac{V'_m - H'_m}{2} \cos^2 \theta + H'_m\end{aligned} \qquad \ldots\ldots \underline{40}$$

The average angle of inclination of the fibres to the plates would have been $\frac{\pi}{4}$ for this case if all the fibres lay in the plane of the paper as in 37. It has been affected as is shown by θ which is the average angle of inclination of the fibres to the plane of the paper.

If ϵ'_m, $(\epsilon'_m)_n$ were determined for paper under the same conditions as V'_1, H' were known for cellulose, then θ could be determined by 39 and 40 and the equations thus checked. This will be discussed further in Results and Discussions.

5. Dielectric Loss of Heterogeneous Materials

(a) General Derivation of Dielectric Loss Formulae from Dielectric Constant Formulae

A general and simple method for the derivation of the dielectric loss ϵ''_m of a binary material from the dielectric losses of the component materials was formulated. In the materials studied in this investigation, the dielectric losses for cellulose and air were taken as ϵ'' and zero respectively. The method allows the substitution of the term $\sqrt{\epsilon''^2 + \epsilon'^2}$ for ϵ' and $\sqrt{\epsilon''^2_m + \epsilon'^2_m}$ for ϵ'_m in an equation between ϵ' and ϵ'_m. The derivation of this method is as follows:

The impedance Z of a dielectric is

$$\frac{1}{G^2 + \omega^2 C^2}$$

where G is the inverse of the resistive component of the dielectric according to parallel notation (41). By basic principles the dissipation factor $D = \frac{G}{\omega C}$ where is the angular frequency of the applied field and $\epsilon'' = \epsilon' D$.

Whence $G = \omega C \frac{\epsilon''}{\epsilon'}$

and $$Z = \frac{1}{\sqrt{(\frac{\epsilon''}{\epsilon'})^2 \omega^2 C^2 + \omega^2 C^2}}$$

and $$Z^{-1} = \frac{\omega C}{\epsilon'} \sqrt{\epsilon''^2 + \epsilon'^2} = \omega \kappa \frac{dxdy}{dz} \sqrt{\epsilon''^2 + \epsilon'^2} \quad .... \underline{41}$$

The inverse of the impedance obeys the same rule for summation in series and parallel as does capacitance. Therefore, since ω, κ are both constant, then integration of a term $\omega \kappa \frac{dxdy}{dz} \sqrt{\epsilon''^2 + \epsilon'^2}$ will proceed in the same manner as will a term $\omega \kappa \frac{dxdy}{dz} \epsilon'$ when integrated with respect to dx, dy, dz over the same spatial arrangement. Hence, if ϵ''_m is a function of ϵ', then $\sqrt{(\epsilon''_m)^2 + (\epsilon'_m)^2}$ is the same function of $\sqrt{(\epsilon'')^2 + (\epsilon')^2}$ for the same composite dielectric.

In the special case in which one component of the dielectric is vacuum or air, it is evident that the corresponding term for $\sqrt{(\epsilon''_m)^2 + (\epsilon'_m)^2}$ is equal to its dielectric constant which is unity. Therefore, for a composite material like paper in which the constituents are cellulose and air, a relation between dielectric losses for cellulose ϵ'' and for paper ϵ''_m can be obtained from a relation between dielectric constants ϵ', ϵ'_m, by substituting in the latter the values $\sqrt{(\epsilon''_m)^2 + (\epsilon'_m)^2}$ and $\sqrt{(\epsilon'')^2 + (\epsilon')^2}$ for ϵ'_m and ϵ' respectively. 42

(b) Dielectric Loss of Cellulose from That of Paper

Three models were discussed in Part 4 of Theoretical Development. The formulae for dielectric loss of these models are derived below from their dielectric constant formulae and formula 42. Following that, the effects of anisotropic fibres will be considered.

(i) Model (a) with Cylinders Parallel to Dielectric Plates

From equations 30 and 42

$$\sqrt{(H''_m)^2 + (\epsilon'_m)^2} = 1 + (e'')^{-1} \left[\frac{\pi/2 + \sin^{-1} eb}{\cos \sin^{-1} eb} - \pi/2 - eb\right] \qquad \text{.... } 43$$

where $e'' = \left[\sqrt{(H'')^2 + (H')^2} - 1\right] / \sqrt{(H'')^2 + (H')^2}$

and where H''_m is the dielectric loss of a composite paper dielectric according to the model on Fig. 6a and H'' is the dielectric loss of cellulose taken radially.

(ii) Model (b) of Square-sectioned Bars Parallel to Dielectric Plates

From equations 32 and 42

$$\frac{1}{\sqrt{(H'')^2 + (H')^2}} = \frac{1}{\sqrt{(H''_m)^2 + (H'_m)^2} + (V_2)^{\frac{1}{2}} - 1} - \left\{(V_2)^{\frac{1}{2}} - 1\right\} \qquad \text{.. } 44$$

(iii) Model of Cylindrical or Square-sectioned Pillars Normal to Dielectric Plates

From equations 33 and 42

$$\sqrt{(V''_m)^2 + (V'_m)^2} = 1 + \left\{\sqrt{(V'')^2 + (V')^2} - 1\right\} V_2 \qquad \text{.... } 45$$

where V''_m is the dielectric loss of a composite paper dielectric according to the pillar model described prior to equation 33, and where V'' is the dielectric loss of cellulose taken with the electric lines of force in the axial direction of the fibre.

When V''_m and V'' are small in comparison with with V'_m and V' respectively, the approximations $\sqrt{(V''_m)^2 + (V'_m)^2} = V'_m + \frac{2(V''_m)^2}{V'_m}$ and $\sqrt{(V'')^2 + (V')^2} = V + \frac{2(V'')^2}{V}$ yield a good approximation for formula 45:

$$V'' = V''_m / \sqrt{V_2 \, (V'_m/V')} \qquad \ldots\ldots 46$$

(c) Anisotropy of Cellulose Fibres re Dielectric Losses

The mean dielectric constant ϵ' of cellulose was previously given (formula 38) in terms of the axial H' and radial V' dielectric constants:

$$\epsilon' = V' \sin^2 \theta + H' \cos^2 \theta \qquad \ldots\ldots 38$$

where θ is the angle between the crystal axis and the plane of parallel dielectric plates. A relationship follows from this for the corresponding mean dielectric loss ϵ'' of cellulose and the axial H'' and radial V'' dielectric losses. This is found by consideration of the complex dielectric constant and loss.

In the Introduction, Part 3, it was established that $= \epsilon' + i\epsilon''$, which is to say that ϵ' is the real and ϵ'' the unreal part of the complex dielectric constant . If H, V represent the complex dielectric constants $H' + iH''$, $V' + iV''$

respectively, then from 38 and from the nature of complex numbers

$$\epsilon = V \sin^2 \theta + H \cos^2 \theta \qquad \ldots\ \underline{47}$$

$$\epsilon'' = V'' \sin^2 \theta + H'' \cos^2 \theta \qquad \ldots\ \underline{48}$$

For if $\epsilon = V \sin^2 \theta + H'' \cos^2 \theta$

then $\epsilon = V' \sin^2 \theta + H' \cos^2 \theta + i(V'' \sin^2\theta + H'' \cos^2\theta)$

This being the case, the real coefficients of ϵ can be equated to give 38 and the unreal coefficients of ϵ can be equated to give 48. In order that there be a unique solution the converse must hold, whence 48 must follow from 38.

Similar relationships are obtained for the dielectric loss ϵ''_m, $(\epsilon''_m)_n$ of sheets measured parallel to and normal to the dielectric plates, respectively. From equation 39

$$\epsilon''_m = V''_m \sin^2 \theta + H''_m \cos^2 \theta \qquad \ldots\ \underline{49}$$

and from equation 40

$$(\epsilon''_m)_n = \left(\frac{V''_m - H''_m}{2}\right) \cos^2 \theta + H''_m \qquad \ldots\ \underline{50}$$

V''_m and H''_m are the composite dielectric losses measured respectively with the sheets normal to and parallel to the dielectric plates, for the case in which all the fibres and crystals are lying in the plane of the sheet.

Equations 48 - 50 when augmented by relationships between H'' and H''_m and V'' and V''_m (equations 43 - 46) are sufficient to calculate H'', V'' and ϵ'' from ϵ''_m and $(\epsilon''_m)_n$. This can be done when the necessary values of dielectric constant have previously been obtained by the formulae given earlier.

In Part 5 of Results and Discussions the calculation is explained in detail.

EXPERIMENTAL

1. Introduction

This section deals with materials and methods of experimentation.

Dielectric measurements were made using two capacitance bridges. They were generally made on dielectric cells which contained specimens of unknown dielectric constant and loss. The bridges, their circuits, their auxiliary equipment, methods of their operation and significance of their readings are discussed. Formulae are given to convert these readings into dielectric values for the unknown.

Specimens based on cellulose nitrate and on cellulose were prepared in such ways that they could be inserted into a dielectric cell. Four such cells have been employed and are described. They were of the immersion type so that their temperature could be readily controlled in liquid baths. Three of them were designed to be vacuum tight so that the specimens could be dried by evacuation or could be treated with vapours.

Conditioning equipment consisted of: (a) devices for thermostatting the dielectric cell at various temperatures and (b) vacuum-tight system for drying specimens and conditioning them with vapours.

2. Electrical Equipment

The values of dielectric constant and dielectric loss for a material were determined from measurements of capacitance and dissipation factor on the dielectric cell in which it was contained. Measurements were made at frequencies ranging from 50 c.p.s. to 10 Mc with a Schering and a twin-T bridge.

Four arrangements of bridges and auxiliary equipment were used as itemized in Table I. The arrangements depended on measuring frequencies. Every arrangement followed customary practice. An electric current of specified frequency was: (a) generated by an oscillator, (b) amplified, if necessary, and (c) fed to an appropriate bridge. The current remaining from off-balance of the bridge was (d) converted and amplified by the detector arrangements into audio earphone signals or into traces on a cathode ray oscilloscope.

From 0.55 to 10 Mc the twin-T bridge was employed. Accuracy of measurement at high frequencies was achieved by avoiding some residual impedances which limit the performance of other bridge circuits. Errors inherent in variable resistors at high frequencies were eliminated by balancing susceptances with specially designed variable air capacitor and a fixed resistor.

The twin-T circuit is illustrated in Fig. 8a. The circuit consisted of two T networks so that they furnished parallel transmission paths, a - b - c and a - d - c. Zero energy transfer from the generator to the detector occurred when the transfer impedances of the two T networks were made equal and opposite and a null balance was obtained. The circuit conditions for this have been determined by Sinclair (56).

Measurements were made by establishing an initial balance without the unknown and a second balance with the unknown in the circuit. The bridge indicated the capacitance of variable condenser C_A for both balance conditions. Conductance of the unknown was determined from the final dial reading G, of a variable condenser C_G. The dial was calibrated directly in units of conductance. Its setting for the initial balance was always zero. Methods to determine corrected values of the dielectric's capacitance and dissipation factor will be given in Part 3 of this section.

The detector for the twin-T bridge was a radio receiver, a hallicrafter S-40. It could, of course, detect a modulated signal. Also, its internal oscillator could generate a signal which produced beats with an unmodulated signal according to the heterodyne principle; the beats so produced were amplified internally and were made audible with earphones. The former type of detection was employed for preliminary balancing of the bridge; the latter was more accurate for final adjustments.

The dual operation of the receiver depended on the oscillator. It was a Clough-Brengle product (Table I) which could generate (a) an unmodulated signal and (b) a carrier signal modulated with a 400 c.p.s. note.

Further details on the operation of the bridge and receiver have been described in the manufacturer's literature and in the theses of previous workers in this laboratory (28)(41).

At all the lower frequencies from 50 c.p.s. to 300 Kc the Schering bridge was employed. Two methods could have been used. The "Substitution" method was shown by Funt (28) to be preferable to the alternative "Direct" method and was accordingly used.

In Fig. 8b the circuit for the "Substitution" method is illustrated schematically. The unknown condenser is represented by a pure capacitance C_{XP} and a pure resistance R_{XP} in parallel. A variable air condenser C_S was balanced against the other arms of the bridge. Its values C', C" were taken with the unknown disconnected and connected respectively. When the unknown condenser possessed a conductance component $(R_{XP})^{-1}$, this was balanced by a change in the variable capacitance C_B. A switch and a dial controlling the condensers C_B were calibrated to read dissipation factors directly. Formulae for corrected values of C_{XP} and dissipation factor will be given under the heading "Electrical Analysis of Circuits and Unknown Condensers."

The variable air condenser C_S was an integral part of the bridge unit. It indicated capacitances from 100 to 1100 uuf, with an absolute accuracy of 0.1 uuf. The capacitor C_P, an external condenser, was a General Radio Co. Type 505, 1000 uuf, mica condenser; it was plugged directly into bridge terminals.

Depending on the measuring frequency, 3 arrangements for auxiliary equipment to the Schering bridge were used. These are clearly shown in Table I. In all arrangements, current from the specified oscillator was conducted directly to the bridge without preamplification. The essential differences were in the two systems employed for detection.

The first, for frequencies from 35-300 Kc, was a well shielded RCA radio receiver whose output went to a cathode ray oscilloscope. Unmodulated signals were fed from the oscillator to the bridge, whose off-balance current proceeded to the receiver. There, an autodyne, which is a type of heterodyne circuit, converted the current to an audiofrequency. This, in turn, was amplified and carried to an earphone jack.

The receiver was highly sensitive. Also, there were filters built into the circuit which provided high selectivity at any frequency in the 35-300 Kc range.

An oscilloscope was used instead of earphones as its trace revealed distortion of the received signal, if such existed. The signal was applied to the 'y' plates of the oscilloscope and was beat against an internal oscillation applied across the 'x' plates (41). This resulted in a sinusoidal trace unless the signal was distorted. Controls were adjusted to give maximum amplitude of generated signal with no noticeable distortion.

The second system for detection was for frequencies from 50 c.p.s. to 20 Kc. The off-balance current from the bridge was selectively amplified with a General Radio assembly (Table I) and fed to the oscilloscope. The assembly consisted of a filter box plugged into an amplifier. A switch on the filter box connected different filter circuits to grids of amplifier tubes in the amplifier. Filtration was selective and was provided at the frequencies: 0.05, 0.116, 0.2, 0.5, 1, 2, 5, 10 and 20 Kc.

This equipment had excellent sensitivity between 0.2 and 20 Kc. At 0.05 and 0.116 Kc the built-in filters were not used; in this range the designers intended a 20 henry coil to be incorporated into the filter circuit. Instead, a 2 henry coil of the filter and appropriate external condensers were employed. Even so at 0.05 Kc measurements were sufficiently precise only when dissipation factors were high. Values at this frequency were thus measured only for cellulose paper above 100°C.

There was some tendency for the balance of the Schering bridge to drift at frequencies up to 0.5 Kc and at 35 Kc. This was so even after prolonged warming up of bridge accessories. At 35 Kc it was evidently due to slight instability of the oscillator at its upper frequency limit. Capacitance balance at the low frequencies was stable; but dissipation factor readings oscillated as much as 0.00002, having a periodicity of about 2 minutes. As the effect was most noticeable on humid days it is believed that it could be eliminated if casings of the bridge and all accessories were modified to receive a deseccant. As it was, average values were taken which are believed to be precise to 0.000002.

While discussing experimental accuracy with the Schering bridge it should be noted that capacitance measurements were accurate to ±0.1 uuf.

Both the twin-T and Schering bridges were previously employed in this laboratory but the second detector arrangement for the Schering bridge was introduced during this investigation. The first such arrangement had been used as low as 10 Kc (41). Even so, below 35 Kc, the second arrangement was more sensitive than the first. It was, of course, applicable to frequencies that were far lower than 10 Kc, that were in fact, as low as 0.05 Kc.

A further electrical apparatus was employed for measuring D.C. resistances of dielectric cells. This was the General Radio Type 1861-A Megohmeter. Dissipation factors were corrected for such resistances if they are high enough to be significant.

3. Electrical Analysis of Circuits and Dielectrics

(a) General

Both the twin-T and Schering bridges yielded results for equivalent parallel capacitance C_{XP} and dissipation factor D_X across their "unknown" terminals. Lead corrections for capacitance and loss were applied to these values in order to find the equivalent parallel capacitance C_m and dissipation factor D_m across the dielectric plates of the cell. From the latter values and the geometric capacitance Ca of the cell, dielectric constant and loss of the contained dielectric were determined.

The "equivalent parallel" notation for an imperfect condenser assumes that it is equivalent to a pure capacitance in parallel with a pure resistance (11).

The dissipation factor D is tan δ , where δ is the phase angle between the voltage and current across the condenser.

(b) Twin-T Bridge

The balance conditions and the evaluation of residual impedances for the twin-T bridge have been discussed in detail by (56) Sinclair.

Capacitance readings for the standard condenser C_A (Fig. 8a) were indicated on a drum scale. Calibration corrections for the scale were supplied by the manufacturers. These were applied to the scale readings to give capacitance readings C', C" when the unknown was respectively disconnected and connected.

The final setting G_o of the conductance dial was frequency-adjusted in order to give a conductance reading G". There was a switch (89) which could be set at different positions of frequency f_o depending on the range of the working frequency f.

$$G'' = G_o \, (f/f_o)^2 \qquad \ldots\ \underline{51}$$

Then the following formulae are readily shown to apply (56):

$$C_{XP} = \frac{\Delta C}{1 + \omega^2 L' \Delta C - \omega^2 L_C \, (C' + C'')} \qquad \ldots\ \underline{52}$$

$$D_X = \frac{G'' \, (1 - \omega^2 L'' C')^2 + \omega^2 R_C \Delta C \, (C' + C'')}{\omega \, C_{XP} \, (1 + \omega^2 L' \Delta C)^2} \qquad \ldots\ \underline{53}$$

where $\Delta C = (C' - C'')$, $\omega = 2\pi f$, and L', L'', L_c, R_c were stray lead impedances.

At the high frequencies attainable with this bridge, corrections for inductance of the leads are necessary. L' was the inductance of the leads from the standard condenser C_A at b' (Fig. 8a) to ground through the dielectric cell. L'' was the inductance between points b, b', and L_c, R_c were the effective inductance and resistance in series with the standard condenser C_A between b' and ground.

A combined tabular and graphical method to calculate C_{XP} and D_X has been suggested by D. Blanchard and was described by Funt (28).

At low frequencies the contributions from L'', L_c and R_c were often negligible. In which case, equations 52 and 53 simplified to

$$C_{XP} = \Delta C / (1 + \omega^2 L'\Delta C) \qquad \ldots\ldots\ 54$$

$$D_X = \frac{G''}{\omega C_{XP} (1 + \omega^2 L'\Delta C)^2} \qquad \ldots\ldots\ 55$$

The value of L'', L_c and R_c were 3.15×10^{-9} henry, 6.1×10^{-9} henry and 0.026 ohms respectively. L' was found for each cell, the lead lengths being unchanged after calibration, from the formula:

$$1/C^* = 1/C_{XP} - \omega^2 L' \qquad \ldots\ldots\ 56$$

where C^* was the apparent value for C_{XP} when uncorrected for L'. Further details of this and other lead corrections will be given after a discussion on the circuit for the Schering bridge.

(c) Schering Bridge

In using the Schering bridge, as with the twin-T, the capacitance readings were designated C', C" after drum scale corrections had been applied.

Readings of dissipation factor instead of conductance were made. The accumulated values of dial and switch settings were taken; these were D', D" with the unknown disconnected and connected, respectively. They were adjusted for differences between the working frequency f and the frequency f' of setting of a range selector switch. Thus the dissipation factor readings corresponding to D', D" were D' (f/f'), D" (f/f') respectively.

The following formulae were applied:

(a) when the uncorrected dissipation factor, $\Delta D = (D''-D')(f/f')$, was less than 0.1,

$$C_{XP} = \Delta C \qquad \ldots\ \underline{57}$$

$$D_X = (C'/\Delta C)\,\Delta D, \qquad \ldots\ \underline{58}$$

where $\Delta C = (C'-C'')$.

(b) when ΔD was greater than 0.1 but $(D''-D')$ was less than 0.1,

$$C_{XP} = \Delta C \cdot \frac{1-(\Delta D)^2(C/\Delta C)}{1+(\Delta D)^2} \qquad \ldots\ \underline{59}$$

$$D_X = \frac{C'}{\Delta C} \cdot \frac{1-(\Delta D)^2(C/\Delta C)}{1+(\Delta D)^2} \qquad \ldots\ \underline{60}$$

(c) when D_X is about unity or higher,

$$C_{XP} = \Delta C \cdot \frac{1+a(D''+D_o)(f/f')}{1+(D''+D_o)^2(f/f')^2} \qquad \ldots\ \underline{61}$$

$$D_X = \frac{C'}{\Delta C} \cdot \frac{\Delta D}{1+\bar{a}(D''+D_o)(f/f')} \qquad \ldots\ldots \underline{62}$$

where $\bar{a} = (D''+D_o)(f/f') - C'(\Delta D/\Delta C)$ and where D_o is the dissipation factor corresponding to the fixed capacitance across each ratio arm of the bridge. For the bridge used, D_o was equal to 0.034.

(d) Cell Calibration and Lead Corrections

The lead corrections for the Schering bridge were identical to those for the twin-T except for the inductance correction already mentioned.

Cells and leads were calibrated at working frequencies using benzene, a material having no dispersion of the dielectric constant in the range of the twin-T. The value of C_{XP} was therefore constant. Plots of $1/C^*$ against ω^2 yielded straight lines. It followed from this and equation 56 that the slope of such a line was $-L'$ and its intercept as ω approached zero was $1/C_{XP}$.

Values C_{XP}, D_X so derived by the twin-T and Schering bridges were identical if the leads to the bridge terminals were the same for both calibration runs.

Calibrations were performed whenever possible by measuring C_{XP} and D_X (a) with the dielectric cell empty and (b) with the dielectric cell filled with benzene. The values were respectively, for case (a) C_e, D_e and for case (b) C_K, D_K.

According to Balsbaugh (57) the geometric capacitance C_a of the cell was in parallel with the capacitance C_d of leads and supporting structures of the cell. Then

$$C_e = C_a + C_d \qquad \ldots\ldots \underline{63}$$

$$C_K = \epsilon_K C_a + C_d \qquad \ldots\ldots \underline{64}$$

where $C_a = \dfrac{C_K - C_e}{\epsilon_K - 1}$ $\qquad \ldots\ldots \underline{65}$

where ϵ_K was the dielectric constant of pure benzene at 25°C. Geometric capacitances were thus found from $_K$ and the experimental values C_K, C_e. Then C_d was also found by equation $\underline{63}$.

The dissipation factors D_d of leads and cell supports were significantly large, but the dissipation factor D_a across dielectric plates in vacuum or, approximately so in air, was of zero magnitude. The dissipation factor of the parallel combination was given to be

$$D_e C_e = D_a C_a + D_d C_d \qquad \ldots\ldots \underline{66}$$

Whence $D_d = D_e C_e / C_d$ $\qquad \ldots\ldots \underline{67}$

from which D_d was evaluated for the cell.

When the cell was filled with material of dielectric constant ϵ'_m and dielectric loss ϵ''_m, it is recalled that their capacitance and dissipation factor were called C_m and D_m. Then since C_m, D_d were in parallel

$$C_m = C_{XP} - C_d \qquad \ldots\ldots \underline{68}$$

Also $D_X C_{XP} = D_m C_m + D_d C_d$ $\qquad \ldots\ldots \underline{69}$

and $$D_m = \frac{D_X C_{XP} + D_d C_d}{C_m}$$

$$= D_X + (C_d/C_m)(D_X - D_d) \qquad \ldots\ldots \underline{70}$$

Thus values for C_m and D_m were obtained, from which the dielectric constant and loss were calculated using the basic equations (11):

$$\epsilon'_m = C_m / C_a \qquad \ldots\ldots \underline{71}$$

$$\epsilon''_m = \epsilon'_m D_m \qquad \ldots\ldots \underline{72}$$

4. Dielectric Cells

(a) Balsbaugh Liquid Dielectric Cell

All dielectric measurements on liquids were made using a special Balsbaugh cell (Fig. 9). A cylindrical type, it was so designed that it could be immersed in a thermostat.

The special feature was its small geometric capacitance of 7 uuf. This was desirable when the cell was filled with solutions of cellulose nitrate in acetone; their conductivity was troublesome. By using this cell, even when filled with such a material, both conductance and capacitance were kept low enough that sensitive bridge balances were obtained.

Concentric nickel cylinders A, B were the dielectric plates. Each was affixed to a glass press C by its lead wire and two other support wires. The press was joined to the end of a glass tube D which was fitted, part way along its length at E, with a male ground glass joint. This constituted a dielectric plate assembly.

It was fitted into a tube F containing the liquid to be measured. The fit was effected using a female ground glass joint at E. The cell was always filled to the same arbitrary level G above the cylinders. This was done to assure reproducibility of cell constants (57). About 25 cc. of liquid were required.

The dielectric plate assembly supported metal leads which went from its cylinders to the exterior of the cell. Tungsten leads were used through glass. They were spot welded to wire leads except for external connections. These were made by means of mercury pools H in cork cups. The latter simply were glued to the outside of the glass. Short and straight pieces were led from these pools to bridge terminals. Electrical leakage with this cell was kept low. A factor which helped was the use of low-electrical loss glass in the press C.

(b) Seidman Paper Cell

A dielectric cell was previously (44) designed in this laboratory for receiving a paper specimen and in which the amount of vapour sorbed on the cellulose sample could be systematically varied. It was a Sayce and Briscoe type of cell (58), the inner member consisting of a glass tube with a cylindrical portion of its exterior platinized. Around this electrode enough of the specimen was wrapped to fit snugly into the outside tube whose interior was correspondingly platinized. Appropriate tubing, ground glass joints and metal through glass leads permitted vacuum or a constantly humid atmosphere to be applied to the dielectric specimen. Because of the small coefficient of thermal expansion of glass, cells of this type have no appreciable thermal coefficient of capacity, even for the temperature range covered in this work.

The cell withstood temperatures from that of liquid air to over 260°F. A portion of the platinum surfacing did have to be repaired but this was easily done by the method recommended by Coffin (59).

(c) Film Dielectric Cell

A dielectric cell for thin solid specimens was designed. It was desired (1) that vapour content could be systematically varied as with the Seidman cell, (2) that temperature control could be effected by immersion in a bath and (3) that this could be done with no electrical leads passing through the bath liquid.

The first requirement promised to be a formidable challenge. It was met, however, by a fortunate discovery: metallized surfaces can be prepared on celluloid sheets which (a) are permeable to vapours of acetone and water, and (b) are sufficiently conductive to act as bona fide dielectric plates. Methods for preparing a condenser with such metallized surfaces and for affixing wire leads to them will be given after a general description of the cell.

The cell is illustrated in Fig. 10. The condenser A is suspended by its lead wires to lead seals C in a glass structure G. A dielectric cell assembly was thus formed much in the manner of the Balsbaugh cell previously described. With the use of ground glass joints this assembly also fitted into a glass tube E.

A smaller tube F made a passageway via a vacuum stopcock to a conditioning system.

Electrical leads connected the condenser A to cell terminals D. The condenser was joined to platinum conductors B at the lead-in-glass seal C and thence to mercury-in-glass pools D. The pools acted as vacuum seals and electrical terminals.

To minimize electrical leakage the platinum wires B were kept in an isolated and evacuated chamber as illustrated.

Metallized surfaces were prepared on specimens by evaporating metal in vacuum and condensing it onto unshielded portions of the specimens.

A metallized sample A and its shields B are shown in Fig. 11. The shields had circular holes and a notch cut in them as illustrated. A sample was sandwiched between the shields and clamped. Then the assembly was placed in a bell jar F (Fig. 12) and metallized first on one side, then on the other. The shields were arranged so that the circular parts were lined up in the sandwich and so that the notches were facing in opposite directions. Thus in Fig. 11 it is seen that there are metallized surfaces C on the top and D on the bottom of the sample and that they form what can serve as circular dielectric plates. The notches in the shields permitted the metallized surfaces to be extended into leads. The leads were taken in opposite directions from the plates to positions where they were later clamped to wire leads. The clamping system will be considered in detail after an explanation of the metallizing apparatus.

The process of metallizing was carried out in a vacuum bell jar (Fig. 12). The sample A was clamped B between the shields forming a sandwich. This was set on the top of a wire cage D. The metallizing metal E was placed on a ribbon filament G which was clamped at H to vacuum sealed electrodes J.

After the sample was placed and some metallizing metal distributed along the ribbon filament, then the jar was evacuated to about 10^{-3} mm. Hg. Current was admitted to the filament until the metal wetted it. At higher currents the metal evaporated and condensed uniformly on the bottom side of the sample, forming a metal coating. No serious oxidation of the coating occurred at sufficiently low pressures in the jar.

Samples thus were gilded or silvered. The filament G which supported both metals was a three-quarters inch length of tungsten ribbon, one-eighth inch wide and 0.01 inch thick. It was found, however, that molten silver would not wet the tungsten. The ribbon was therefore indented in four or five places with a bluntly pointed tool. Thus pockets were formed to contain the silver and the method worked well.

The layers of metal were made to a thickness corresponding to about 100-200 mg./sq.cm. Experience showed that when the electrical resistance across a 1-1/4 inch diameter disc was 2-15 ohms it behaved satisfactorily.

The metal coatings were easily abraded and making electrical contact to them was difficult. If the dielectric plate portion of the coating was even slightly abraded the dielectric values for the sample were affected. However, the lead portion (Fig. 11) of this coating could be somewhat abraded and still exhibit high conductivity. Only extensive damage to it would affect dielectric measurements on the sample.

The upper and lower leads of the sample were thus able to withstand the clamps A of Fig. 13 so that electrical contact was made from them to wire leads G. The latter was silver-soldered to the body of the clamp. The metallized surfaces of the sample B are shown by cross-hatches. Their lead portions were protected from abrasion by cushions C of electrically conducting acetylene black. The opposite non-conducting faces of the sample were insulated from the clamp with small pieces D of teflon. Clamping was effected by tightening the screw E on the plunger F. The plunger was used to dampen torque from the screw to the sample. Parts A, E, F and G were all made of brass or copper for good electrical conductivity.

The whole assembly shown in Fig. 13 is the condenser A of Fig. 10; it was connected to the leads from C (Fig. 10) with soft solder. With this in place, the film dielectric cell was complete.

Optimum electrical contact was made by this method of condensing electrodes directly on the specimen. When it is recalled that the electrodes were permeable to vapours it may seem unreasonable that there was complete electrical coverage of the metallized sample surface. It was evident that gaps or holes were scattered throughout the condensed metal layer and that they acted as passageways for the vapours. Yet these were so small that, insofar as dielectric measurements are concerned, there was complete electrical coverage of the whole metallized surface. This will be shown, since celluloid specimens were used to work out the method, in a section "Results and Discussions, Part 2a." That these electrodes are dielectrically satisfactory would be expected by comparison with Sayce-Briscoe cells. The metal coatings on their glass surfaces are not much different than these coatings and they have been generally accepted as good cells.

(d) Modification of Film Dielectric Cell for Paper

A condenser suitable to receive paper samples (Fig.14) was substituted for the one (A in Fig. 10; cf. Fig. 13) in the film dielectric cell. Sheets were prepared of cellulose nitrate which had low mechanical strength. These could not be loaded into the Seidman cell without damage both to cell and specimen, but they were loaded into this cell conveniently and without damage.

The condenser was a stacked sandwich type which had five discs of paper A in parallel (Fig. 14). This required six circular dielectric plates B in the sandwich. Alternate plates were connected together with flexible wiring; one set of three was connected to the ground terminal of the cell and the other set was connected to the high tension terminal.

The sandwich was clamped with a bolt C passing centrally through it and a nut D. Teflon washers E, insulated the nut, bolt and metal washers F from the dielectric plates. The outside plates were stiff, being 3/16" thick and of brass, and did not distort structurally on clamping. Intermediate plates were of 0.015 inches brass shim. As they were connected with flexible wiring, loading was accomplished by laying a paper on a plate and folding the next plate over and on top of it. Finally the assembly was clamped as shown.

The geometric capacitance of the cell was found after determining the average plate separation and five times the average plate area. These values were used in the standard formula (11) for geometric capacitance of a parallel plate condenser in place of the plate separation and plate area respectively.

5. Materials

(a) Acetone

Chemically pure acetone from Anachemia Chemicals was further purified by a method similar to that of Reynaulds and Kraus (66). After drying with calcium chloride, it was refluxed for two hours over activated alumina and then distilled. The middle third of the distillate was heated with activated alumina in the same way and the middle third of that distillate accepted. At 25°C the specific electrical conductivity was thus reduced to 5×10^{-8} mho/cm. at 1000 cps; the dielectric constant at 100 Kc was 20.3 ± 0.1; and the viscosity was 0.306 ± 0.001 cps. The corresponding values given by Reynaulds and Kraus were 2×10^{-9} mho/cm., 20.47 ± .05 and 0.3040 ± 0.0008 cps.; they were the criteria of purity for acetone.

(b) Benzene

Chemically pure benzene from Anachemia Chemicals was dried for ten days over sodium wire, then distilled. The middle third was collected and used for cell calibrations. The dielectric constant was taken to be 2.274 at 25°C (60).

(c) Cellulose Nitrate

The following samples of cellulose nitrate were investigated:

No. 1. Short fibred cellulose nitrate of 12.2% nitrogen content-a purified grade "D" material, lot 5527-Y of the Hercules Powder Company, Parlin, N.J. It was purified by treating in a Waring Blendor with distilled water at room temperature, then precipitating from solution in purified acetone into excess distilled water at room temperature. It was given a final washing with distilled water and dried in a vacuum desiccator. The material had a degree of polymerization of 148 according to a method used by Jorgensen (61).

No. 2. Cellulose nitrate similar to sample No. 1 except that in its purification the distilled water was at 80°C instead of room temperature. Viscosities were determined of solutions in acetone of 0.05, 0.025, 0.0125 and 0.0062% weight by volume. The ratios of specific viscosities over concentration was plotted against concentration and extrapolated to zero concentration to determine a value for intrinsic viscosity. This value was multiplied by Jorgensen's factor 100 to give the degree of polymerization. The average degree of polymerization from two experiments was 148 with a mean deviation of 7.

No. 3. Cellulose nitrate similar to sample 1 except for the method of purification which was different. It was treated in a high speed Waring blendor and washed with distilled water at 85°C; the treatment was repeated five times and the material dried in a vacuum desiccator.

No. 4. Short fibred cellulose nitrate of 12.6% nitrogen content. It was purified in the same manner as sample No. 3 from grade "D" material, lot 5380 Y of the Hercules Powder Company, Parlin, N.J.

No. 5. Long fibred cellulose nitrate of 11.66% nitrogen content. The nitrate was prepared from dewaxed staple cotton fibre from the Hercules Powder Company, Parlin, N.J. and was thus considered to have a degree of polymerization of about 3000 (62). It was nitrated with a standard Alexander and Mitchell (63) nitrating mixture at -35°C for about twenty minutes. The nitrate was washed with ice-water and thrice refluxed for five minutes in 50% methanol-water. It was subsequently washed with water, dried for two hours in a vacuum oven at 60°C and stored in a vacuum desiccator. The reported nitrogen analysis was for nitrate nitrogen and was made by a modified micro-Kjeldahl method (92). The same analytic procedure was used for sample No. 6.

No. 6. Long fibred cellulose nitrate of 14.13% nitrogen content. Some dewaxed cotton as used for sample No. 4 was nitrated for 5 hours at 0°C. The nitrating mixture contained 44,31 and 25% by weight of nitric acid, acetic acid and acetic anhydride. It was then stabilized by the same treatment given sample No. 5 but was kept wet under ice-water. It could thus be made into handsheets as a section on "Preparation of Samples" will show.

(d) Celluloid

Celluloid sheet 0.005 inches thick from Anthony Foster and Sons, Montreal, P.Q., contained 40% camphor, 60% nitrocellulose of 11.2% nitrogen and a minor amount of retained alcohol. The degree of polymerization was not specified but for this kind of material it is generally 500-600 (64).

(e) Cellulose Paper

Cellulose paper was from the same source as that used earlier in this laboratory (44), namely, Schleicher and Schuell, No. 589 Red Ribbon quantitative filter paper of an extra dense quality, and with a specified ash content of 0.007%. Seidman (41) reported that:

(i) it analyzed for 98.4% alpha-cellulose and 1.1% pentosan;

(ii) its cupriethylene diamine viscosity was 15.7 centipoises;

(iii) microscopic examination indicated it to be a rag furnish containing 75% bast fibre and 25% cotton.

6. Preparation of Samples

(a) Cellulose Nitrate-Acetone Solutions

Three solutions were investigated. They consisted of:
(1) Sample No. 1 of cellulose nitrate in purified acetone at a concentration of 3.09 grams of the nitrate per 100 cc. of solution. The nitrate had been dried to constant weight in a vacuum desiccator and then was made up into solution in a volumetric flask. The operations with dry nitrocellulose in air were performed quickly to minimize sorption of water vapour.
(2) Sample No. 2 of cellulose nitrate in purified acetone at a concentration of 3.00 grams of the nitrate per 100 cc. of solution. It was prepared in the same manner as solution No. 1.
(3) Sample No. 2 of cellulose nitrate in purified acetone at a concentration of 17 grams of the nitrate per 100 cc. of solution. It was prepared in the sample tube F (Fig. 9) of the Balsbaugh cell. The nitrate dissolved slowly so the system was stoppered from the atmosphere by assembling the whole of the cell. Air bubbles worked out of the system and after a few days it appeared to become homogeneous. The solution was very thick and tended to set into a gel.

(b) Low-Camphor Celluloids

Celluloid samples having camphor contents of 35.3, 29.8 and 27.2% were prepared from the commercial material having 40%

camphor. The camphor was steam distilled from sheet samples which were kept from curling badly by clamping in a folded-wire cage. The loss of camphor was determined from dry weights before and after the extraction to 0.1%.

(c) Films

Pure nitrocellulose films were cast on the surface of a piece of plate glass one half inch thick. A circular portion A (Fig. 15) on the glass surface, three inches in diameter, was surrounded by a trench B one quarter inch wide and deep. Mercury in this trench made a seal between it and a stainless steel cover C whose walls rose one and a half inches vertically. An opening D in the top of this cover allowed the admission of nitrocellulose solution. The opening was then partly closed and other ventilation holes E were made in the cover to control evaporation.

The evaporation had to be kept slow enough that the film would not wrinkle, the optimum drying time being about two days. Moist air was eliminated by maintaining the solution in the solvent atmosphere and on very humid days by enveloping the drying vessel in a partially desiccated atmosphere. Excess humidity caused a white haze to appear which rendered the otherwise transparent and slightly yellowish films an opaque white.

Such a haze was artificially induced into film by the addition of 4% water to the acetone used in film preparation. A thin film was made with 0.08 gm. of 12.2% nitrogen cellulose nitrate, 25 cc. acetone and 1 cc. water. The haze was very prominent and the film had frayed edges that at first sight appeared fibrous. Under closer examination with a microscope, spherical cavities were seen all through the material. Otherwise it appeared homogeneous with no indications of a truly fibrous nature. With a polarising microscope the material appeared to be as isotropic as a clear control film prepared as above but without the water. It is likely that this haze is due to a phase separation of water droplets from a nitrocellulose-acetone solution or from a gel during drying of the solution into a film. After the film took form, the water droplets evaporated leaving a multitude of microscopic voids. The amount of light scattered by such a material was ample to make it opaque. The haze in this sample was accented by using a large proportion of water. Haze, as it normally occurs with less water, is likely due to the presence of smaller, submicroscopic voids.

Stress hazing would also occur if the plates were not adjusted level for the drying process. This appeared as milky streaks and sheets in the film. Evidently it was somehow formed by uneven forces which developed in the film if there were marked differences in its thickness from place to place. Accordingly the plate glass base (Fig. 15) was fitted with levelling screws through diamond-drilled holes.

(d) Papers of Cellulose Nitrate

It was interesting to find that hand sheets of cellulose nitrate could be formed from water or methanol in water having sufficient strength for handling. The cellulose nitrates having nitrogen contents of 12.2 and 12.6% were of very short fibres and were probably made from cotton linters. The sheets made from them were of excellent formation but of too low a mechanical strength to be at all practicable in the Seidman cell. They were satisfactory for the film dielectric cell as modified for paper.

However, handsheets from the 11.66% nitrogen material were strong enough, by careful handling, for insertion in the former cell. The fibres were cut into 2-4 mm. lengths so that flocs of them could be broken up. The cellulose nitrate at a consistency of about one gm. per 100 cc. in distilled water was beaten in a Waring blendor until any noticeable flocs had disintegrated. The slurry was then made into 2-3 gm. sheets of nine inches diameter with distilled water in a British hand sheet machine. They were pressed between blotting paper in a screw-press and dried at room temperature.

The 14.13% nitrogen nitrocellulose was treated in the same manner as the last material except for a couple of variations. The fibres were never allowed to dry after nitration until the handsheet had been formed, and it was necessary to use 30% purified methanol in distilled water during the beating process. After the fibres were once dispersed, this methanol was twice washed and beaten out of the fibre with distilled water before the sheet was formed. If the fibres had been cut prior to nitration the use of methanol at this stage may not have been necessary. This sheet, because of its low affinity for water, was almost as weak as those made with short fibres; however, it could readily be handled for preparation and insertion in the film cell as modified for paper dielectrics.

7. Procedures

(a) General

The following variables were controllable for dielectric experiments: frequency, temperature, non-volatile composition, physical structure of sample, dilution with solvent and the amount of vapour sorbed. The dependent variables were the dielectric constant and loss.

Once a sample was inserted into a dielectric cell, frequencies and temperatures were altered at will, but neither its non-volatile composition nor its basic physical structure was changed; nor was the solvent content of a solution changed. However, the amount of vapour sorbed on solid specimens could be varied in any of the three cells which have been described. Indeed, holding this amount constant while varying temperature was a special problem for the systems celluloid-acetone and cellulose nitrate-acetone.

The electrical equipment for controlling frequency and with which dielectric constants and losses were determined has been discussed previously. Sections follow which describe the temperature regulating and the vapour-conditioning systems.

(b) Constant Temperature Regulation

Dielectric cells were all of the immersion type. They were designed in this manner so that their temperatures could be controlled in thermostatted liquid baths. Baths were held at temperatures from that of liquid air to over 260°C. Admittedly the bath at liquid air temperature was liquid air, but baths of organic liquids were held at temperatures down to -155°C.

Four systems were employed:

(i) At temperature above 70°C voltage was manually regulated across an immersion heater to give a constant temperature.

(ii) From 70°C to room temperature conventional thermostatting was employed but with no coolant.

(iii) From room temperature to -65°C, control was helped with a non-conventional toluene thermoregulator and a cooling device which used dry ice.

(iv) Below -65°C manual cooling with liquid air was effected.

Bath liquids were contained in a four litre modified Thermos flask.* A variable speed electric stirrer kept temperatures uniform to less than 0.05°C throughout the bath. Variable voltages were fed to a 125 watt capacity immersion heater. Cooling was supplied with a cold finger dipping into the bath. Bakelite lids were constructed for the bath. They minimized

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* Fisher Scientific Company, Ltd., Cat. #10-197

evaporation of bath liquids and supported the dielectric cells. Holes, of course, were provided for the thermostatic equipment.

The following bath liquids were used with the foregoing thermostatting systems: (i), (ii) mineral oil, (iii) toluene, and (iv) isopentane.

System (i) requires no further explanation; extra precautions in case of fire or implosion were taken at the high temperatures. For system (ii) it need only be mentioned that a mercury thermoregulator was employed. System (iii) on the other hand, required special apparatuses as already mentioned.

Fig. 16 illustrates the thermoregulator. It was constructed of a bulb A, 1-2 mm. capillary glass tubing, a stopcock B, reservoirs C and D, and electrical leads E and F. Toluene filled the bulb A and capillary tubing up to the mark G. The rest of the capillary to H was filled with mercury. Toluene in A expanded and contracted thus making and breaking electrical contact at H.

The bulb of the regulator and capillary tubing up to J were immersed. It was necessary to keep the mercury at room temperature instead of in the bath where it would have frozen at the low temperatures. Capillary tubing was used to minimize drifting of control temperatures as a result of specific volume changes in the capillary. Such would be caused by fluctuations in room temperature.

The reservoirs and the stopcock were used to facilitate (1) filling of the regulator and (2) readjustment to a different control temperature.

The bulb A as illustrated, is disproportionately small. As used, the regulator held temperatures to less than 0.1°C. To give an example of its ease of manipulation this degree of control was reached in 5-10 minutes after a 10°C change in temperature.

The other apparatus (Fig. 17) is a combination of a cooling finger A and an insulated reservoir for dry ice. It was constructed of pyrex glass. The cooling finger was immersed partially or completely in the bath to afford different rates of cooling. The reservoir contained crushed ice and a little acetone C. The acetone was ag [illegible] of carbon dioxide gas which was released in the cooling finger. The agitated acetone in its turn kept washing the dry ice down to the bottom of the reservoir. Thus cold temperatures persisted in the cooling finger.

Insulation was provided with an evacuated jacket D formed with a double wall. Its interior surfaces were silvered to minimize radiant heating of the device's contents. An extension E of the cooling finger was likewise insulated by an extension of the same jacket. This extension was built into the apparatus to save space around the top of the bath; there was not enough room in this region for the bulky part of the reservoir.

As illustrated, sections A and E are disproportionately short. For example, A was 16 mm. in diameter and 12 cm. in length. Total capacity of the device was one litre. Under normal conditions it had to be refilled every three hours. It supplied sufficient cooling for thermostatted control of the bath at -65°C. By analogy to dewar-flasks and its function as a cooling finger the device was called a dewar-finger.

With proper annealing facilities it would be possible to make dewar-fingers for use with liquid air. Isopentane in place of toluene in the thermoregulator (Fig. 16) would then permit this method to be used for thermostatting baths to about -155°C.

In practice, however, it was necessary in the case of system (iv) to manually control temperatures below -65°C. This was effected by pouring liquid air into a pyrex glass tube which was inside another pyrex glass tube. The latter tube was 16 mm. diameter and was sitting in the bath as a cooling finger. Cooling in this manner was slow enough that liquid air persisted in the inner tube for 2-4 minutes. Temperature was thus held within 0.2°C when checked every five minutes. This was the case to temperatures of about -110°C. At -155°C temperatures were held to ½°C.

Toluene, alcohol and mercury thermometers were used which were calibrated with respect to dry ice point, ice point, boiling point and/or a mercury thermometer which was standardized at 25.00°C at the National Research Council, Ottawa.

(c) Vapour-Conditioning System

(i) General

The The vapour-conditioning system is schematically shown in Fig. 18. The vapour source V_1 was maintained in a bath

W_1 and was interconnected to: C_1, a dielectric cell in the thermostatted bath W_2 just discussed which was at the dielectric bridges; C_2, a dielectric cell in a bath W_3 kept at 25.00 ± .03°C; B_1, a torsion balance in W_3; B_2, a quartz spiral balance in a bath W_4; M, a mercury manometer; S, a spiral mercury gauge; and R, a reservoir for vapours.

There was a second vapour source V_2, a line to vacuum, and a line from atmosphere via a drying tube A which was filled with flakes of caustic soda.

As soon as a solid sample was placed in a dielectric cell and the cell assembled, it was affixed to the system at C_2 and evacuated at 25°C until dry. Long electrical leads were brought to the cell from the Schering bridge. The criterion for dryness was that there was no indicated change in dielectric properties in a 24 hour interval. Then, while still evacuated, pure vapours were allowed into the cell from V_1 or V_2. The vapours were held at a constant pressure as indicated with the manometer. When dielectric equilibrium had been reached the cell was stoppered and removed to bath W_2 for proper dielectric measurements to be taken on it.

To determine the amount of vapour sorbed on such a specimen, another sample of the same material was taken. It was weighed in B_1 or B_2 then evacuated until there was no detectable change of weight in two consecutive days. Then vapours were sorbed at the same pressure as for the dielectric specimen until equilibrium was reached. Thus the vapour content of the gravimetric specimen was determined and was assumed to be the same as for the dielectric one.

An oil pump was capable of reducing pressures to 0.0003 mm. Hg as measured by the spiral gauge S. The pressure of a system would be down to this value when samples had been taken to dryness.

The interconnected system (Fig. 18) thus permitted simultaneous conditioning of dielectric and gravimetric specimens. Either of the balances B_1, B_2 could be connected to either of the dielectric cells C_1, C_2 then either set evacuated or exposed to vapours from V_1 or V_2.

Some sorption processes required weeks or months before equilibrium was reached. In these cases the reservoir R was used continuously as a source of vapour and its pressure was adjusted slightly as required.

The system described by Seidman (41) for maintaining constant vapour pressure was not wholly satisfactory. On eliminating unnecessary constrictions and by using magnetic stirring, fluctuations in vapour pressure found with this method were eliminated. To maintain constant pressures of water vapour, saturated solutions of inorganic salts were used. These often evaporated down into thick slurries in which the stirrer tended to stick.

A much more exact and dependable control is that of thermostatting the pure deaerated liquid. Conventional and low temperature thermostatting as described in the last section were used. Pure condensed vapour was added to V_1 and the system evacuated. This was continued for about five minutes until all bubbling, which was obviously due to deaeration, had subsided. On isolating this system from the pump the pressure reached in the system was the vapour pressure of the vapour at the temperature of the bath W_1. The temperature was easily adjusted to give fine control of the pressure.

Two quartz spirals and two torsion balances were used during these investigations. The full length of the quartz spirals were measured between marked points at the extremities of each. Respectively they obeyed Hooke's Law up to loads of 100 and 70 mgm., and had calibrations of 2.33 mgm./mm. and 0.454 mgm./mm. Using a cathetometer accurate to 0.05 mm. the sensitivities were 110 and 23 micrograms respectively.

Torsion balances are more sensitive and carry much heavier loads than quartz spirals. They are especially valuable in determining small differences in weight.

(ii) Maintenance of constant Composition for High Sorbate Concentrations

It was previously mentioned that the problem arose in this investigation of maintaining a constant sorbate composition in the dielectric specimen C_1 while its temperature was changed. This was no problem (41) with the Seidman cell for the free space in the cell was so small relative to the amount of water present in a sample. However, with the film dielectric cell, a small sample is used and a large free space exists in the cell.

The bath W_4 was equipped with thermostatting as versatile as that of bath W_2. the quartz spiral at B_2 was replaced with a torsion balance and the line opened from the balance to C_1, M, and V_1. Temperatures of W_2 and W_4 were changed concurrently. Minute changes in weight of the gravimetric specimen were detected and the vapour pressure was rapidly adjusted to compensate for it. At the new temperature of W_2 and W_4 the new equilibrium vapour pressure, wherewith there was no weight change of the gravimetric sample, was maintained.

This operation was repeated for every temperature change during the dielectric investigation of the sample. Thus, to speed experimentation, frequencies were spanned at constant temperature instead of the previous practice in this laboratory. That was to vary temperatures at constant frequency.

(iii) Torsion Balance

The torsion balance, Figs. 19 and 20, was contained in a chamber with a vapour system outlet at one end and a flatly ground face at the other. The torsion balance was inserted via this open end by an optically flat plate glass A which was sealed to the balance chamber with Apiezon "Q" sealing grease B. Overhead ground glass plugs K permitted the counterpoise C and sample D to be replaced. Small quantities of thallium 204 were placed on aluminum plates under collodion and inserted at E. The strong β-radiation broke down static charges on the specimens but was perfectly shielded by the glass walls from the experimenter. No appreciable γ-emission was involved. Finely drawn extended glass hooks F supported the sample and counterpoise on the balance.

The balance itself was constructed from pyrex glass and 0.002" diameter tungsten wire. The torsion wire was wrapped around and strung between the middle uprights F of the frame. It was sealed into place with horny silver chloride and taughtened with spring wire between the uprights while the latter were being heated at their bases. The balance beam G was constructed of a 2 mm. diameter glass rod with forked ends, across which short pieces of tungsten wire were strung. Tungsten hooks hung down from their midpoints, being also sealed with silver chloride. Similarly the balance beam was attached symmetrically to the torsion wire. At one end a scale was constructed using tungsten pointers on the balance beam and on the curved arm H of the frame. The curvature keeps the beam pointer J in focus with the reference pointers when viewed with a travelling microscope through the plate A.

The counterpoise was adjusted within 5 to 10% of the density of the gravimetric specimen to avoid the necessity of buoyancy corrections; and the weight of the specimen was adjusted for proper balance. The sensitivity used was 6 micrograms and could easily have been increased by bending the balance beam upward at its extremities. Less interference vibration was found at the same sensitivity using 0.004 inch diameter and 55 mm. long torsion wire and a 14 cm. long beam by resorting to this technique.

The torsion balance was held rigidly in place by sealing it to the chamber wall at a couple of spots with Pyseal. Aluminum balance pans and gold and silver coatings on film specimens were found to pick up considerable quantities of mercury so coatings were avoided on gravimetric specimens. There was no indication of such trouble with tungsten. The counterpoise was found to be easily made by using 2 mm. pyrex tubing with a tungsten hook. After the ends were sealed surface forces were strong enough to partly collapse the air pocket against internal pressure and it could thus be adjusted to the required density. A calibration curve is shown in figure 21 for the balance with the 0.002 inch diameter torsion wire when loaded with 106.3 mgm. at the arbitrarily selected zero reference pointer. The weight corresponding to this zero reference should change only with counterpoise weight. Calibration was made by adding weights to the sample end of the balance beam rather than the counterpoise end in case it was not suspended perfectly symmetrically. It should be noted that the sensitivity changes quite markedly with the load. The balance is much more rugged and easier to build than a torsion balance of silica glass (65).

8. Specific Procedures

(a) Introduction

Minor variations of the General Procedures will be mentioned in Results and Discussions. This section will describe more extensive variations from the General Procedures which were necessitated by the varying properties of the different materials studied. The following specific procedures will be discussed:

Cellulose nitrate-acetone solutions: direct variation of bath temperatures
Celluloid: performance of the film dielectric cell
Cellulose nitrate films: concentration of acetone in films
Cellulose papers: drying and heating of samples

(b) Cellulose Nitrate - Acetone Solutions

Solutions No. 1 and No. 2 (see preparation of samples) were poured into the Balsbaugh liquid dielectric cell and the cell was assembled. The third solution was prepared in the cell. In each case the cell was placed in a toluene bath and connected to a bridge.

The bath which was used for solutions was not thermostatted according to the method given in Part 7 of this section. It was cooled by having dry ice added directly to it. It was electrically heated with a variable voltage supply to an immersion heater. Temperatures were raised or lowered to successive values in about 2½ minutes. A longer time was allowed at the new temperature before measurements were made.

When both bridges were used the cell and bath were moved from one bridge to the other. The same short leads were used to connect the cell with each bridge so that lead corrections would be the same for both bridges.

The frequency and temperature ranges of runs for the individual solutions are given in Results and Discussions.

(c) Celluloid - Performance of the Film Dielectric Cell

Preliminary measurements on celluloid were made with the Seidman cell as described in Results and Discussions. Refined measurements were determined using the film dielectric cell. It was necessary to make this change before studying hard brittle films because the electrodes of the Seidman cell were easily scratched even by a highly plasticized celluloid. As was mentioned earlier (Experimental, Part 4) the design and techniques for the film cell were developed using celluloid specimens. The following characteristics of the cell will be discussed:

(i) Performance of the metal coatings as dielectric plates or electrodes

(ii) Permeability of the metal coatings to water and acetone vapours

(iii) Amalgamation of the metal coatings in the conditioning system

(iv) Thermal equilibration of dielectric specimens in the cell

(v) Celluloid with 4.1% sorbed acetone.

(i) Performance of the metal coatings as electrodes

It will be recalled that the electrodes in this cell were metallic coatings on each side of the sample which were thick enough to be electrically conductive, but also thin enough to be permeable to vapours of acetone and water (Experimental, Part 4). Electrical contact between the condensed metal coatings and the samples was, of course, optimum.

It is reasonable to doubt that the true capacitance of the sample could have been determined with these permeable electrodes, since they must have been riddled with openings which acted as vapour passages. However, the considerations listed below convinced the author that the openings in the electrodes did not cause a significant variation in the field within the dielectric.

(1) The capacitance of similar specimens was the same when using metallic film electrodes or provisional sheet steel electrodes

(2) Similar specimens of celluloid were prepared with film electrodes. They were placed in a film dielectric cell

and evacuated to eliminate sorbed water. Their dielectric constants were then determined and found to be constant to a good precision as shown in Table II.

(ii) Permeability of the metal coatings to water and acetone Vapours

The metal coatings were permeable to vapours although they inhibited the rates of sorption and desorption. The samples cited in Table II had been stored at atmospheric conditions and then they were evacuated to dryness in the dielectric cell until they had reached the conditions for which their dielectric constants were reported (Table II). Celluloid between the metal coatings had dried during evacuation; this was evident since dielectric constants of the samples had dropped by about 0.95 units. Steady values of C were obtained in a couple of days when the pressure of the system had finally dropped to its lower limit of 3×10^{-4} mm. Hg. The sample was then considered to be dry for the ordinary purposes of this investigation.

Sample S-3 was evacuated only to a pressure of 5×10^{-3} mm. Hg. Drying was not as complete for it as for the other samples of Table II. Evidence for this was the higher value of the dielectric constant.

The rate of desorption for the coated samples was qualitatively compared to that of uncoated samples. The latter were placed on a torsion balance and the system was evacuated. They arrived at constant weight in one-half to one-quarter of the time required for coated samples to become dry.

(iii) Amalgamation of the metal coatings in the conditioning System

Gold and silver were used in metallizing the surfaces of celluloid. At pressures approaching 3×10^{-4} mm. Hg, the metal surfaces had a tendency to sorb mercury vapours and to be converted into microscopic droplets of amalgam. This amalgamation would have ruined the samples for dielectric measurement. Two principal sources of mercury vapours were the mercury manometer M and the spiral pressure gauge S (Fig. 18). The destructive amalgamation was prevented by separating the manometer and the gauge from the rest of the system except during periodic pressure measurements. In order to circumvent this difficulty for gravimetric determinations of sorption, all those measurements were made with uncoated samples.

(iv) Thermal equilibrium of dielectric specimens in the cell

Temperatures in the film dielectric cell were adjusted by intervals of approximately ten centigrade degrees. On a test sample these adjustments were made in about six minutes, a total of twenty minutes being allowed between readings. At an operating frequency of 100 Kc both temperatures were lowered from 80°C to -40°C and raised again to 80°C. Figs. 22 and 23 show that throughout most of the temperature cycle the values of $D_X.C_{XP}$ and of C_{XP} are reproducible. Hence sufficient time has been allowed for the sample to reach the temperature of the bath.

At temperatures above 50°C the values for C_{XP} (Fig. 23) began to diverge. This was attributed to enhanced drying of the sample at the higher temperatures. This was probably the case, for the vacuum on this sample was maintained by continuous evacuation. It is possible, of course, that there was some contribution from loss of camphor by evaporation or from decomposition.

This sample was dried to a pressure of only 0.02 mm. Hg at 25°C. Other samples were taken to a pressure of 3×10^{-4} mm. Hg at 25°C by drying for the two-day period mentioned previously. The temperatures of those samples were never brought above 25°C so that spurious results due to extra heating were prevented.

Up to this stage in the work reliable results could not be obtained atfrequencies below 100 Kc. the author decided to modify the dielectric apparatus so that lower working frequencies could be used. The Experimental section contains the description of how this was done. Dispersions could then be spanned at lower frequencies without subjecting the sample to temperatures higher than 25°C. Measurements with the modified equipment were made according to the convention described in the experimental section on procedures. When bath temperatures were changed, a full half hour was given for the temperature of the sample to come to that of the bath. The bath, as was mentioned before, was thermostatted and measurements were made over a range of frequencies at each temperature.

(v) Celluloid with 4.1% sorbed acetone

A specimen of celluloid was dried to constant weight at 3 x 10^{-4} mm. Hg. and 25°C; to this was sorbed 4.1% by weight of acetone (Experimental, Part 7c). The concentration of acetone was kept constant at different temperatures of a dielectric run by the method for high sorbate concentrations given in Experimental, Part 7c.

(d) Cellulose Nitrate Films - Concentration of Acetone in Films

(i) General

Concentration of acetone in film samples was determined on the basis of 'dry' films. 'Dry' films were evacuated to constant weight for 3½ days at 25°C in a system whose pressure was lowered to 3 x 10^{-4}mm. Hg. Films were also considered to be 'dry' when evacuated at 25°C in a vacuum desiccator over P_2O_5. Fibres of nitrocellulose subjected to the latter treatment contained no acetone and were designated 'bone dry'. The difference in acetone content of 'dry' and 'bone dry' samples was determined for nitrocelluloses of various degrees of nitration. 0.14 gram aliquots of nitrocellulose fibres were weighed into 10 ml. beakers and dried for a week to constant weight by the P_2O_5 treatment. 10 cc. of acetone were added to each sample of nitrocellulose and solutions or partial solutions were affected in an undesiccated desiccator at standard pressure. The acetone was then allowed to dry out over $CaCl_2$ with the desiccator lid slightly ajar. In this way films were formed on the bottom of the beakers. They were left in the beakers and exposed to room atmosphere for several weeks and finally dried in a vacuum desiccator over P_2O_5 to constant weight in eleven days. An increase in weight was found over that for the dry fibres and it was attributed to retained acetone. The grams of acetone per gram of 'bone dry' fibre were thus determined (Table XXXVII).

Maximum inclusion of acetone in the nitrocelluloses occurs for a degree of substitution (D.S.) of 2.4. At approximately the same D.S. there is the least tendency towards crystallinity of nitrocelluloses; that is, there is "a minimum in the attractive force between chains," (4).

A sorption isotherm for acetone and nitrocellulose of D.S. 2.33 was determined on a torsion balance (Table XXXVIII), the relative weight sorbed being given as grams acetone sorbed per gram of 'bone dry' nitrocellulose. The isotherm was in accord with those determined by Dreschel and coworkers (67) for degrees of substitution 2.27 and 1.97. This work is complemented by that of Schulz (68). Although the D.S. of his nitrocellulose was not given, the curve calculated from his data is joined by dotted lines to that of D.S. 1.97.

The isotherms are somewhat similar in shape to those for water-cellulose. At low vapour pressure there is a hump which is characterized by the occurrence of solvate formation with the very first sorbed molecules, and then of simultaneous solvate formation and dissolution. At a relative weight of about 90% Schulz found a break in swelling properties which he attributed to the existence of a solvate having four molecules of acetone per C_6 unit. Little significance seems to have been attached to this postulate by other workers; Spurlin ignores it (41).

(ii) Nitrocellulose film with 16% sorbed acetone

The composition of nitrocellulose films with 16% sorbed acetone was kept constant at the different temperatures of the dielectric run by a method previously described for high sorbate concentrations (Experimental, Part 7c); the vapour pressure of acetone was adjusted. A curve of log vapour pressure vs 1/T was found to be linear (Fig. 25). Such plots (isosteres) have been used to determine heats of sorption of water-cellulose (48). Similarly, after subtracting the heat of vaporization from the heat of sorption (from Fig. 25), the heat of swelling was found to be 4,400 calories per mole at 56°C. Calvet found a value of about 3,900 calories per mole by calorimetric measurements at room temperature (4).

At lower concentrations of acetone, the dielectric cell was isolated from the rest of the conditioning system during a dielectric run. At the highest concentration among these (9.9%) there were complications which will be discussed later (Results and Discussions, Part 3).

(e) Cellulose Paper

(i) Cellulose paper (a)

The dielectric properties of cellulose paper were measured in a Seidman paper cell which was used previously in this laboratory (44). A sample of paper whose dry weight was 1.639 grams made exactly four layers when wrapped around the inner compartment of the paper cell. Free volume between dielectric plates in the cell was 3.61 cc. so that the partial specific volume $\bar{V}_2$ of cellulose between dielectric plates of the cell was 0.293 when the density of the cellulose was assumed to be 1.55 grams/cc. (2).

The sample was evacuated while its temperature was raised to 90°C. The evacuation proceeded in this way for thirty hours, by which time its dielectric properties were constant and the pressure had dropped to 3×10^{-4} mm. Hg. Dry air was then admitted into the system with no apparent change in dielectric properties. This was done to ensure good thermal equilibrium between sample and bath. At this point the sample was termed cellulose paper (a) and dielectric measurements were made which are reported in Results and Discussions.

(ii) Cellulose papers (b) and (c)

The paper sample which was designated cellulose paper (a) for measurements of ϵ'_m ϵ''_m taken at 90°C was termed cellulose paper (b) for measurements made at 125, 149 and 174°C over a frequency range from 0.1 to 20 Kc. It is understood that the composition of the sample varied as heating increased, but it is felt that these measurements could be appropriately grouped together.

The same sample was held at 174°C and was evacuated to a pressure of 3×10^{-4} mm. Hg in three hours. It was then allowed to cool to room temperature under evacuation. Dry air was then admitted to the sample, which after this conditioning was termed cellulose paper (c). ϵ'_m ϵ''_m were determined at temperatures from 91 to +264°C. Further details of the experiment are given in Results and Discussions.

RESULTS AND DISCUSSIONS

1. Cellulose Nitrate - Acetone Solutions

(a) General

Cellulose nitrate in solution was the subject of the first part of this investigation. Solutions No. 1, 2, and 3 were used (Experimental, Part 6). They contained respectively 3.09, 3.00 and 17 grams of cellulose nitrate (D.S. 2.32) per 100 cc. of solution with acetone. Dielectric constant ϵ'_m and loss ϵ''_m of the solutions were determined within a temperature range of -75° to 45°C and a frequency range of 0.1 to 18 Mc.

Four effects were observed:

(i) Dielectric constant and loss increased with decreasing frequency. Curves of $\epsilon'_m - f^{-1}$ approached those expected from D.C. conductivity. In the limit at low frequencies they were linear and passed through the origin. This dispersion was therefore attributed to D.C. conductivity.

(ii) At frequencies above 1 Mc there was dielectric dispersion of the solvent, acetone.

(iii) Near 200 Kc there were indications of a third dispersion of small magnitude. This was compared to (a) two sharp dispersions found by Scherer and Testerman for 3% solutions of nitrocellulose in acetone and (b) a number of dispersions of impure acetone noted by Cole, the numbers being 0, 1 or 2 depending on the source of the acetone.

(iv) A dispersion against frequency similar to that in (iii) was observed at -75°C. This was believed to be a true nitrocellulose dispersion.

Dispersions were observed with both temperature and frequency as parameter. The latter method yielded more informative data because the effect of D.C. conductivity could be estimated according to (i).

(b) Solution #1

Solution #1 was held at 24.4°C and measurements were made on it from 175 to 300 Kc. The conductivity of the solution was too high to permit measurements below 175 Kc with the Schering bridge or to permit any measurements with the twin-T bridge.

Results of the dielectric constant ϵ'_m and loss ϵ''_m are shown in Table III. Plots were made of ϵ'_m against frequency (Fig. 26a) and of ϵ''_m against the reciprocal of frequency (Fig. 26a). The former shows a strong frequency dependence which is evidently due to polarization. An attempt to measure the D.C. conductance substantiated this conclusion; polarization effects were so strong that D.C. measurements were impracticable.

The ϵ''_m - 1/f plot would be linear--as exemplified by the drawn line in Fig. 26b--if the conductivity G of the solution were constant, that is, if the dielectric loss were due only to a D.C. resistance (1/G). By the parallel notation for leaky condensers (11)

$$\epsilon''_m / \epsilon'_m = G/\omega C_m \qquad \text{.... 73}$$

Hence, $\epsilon''_m = G/\omega C_a = G/(2\pi f C_a)$

and $\epsilon''_m \propto 1/f$ 74

The frequency dependence of ϵ''_m can therefore be attributed to D.C. conductivity; (a) in a frequency range, if one is found, where a plot of $\epsilon''_m - 1/f$ is linear and (b) if, on extrapolation, the plot passes through the origin.

The plot of experimental points for Fig. 26b does not fall on the straight line drawn through the origin and therefore there is a contribution to the loss over that of D.C. conductivity. This is probably caused by polarization.

(c) Solution #2

Solution #2 was more highly purified than #1 but was otherwise essentially the same. Measurements were obtainable down to 100 Kc with the Schering bridge and at 3 and 10 Mc with the twin-T bridge.

Two runs were made, one at various frequencies at 26.0°C (Table IV), and one at various temperatures at 100 Kc (Table V). For the latter run, readings were taken at 10 minute intervals while the temperature was lowered progressively from 19.6°C to -70.2°C. From the results of the first run plots were made of ${}'_m - f$ (Fig. 26c) and for $\epsilon''_m - f^{-1}$ (Fig. 26d). Both showed a great reduction of polarization effects from the plots for solution #1 (Fig. 26a, 26b) although there was still a discernible increase in ϵ'_m at low frequencies.

This increase was comparable in magnitude to that found by Scherer and Testerman (36). They found an increase in ϵ'_m as the frequency was decreased from 500 Kc until in the neighbourhood of 150 Kc, ϵ'_m remained at a constant value. At frequencies below this 'plateau' region of constant ϵ'_m, the values of ϵ'_m again increased and levelled off at 100 Kc. By looking at the plotted experimental points in Fig. 26c, a similar trend in ϵ'_m - f can be detected.

However, the plateau region in this curve is not significant. Possible errors in ϵ'_m are too large, being ± 0.03 in a total of 20 without including errors for geometric capacitance of the cell. This figure is composed of the following possible errors: ± 0.1 uuf in C'; ± 0.1 uuf in C"; hence ± 0.2 uuf in C' - C" (of average value 140 uuf). The line in Fig. 26c is therefore drawn with a very gradual slope at higher frequencies--see values of ϵ'_m at 3 and 10 Mc in Table IV--with a steepening of the slope near 100 Kc. The author believes that ϵ'_m would continue to increase at lower frequencies because of polarization.

Scherer and Testerman worked with a cell which gave two and a half fold higher values of capacitance than did the Balsbaugh cell. This would have improved their accuracy accordingly. However, they employed a resonant circuit which is purported to be useful for conducting liquids (12), but which is normally not so accurate as the heterodyne beat circuits. A precision of ± 0.1 in 350 uuf was claimed for the capacitance of their cell. There was a variation of ± 0.05°C in the temperature of their thermostatic bath, which in itself produced an error of this magnitude. Two bridge balances per determination of ϵ'_m are necessary when measurements are made at different frequencies. It is doubtful that their bridge yielded a significant precision of better than ± 0.2 in 350 uuf. These possible errors when added together amount to ± 0.3 in 350 uuf.

The plateau found by Scherer and Testerman was accordingly subject to less error than that of the present work. However, their errors were so large that the shapes of the ϵ'_m - f curve for their two dispersions has little significance; each dispersion occurred over only a 3 uuf interval. For the present, therefore, no importance should be attached to their relationship between the shape of such curves and curves of molecular weight distribution for nitrocellulose,

The dispersions found by Scherer and Testerman may have been due to the phenomenon suggested by them, but more probably they were produced by impure acetone as was indicated in the Introduction. Cole (69) noted that acetone displayed one or two dielectric dispersions in the 100-1000 Kc region, but that neither persisted after the acetone was highly purified. Scherer and Testerman did not purify their acetone and there is little doubt that impurities were introduced from their cellulose nitrate, even though they took pains to purify the nitrate before dissolving it. They did not give specific conductivities or dissipation factors (36) which could be used as criteria for the purity of their solutions. If, instead, we use the percentage increment in dielectric constant from 100 to 500 Kc, then their solutions were even less pure than solution #2 of this work. The increments were respectively 1.7 and 1.3%. There was probably enough impurity in both these solutions to induce the effect observed by Cole (69).

Results for the temperature run at 100 Kc (Table V) are illustrated in Fig. 27. ϵ_m' and ϵ_m'' were determined at decreasing temperatures, then at increasing temperatures. The bath temperatures were changed rapidly and then held constant for the sample to reach the new bath temperature. There were variations in the intervals of temperature and of time between successive readings. They are recorded in Table V.

Dielectric dispersion in the region of 26°C and 100 Kc was detected from the curve of $\epsilon_m' - f$ (Fig. 26c). Corresponding to this, there should have been a dispersion against temperature in the region of 26°C at 100 Kc.

Fig. 27a shows that there is linearity of ϵ_m against t between -70 and +10°C. A temperature coefficient in ϵ_m of this nature is normal for acetone. Above 10°C there is a deviation from linearity for the solution. Scherer and Testerman reported that the temperature coefficient of acetone's dielectric constant was invariant from 16 to 35°C. Part of the curvature in Fig. 27a must therefore be due to dispersion. This fact confirms the results obtained against frequency at 26.0°C for run (b).

The curve of ϵ_m'' against t (Fig. 27b) shows no indication of effects from a dispersion region. Although such a region must exist above 10°C, contributions to ϵ_m'' by dispersion effects are masked by the high D.C. conductivity.

(d) Solution #3

This was a 17% solution made from the same material as solution #2. The following runs were made in which ϵ_m', ϵ_m'' were determined:

(a) At 21.9°C and from 115 Kc to 10 Mc, (See Table VI, Fig. 28a, Fig. 28b)

(b) At 23.4°C and from 1.8 to 18 Mc, (See Table VII, Fig. 28c, Fig. 28d)

(c) At 45.4°C and from 1.5 to 18 Mc, (See Table VIII, Fig. 29a, Fig. 29b)

(d) At -75.0°C and from 100 Kc to 16 Mc, (See Table IX, Fig. 29c, Fig. 29d)

(e) At 130 Kc and from -63.3 to 24.7°C, (See Table X, Fig. 30a, Fig. 30b)

(f) At 16 Mc and from 18.3 to -60.9°C (See Table XI, Fig. 31)

(g) At 16 Mc and from -60.9°C to 19.5°C, (See Table XI, Fig. 31)

Run (a)

Fig. 28a shows that the dielectric constant began to increase at frequencies below 180 Kc. The rate of this increase was 0.7 uuf per 100 Kc. A corresponding increase for solution #2 (Fig. 26c) was about 0.25 uuf per 100 Kc. Since the rate of increase changed in the same direction as the concentration of nitrocellulose and therefore of nitrocellulose impurities, it is probable that both increases were due to impurities. The curve $\epsilon_m'' - f^{-1}$ (Fig. 28b) appeared to be linear, indicating an absence of polarization effects. However, a slight deviation from linearity was detected which corresponded to a peaking of the dielectric loss after corrections for D.C. conductivity were made. This will be considered later in a general discussion of the solutions.

Run (b)

Like Fig. 28a for run (a), Fig. 28c shows a gradual decline in dielectric constant between 0.2 and 5 Mc. At the higher frequencies the decline is sharper due to dielectric dispersion of acetone. At the same frequencies and for the same reason the dielectric loss increased sharply (Fig. 28d) over that attributed to D.C. resistance. Parallel effects in pure acetone will be discussed in the general discussion on solutions.

Run (c)

Curves were plotted for the run at 45.4°C (Fig. 29a and b)which were similar to the curves for the higher frequency runs at room temperature. The effects were less pronounced, but this was expected since dispersion regions normally shift to higher frequencies at higher temperatures.

Run (d)

Of course the effects were more pronounced at -75°C (Fig. 29c and d) than at the higher temperatures. When allowances for the differences of scale are made, this intensification of effect can be clearly seen in the lower left corner of Fig. 29d. This figure reveals another dispersion at values of 2-10 reciprocal megacycles. The author believes that this is due to cellulose nitrate rather than to impurities. It will be isolated later by correcting for the dispersion of acetone and for the D.C. resistance.

Run (e)

This run was made against temperature at 130 Kc. The plots of ϵ''_m and ϵ'_m against temperature (Fig. 30a and b) revealed no significant inflections. Although some inflection was expected near room temperature to correspond to the apparent dispersion of Fig. 28a, the plot of ϵ'_m - t was, in fact, apparently linear.

Runs (f) and (g)

These runs were made at 16 Mc. For run (f) the temperature was decreased in increments. Run (g) was a continuation of run (f) in which the temperature was raised in increments to complete a temperature cycle. The time interval between readings was only ten minutes. Even so, the temperature hysteresis in values of ϵ'_m was small. The curves of ϵ'_m - t (Fig. 31) were linear. Like those at 130 Kc they indicated that no dispersions were spanned in this temperature range of 20°C to -60°C. Values for ϵ''_m were not determined because the conductance for temperatures below 4°C was higher than the calibrated range of the twin-T bridge.

(e) General Discussion of Cellulose Nitrate Solutions in Acetone

There are large contributions to ϵ''_m from the D.C. conductivity of cellulose nitrate solutions. Unfortunately the D.C. conductivity cannot be measured on a D.C. resistance bridge because of polarization effects. The best way to estimate the contribution is to plot ϵ''_m against the reciprocal of the frequency. If there is only a D.C. contribution the plot will be linear and will pass through the origin. This kind of plot has been made for the foregoing experiments. The D.C. contribution has been estimated by the drawn lines in the curves of ϵ''_m - 1/f (Figs. 26b, 26d, 28b, 28d, 29b, and 29d). These contributions have been subtracted from experimental values of ϵ''_m for the runs corresponding to Figs. 26d, 28b, 28d, and 29d. Table XII gives corrected values for ϵ''_m.

From these values solutions #2 and #3 show dispersions at room temperature. Their magnitude is not great and is of questionable significance. Nevertheless, they do give support to the thesis that there is a dispersion at frequencies between 100 and 300 Kc. No confirmation was found for a second dispersion which was faintly indicated in Fig. 26c. It has already been suggested that both dispersions reported by Scherer and Testerman resulted from impurities in their acetone. It is felt that the dispersions observed here can be accounted for in the same way, except those at high frequencies where acetone itself displays a dispersion, and in the results for solution #3 at -75°C.

For simplicity of discussion the three dispersions observed by the writer will be referred to as dispersions S1, S2 and S3 respectively. The above remarks on the effects of D.C. conductivity apply to dispersion S1.

There is some dispersion (dispersion S2) of the dielectric constant for acetone at frequencies above 1 Mc. It is of small magnitude, but it makes the predominant contribution to ϵ_m'' at frequencies over 10 Mc. Values of ϵ_m'' for acetone at 20.6°C are given in Table XIII. Compare these values with those for solution #3 at 23.4°C and at high frequencies (Table XII). The comparison confirms the statement that dispersion of acetone is responsible for the increasing losses at high frequencies. Such losses are also evident in solution #3 at 45.4°C, (Fig. 29b) and at -75°C (Fig. 29d) and Table XII.

When values from Table XII are plotted against log frequency, a dispersion effect (dispersion S3) is seen (Fig. 32) which is additional to that expected for acetone. Its presence was also noticed in Fig. 29d.

If the dispersion is symmetrical with respect to frequency, then the curve of ϵ'' - f (Fig. 32) has been cut off on the low frequency side. That is, the value of ϵ'' at 100 Kc should be positive instead of zero. Such a cut-off has probably been effected by overestimation of the D.C. resistance from Fig. 29d. Even as shown this dispersion spans two cycles of frequency and might easily span another two if proper D.C. resistance corrections were made. The dispersion is in this way similar to Debye type dispersions rather than to resonant type dispersions. Dispersion S1 was claimed to be of the latter type (36). Even if it were the Debye type it probably would have shifted to frequencies much below 100 Kc at -75°C and therefore is probably distinct from dispersion S3.

The author believes that dispersion S3 (Fig. 32) is due to solvated nitrocellulose. It is suggested that further work in solutions be performed with more highly purified nitrocellulose (9) at low temperatures and perhaps with ethyl acetate instead of acetone (12).

2. Celluloid

(a) General

Measurements on solutions of cellulose nitrate revealed little about the nitrate. One dispersion which was believed to be caused by the nitrate was found at -75°C. At higher temperatures this dispersion probably shifted to higher frequencies where it was masked by the dispersion of acetone. At lower frequencies ionic conductance in the solutions masked dispersion effects. It was considered that the dispersion of cellulose nitrate could be more easily investigated in the solid state because:

(a) Ionic conductance would be reduced
(b) Dispersion effects by acetone would be eliminated
(c) The high viscosity of the medium would lower the frequency of the dispersion into a region where measurements could be made more easily.

The investigation of solid cellulose nitrate was begun with celluloid. Preliminary measurements were made in the Seidman paper cell and subsequent measurements in the film dielectric cell. Dielectric dispersions of the Debye type were detected. As described in Experimental, Part 8, the performance of the film cell was tested using celluloid as the dielectric. Four celluloids were investigated, Their camphor concentrations were 27.2, 29.8, 35.3 and 40% (Experimental, Part 5). There were indications that peaking of the parameters of activation ΔF^*, ΔH^*, ΔS^* occurred at 35% camphor. This was explained on the basis that complex formation between camphor and nitrocellulose occurred at this concentration. A second dispersion region was detected and was designated dispersion D.

(b) Preliminary measurements

Preliminary measurements were on commercial celluloid containing 40% camphor and 60% cellulose nitrate. The sample was first conditioned at atmospheric temperature and humidity and then inserted in the Seidman cell. The cell was stoppered and set in a bath. It was held at a constant frequency while the temperature was varied, an interval of fifteen minutes being allowed between readings. Values of ϵ_m', ϵ_m'' against temperature were determined at frequencies of 10, 100 and 1000 Kc (Table XIV). They were plotted in Fig. 33 where distinct effects of dielectric dispersion are displayed. Curves ϵ_m' - t and ϵ_m'' - t have inflections and peaks respectively. For the same working frequency the temperatures t_m of inflection and of peaking are coincident within experimental error. Furthermore, the values of t_m decrease with lowering of frequency.

(c) Refined Measurements

(i) General

Results were obtained for celluloids whose cellulose nitrates were plasticized with different proportions of camphor and on regular celluloid (having 40% camphor) which was further plasticized with acetone. Measurements were made at temperatures ranging from 25°C to -68°C and over a frequency range from 0.2 to 300 Kc. Values of ϵ' and ϵ'' are presented in Tables XV to XXIV. The data reveal a number of expected features.

(ii) Dielectric dispersion in celluloids

In all these tables the temperature coefficient of ϵ' is positive. In some cases an absorption region is spanned as indicated by peaking of the values of ϵ''. The temperatures t_m of the peak value ϵ''_t in these curves is particularly significant. For a given celluloid, a decrease in frequency causes a shift in t_m to lower temperatures. It also causes an increase in ϵ' at a particular temperature. These effects are illustrated for regular celluloid in Fig. 34 and 35 and for celluloid-acetone in Fig. 36 and 37. They are qualitative indications of dielectric relaxation which is due to dipole orientation according to Debye concepts (14).

Corresponding to these features are those for plots against log f. Fig. 38 and 39 for celluloid with acetone are examples. The log f coefficient of ϵ' is negative. At the same time, the frequency f_m corresponding to the maximum in ϵ'' decreases with a shift to lower temperatures. These features are also in accord with Debye concepts.

The effect of 4.1% acetone sorbed on regular celluloid is to shift t_m to lower temperatures (Fig. 34 and 36) and f_m to higher frequencies (Table XVI, Fig. 38). Also the dispersion peaks become higher and sharper. These are the normal effects of plasticization (10)(70)(71).

(iii) Complex formation between nitrocellulose and camphor

On the other hand, striking effects were obtained with changes in the concentration of camphor. t_m was a maximum at 35.3% camphor (Tables XV and XXII). This unusual shift in t_m with composition is illustrated in Fig. 40. The author attributes it to solvate formation between camphor and cellulose nitrate.

Before these experiments were performed the formation of a distinctive solvate between camphor and nitrocellulose was expected (Introduction, Part 2). It was expected that the solvate would be quite stable and detectably crystalline, that it would be composed of one camphor molecule per anhydroglucose unit and that with the nitrocellulose of these celluloids, the solvate would correspond to a camphor concentration of 35% (Introduction, Part 2). The experiments were performed in the hope that an effect distinguishable as solvate formation would be detected. Such a strong effect as that described above was not expected.

The Eyring rate theory offered a possible explanation for these effects of solvate formation and plots were made of log $(1/2\pi f)$ against $1/T_m$ to test its applicability. (T_m in °K is the same temperature as t_m in °C). Values for t_m are given in Table XXV and the rate plots are shown in Fig. 41. No values for t_m were obtained for the sample with 35.3% camphor. They were over 25°C, the experimental limit. In Fig. 41 the plot for this sample would lie off the graph, beyond its upper left hand corner. Nevertheless, the results are of interest.

The nearly-linear plots for the other celluloids indicate that the rate theory does apply. The slopes of the plots indicate that they would be at a maximum near 35% camphor. More significant than these slopes, however, are the thermodynamic values which have been derived from the plots and the absolute rate theory.

The Eyring rate theory was discussed in Introduction, Part 3. It led to the following relationships for the free energy of activation ΔF^*, the enthalpy of activation ΔH^* and the entropy of activation ΔS^*:

$$\begin{aligned} \Delta F^* &= 2.303\ RT \log (kT\tau^*/h) \\ \Delta H^* &= 2.303\ R\,[\log \tau^*/(1/T)] - RT \qquad \ldots\ldots\ \underline{21} \\ \Delta S^* &= (1/T)(\Delta H^* - \Delta F^*) \end{aligned}$$

where k, h, and R are respectively the Boltzman, Planck and gas constants, and T is the absolute temperature. $(1/\tau^*)$ corresponds to a rate constant where τ^* has the magnitude of a relaxation time and is taken as $1/2\pi f$. The value of $[\partial \log \tau^*/\partial(1/T)]$ is that of the slopes for the curves log $1/2\pi f$ versus $1/T_m$, or the curves log $(1/2\pi f_m)$ versus $1/T$.

The curves of Fig. 41 were extrapolated to $1/T_m = \frac{1}{298^{\circ}K}$. From the slopes and the values for $1/2\pi f$ at $298^{\circ}K$, the values for ΔF^*, ΔH^* and ΔS^* were determined. (Table XXVI).

ΔF^* has a maximum at a concentration of about 35% camphor. From the limited data it appears that ΔH^* and ΔS^* also have maxima at about the same concentration.

For the composition of maximum ΔS^*, there are a maximum number of bonds broken per relaxation of a single dipole. This phenomenon would occur at the composition of the nitrocellulose-camphor complex, so that the maximum found for ΔS^* is reasonable.

The enthalpy should also be a maximum when there are a maximum number of bonds broken per dipole relaxation. This assumes that the enthalpy of activation per bond broken changes more slowly with respect to composition than does the number of bonds broken per dipole relaxation. This is a necessary consideration for the enthalpy of activation to break a bond tends to diminish with increasing amounts of a plasticizer (41).

The net effect is apparent in the free energy of activation. Its value definitely has a maximum, a fact which is attributable to the predominant effect of the maximum in the number of bonds broken per dipole relaxation. That this should be so is reasonable, for at this composition a solvate is formed, which is distinctive enough to have crystalline characteristics (9). When the concentration of camphor deviates from the composition of the pure solvate, then, of course, the solvate is contaminated with camphor or with nitrocellulose, so that its crystalline character is disrupted. The number of bonds broken per dipole relaxation are understandably at a maximum for such a crystalline material.

(iv) 4.1% acetone sorbed on celluloid

The effect of adding 4.1% acetone to regular celluloid (40% camphor) was likewise observed (Fig. 41, Table XXVI). The entropy of activation more than doubled, the enthalpy increased somewhat and the free energy diminished. Presumably then, the acetone was solvating the celluloid, the number of bonds broken per dipole relaxation were increased, but at the same time the enthalpy of activation per bond broken was strongly diminished.

(d) Dielectric Dispersion D

A second dispersion, which is designated Dispersion D, was discovered with all the dry celluloids at temperatures below -40°C (Fig. 42). Absorption peaks were witnessed only for absorption curves at high frequencies; the other peaks occurred at temperatures below the limits of experimentation (Fig. 40). A few values of t_m were obtained but they were badly masked by interference of the first dispersion and therefore are of only qualitative significance. The dispersion behaved as a normal Debye type in that (a) t_m decreased with frequency, (b) t_m decreased to such an extent with 4% sorbed acetone that the dispersion was no longer evident within the limits of experimentation, and (c) both dielectric absorption and dispersion of the dielectric constant occurred in the same ranges of low temperature and high frequency.

3. Cellulose Nitrate Films

(a) General

Cellulose nitrate was next investigated in the form of films cast from solutions of purified fibres of cellulose nitrate in acetone. The following factors were studied:

(i) film drying temperature
(ii) presence of moisture hazing in a film
(iii) variation in degree of substitution of cellulose nitrate (D.S. 2.33 and 2.46)
(iv) concentration of sorbed acetone.

The preparation of the films was described earlier. Samples 3 and 4 of cellulose nitrate were used. Their degrees of substitution (D.S.) were 2.33 and 2.46 respectively. The films, which were transparent and yellowish, became dry to the touch after two weeks of drying in air. One exception was a moisture hazed film which was milky white. It was prepared by adding 4% water to the acetone used in dissolving the nitrocellulose.

These are the samples for which the film dielectric cell was primarily designed. After a preliminary drying in air the samples were coated with thin metal films which served as dielectric plates (Experimental). The sample was then placed in the dielectric cell and was further dried by evacuating at 25°C for three and a half days, the last two and a half at a pressure of 3×10^{-4} mm Hg. As has already been mentioned, drying proceeded by permeation of volatiles through the thin dielectric plates and therefore could proceed in situ as described. On the third and final drying day changes in the dielectric properties of the film were almost negligible.

In general, dielectric measurements were made from 25 to -68°C, and from 0.2 to 300 Kc (Experimental, Part 7).

None of these films was completely dried of acetone, although drying proceeded further at 45 than at 25°C. All films displayed a dispersion similar to the principal one for celluloids. There was interference with this dispersion from a second dispersion when the concentration of acetone was low. The dispersions were designated A and B respectively.

Slight differences in degree of substitution (D.S. 2.33 and 2.46) yielded slightly different values of ΔF^*, ΔH^* and ΔS^*. These differences were considered insignificant. Effects due to differences in concentration of residual or sorbed acetone in the films were considered in the light of the assumption that an acetone-nitrocellulose complex was formed at the same time as a solid solution of nitrocellulose.

A third dispersion designated dispersion C was detected at low frequencies and near 25°C in highly plasticized nitrocellulose.

(b) Film Drying Temperature

One nitrocellulose film was dried at 25°C (film #1) and then further dried at 45°C (film #2). A set of dielectric measurements as outlined above was made at each temperature.

The drying at 25°C proceeded for only 41 hours. The final drying pressure was high, about 6×10^{-3} mm Hg. However, there was no detectable change in dielectric properties of the film during the last eleven hours of drying. The results (Tables XXVII and XXVIII) yielded a rather odd looking set of plots of $\epsilon'' - t$ (Fig. 43), the curves being for different frequencies. The shift in t_m with frequency appeared rather small.

The sample was then dried at 45°C and a pressure of 3×10^{-4} mm. Hg for 5-1/3 days. Drying was discontinued then because it was feared that the nitrate might begin to decompose. A non-metallized sample of the same material was conditioned similarly on a torsion balance. At the end of the treatment it was still losing weight at the rate of 0.06% per day. The dielectric sample was undoubtedly drying at the same rate, its metal coatings having no effect on these slow rates of desorption.

Consider Fig. 44 which shows, as functions of time, the loss in weight and in ΔC of the uncoated and coated samples respectively. That the curves have essentially the same shape indicates that the controlling factor in the samples' drying is the same and hence that the coatings do not interfere with this particular drying process.

Presumably the process is controlled by diffusion of acetone from the bulk of the material to its surface. Dielectric measurements were begun at 45°C and were carried down to -27°C. The frequencies were varied from 0.2 to 300 Kc (Tables XXIX and XXX).

The increased drying (compare Table XXVII and XXVIII) reduced the dielectric constants, the peak values of dielectric loss, ϵ''_T, and most of the corresponding temperatures t_m. These trends are normal for reduced plasticization. However, the surprising fact was that two sets of peaks were detected. These are shown in Fig. 45 where graphs are drawn of ϵ'' - t for all ten experimental frequencies. Values of t_m are indicated with arrows. There is little doubt that the two sets of peaks are produced by two distinct mechanisms causing two distinct dielectric dispersion regions. Each mechanism tends to have its own curves of ϵ'' - t and its own values of t_m. Although obscured by mutual interference of the mechanisms, t_m has been determined for each one as listed in Table XXXI. The dispersion which predominates at lower frequencies is designated in the table and subsequent text as dispersion A, and that at higher frequencies as dispersion B.

A single set of t_m for the less dry film (Fig. 43) was also determined (Table XXXI). The interference of the two dispersions was so strong that only one peak could be found for any curve of ϵ'' - t.

This is seen from plots of log (1/2πf) against 1/T (Fig. 46a). Curves 2 and 3 respectively are for the dispersions A and B of the drier film. Curve 1 is for the less dry film. Part of the curve is parallel to and near Curve 3; it then moves into the vicinity of curve 2. In this way, the predominant dispersion is seen to be firstly B, and then A.

On curves 1 and 3, dispersion B is seen to move to lower frequencies for the drier film. This is consistent with a reduction in plasticization.

(c) Presence of Moisture Hazing in a Film

A moisture hazed film (Film #3) was referred to earlier in this section. It was dried conventionally at 25°C for 3½ days and down to a pressure of 3×10^{-4} mm. Hg. Results for ϵ' and ϵ'' are given in Tables XXXII and XXXIII.

Dispersions A and B are both evident in curves of ϵ'' - t (Fig. 47). A is predominant. The frequency characteristics of t_m (Table XXXI) are plotted in curve 4 of Fig. 46a. The deviation from curve 3 is believed to be due partly to the presence of submicroscopic air pockets in the film, and partly to a reduction in the residual acetone of this film compared to film #2. The porosity and the presence of water in preparing film #3 may have assisted in freeing acetone from the film.

(d) Variation in Degree of Substitution of Cellulose Nitrate (D.S. 2.33 and 2.46)

Film #4 was prepared with nitrocellulose of 12.6% nitrogen content (D.S. 2.46). It was dried conventionally as in (c). A number of nitrocelluloses covering a wide range of degree of substitution were mentioned in Table XXXVII (Experimental, Part 8d). It was intended to prepare films with all of these but the ones of D.S. other than 2.33 and 2.46 were inhomogeneously nitrated. They did not completely dissolve in acetone so that it was not possible to prepare film specimens good enough for dielectric measurements.

Results of ϵ' and ϵ'' for film #4 are tabulated in Tables XXXIV and XXXV. Dispersion A was predominant although there appeared to be some interference due to dispersion B (Fig. 48). The frequency characteristics of t_m (Table XXXI) are plotted in curve 5 of Fig. 46a. The deviation from curve 3 for nitrocellulose of D.S. 2.33 is slight. From Fig. 46a thermodynamic functions of activation have been calculated (Table XXXVI). Values for ΔH^* and ΔF^* are slightly lower and for ΔS^* slightly higher with the more highly nitrated material. These differences are so small that they are not significant.

The next part of this section deals with two more nitrates (D.S. 2.16 and 3.00) which were investigated in the form of nitrocellulose sheets. The effects of degree of nitration will be discussed there.

Values of t_m for all four samples are given in Table XXXI. Plots of log $(1/2\pi f)$ - $1/T_m$ were linear (Fig. 46). They yielded the thermodynamic properties of dielectric relaxation which are presented in Table XXXVI and which are plotted against concentration of acetone in Fig. 49. The points for 0% acetone were those found for nitrocellulose paper in the next part of this section. The curves are similar in character to those determined by Seidman and Mason (41)(44) for water, methanol and ethanol sorbed on cellulose. The only difference is that their system displayed no peaking of the ΔF^* - % curve whereas the system nitrocellulose-acetone displays a distinctive peak.

Several postulates have been made as to dipolar groups and mode of relaxation in dielectric dispersion of cellulose and its derivatives. Whatever these factors may be, they are strongly affected in both the parent compound and in nitrocellulose by low and high molecular weight plasticizers.

Camphor affixes itself to cellulose nitrate (9), firstly by forming a complex which has one mole of camphor per anhydroglucose unit, and secondly by forming a solid solution with this complex. With perfect mixing an essentially pure complex of nitrocellulose and camphor can be formed, and at other concentrations solid solutions are formed between this complex and either nitrocellulose or camphor. It is possible, of course, to have a mixture which has been so poorly blended that both the pure complex and the solid solutions just described are formed.

(e) Concentration of Sorbed Acetone

The effect of sorbed acetone on dielectric properties of cellulose nitrate was very pronounced. The degree of substitution was 2.33 in all samples and the acetone concentrations were 0.7, 4.3, 9.9 and 16.0 grams acetone per gram of 'bone-dry' nitrocellulose (films #2, #5, #6, #7). The manner in which these acetone concentrations were determined is described in Experimental, Part 8. The concentrations of acetone in the samples are given in Table XXXIX, in terms of relative weights, moles per anhydroglucose unit and moles per nitrate group.

The values of ϵ', ϵ'' for 0.7% sorbed acetone are given in Tables XXIX and XXX (see Fig. 45). Those for 4.3, 9.9 and 16.0% sorbed acetone are presented in Tables XL to XLVII.

For 9.9% acetone-nitrocellulose the values of ϵ', ϵ'' were time dependent as is shown by a comparison of a cooling-heating cycle that took 34 hours (Tables XLII to XLIV) with one that took 3 hours (Table XLV). Evidently sorption and desorption was taking place between the sample and the surrounding acetone atmosphere. However, there was no significant difference in the values of t_m from ϵ'' - t curves. Thus the values for t_m found from the data of Table XLIII are presumed to be correct.

The values for t_m for the 4.3 and 0.7% acetone-nitrocelluloses are undoubtedly correct. Even the values of ϵ', ϵ'' have only slight errors since the rates of acetone diffusion for these low-acetone-concentrations are very slow.

Laboratory observations have revealed a similarity between the action of acetone sorbed on nitrocellulose and that of water, methanol, or ethanol sorbed on cellulose. There is a tendency for a complex to be formed, but its composition has not been established because, at equilibrium, regions of complex coexist with those of solution and of unsolvated polymer. In the case of nitrocellulose and acetone, for instance, it is reasonable to suppose that the first complex formed has one mole of acetone per anhydroglucose unit. At very low concentrations of acetone, these complexes exist among bare anhydroglucose units and a small number of free molecules of acetone which are dissolved but not solvated by the nitrocellulose. The proportion of free acetone over solvated anhydroglucose units is small at low concentrations of sorbed acetone, but it increases with the concentration.

Thus in the low concentration region, the effects of solvate formation are pronounced, but at concentrations of more than 3%, the plasticizing effects of dissolution are stronger than the inhibition to relaxation of solvate formation. ΔF^* has a peak value as it does with camphor-nitrocellulose. Solvate formation in the former case is not as strong as in the latter; but it is stronger than in the cellulose-sorbate systems because Seidman and Mason (44) found no peaking in their ΔF^* - % curves. The effects of sorbates were described (41) by referring to the number and strength of the bonds which were broken during a dipole relaxation. At the maximum point in the ΔS^* - % curve a maximum number of bonds was broken per orientation of a single dipole. The enthalpy per bond broken was less than that for lower sorbate contents. At sorbate concentrations greater than that of the maximum, the cellulose molecules had separated in such a way that fewer bonds were broken per dipole orientation and ΔS^* was reduced in magnitude. At the same time the enthalpy incrementsper bond broken became even smaller so that there was a corresponding decrease in ΔF^* and hence in relaxation time.

These principles also apply to the acetone-nitrocellulose system, regardless of the dipole or mode of relaxation responsible for dielectric dispersion.

The discussion thus far has been largely restricted to dispersion A. It is probable that dispersion B is affected by dissolution and solvation in essentially the same way as is dispersion A. In highly plasticized nitrocellulose the two dispersions interfere to such an extent that dispersion B is indistinguishable and a single loss peak is evident (Fig. 50 and 51).

(f) Dispersion C

A third dispersion region - designated dispersion C - was detected in highly plasticized nitrocellulose (Fig. 51, 16.0% acetone-nitrocellulose). Its existence is indicated by a sharp increase in ϵ'' with temperature at low frequencies. The curve at 0.116 Kc shows this particularly well. The peak of ϵ'' for dispersion C is well out of the range of the experimental equipment used. This dispersion may be assumed to exist with all the nitrocellulose films reported here, the peak being at such low frequencies and high temperatures that the positive signs of dispersion become apparent only in the plasticized state. Plasticization, of course, increases the peak frequency f_m and lowers the peak temperature t_m. Under these conditions dispersion effects were observable, even though the dispersion peak was not spanned.

4. Nitrocellulose Papers

(a) General

Thus far four dispersion regions, designated A, B, C and D, have been identified for the nitrocellulose-camphor-acetone system. Dispersions A and B showed separate and distinct absorption peaks for dry nitrocellulose films, but merged into a single peak with 10% or more sorbed acetone and with celluloid which was plasticized with camphor. Effects of dispersion C (high t, low f) were observed in highly plasticized nitrocellulose film, while dispersion D (low t, high f) was noted in the celluloid samples.

Nitrocellulose papers were investigated in order to avoid traces of acetone which were present in the nitrocellulose films. This was done though the measurements were complicated by the composite nature of the paper dielectric. Handsheets of fibrous nitrocellulose were prepared and their dielectric properties measured in a modification of the film dielectric cell (Experimental, Parts 4, 5). Dispersions A and B were apparent. The thermodynamics of relaxation of the former were compared for the samples of different degrees of substitution. A fifth dispersion region E was detected. It may or may not be different from dispersion D.

(b) Results

Nitrocelluloses nos. 5 and 6 were investigated. They analyzed for 11.66 and 14.13% nitrogen content, their degrees of substitution being 2.16 and 3.00 respectively. Measurements were made from 0.2 to 4000 Kc and from 15°C to -155°C. The paper was dried in the following manner. It was placed in a cell and evacuated to dryness at room temperature. Next the temperature was gradually raised to 65°C over a 5 to 10 hour period, and then evacuation was allowed to proceed for another 3 to 10 hours, at a pressure of 3×10^{-4} mm. Hg, until no further changes in dielectric properties could be detected. At that point an atmosphere of dry air was admitted into the cell to aid thermal equilibration of the sample and bath. Resulting values for ϵ' and ϵ'' are collected in Tables XLVIII to LI.

The plots of ϵ''_m - t (Fig. 52, 53) show two distinct sets of peaks. They are doubtlessly the same dispersions A and B which were found in weakly plasticized nitrocellulose films. The peaks found with paper are more distinct than the film peaks. This was anticipated, since even the driest film contained some acetone, and with 10% or more of sorbed acetone, dispersions A and B merge. Plots of ϵ' - t corresponding to those of ϵ''_m - t are given in Fig. 54, 55.

Table LII gives values of t_m which were taken from the peak values of ϵ''_m shown in Fig. 52 and 53. From these, plots were made of log$(1/2\pi f)$ - $1/T_m$ (Fig. 56), and the absolute rate theory was employed to calculate the thermodynamic parameters for the relaxation process (Table LIII).

The characteristics of dispersion A for the two degrees of substitution 2.16 and 3.00 were compared. The most significant difference between these materials is the higher degree of lattice order which is known to exist in the trinitrate. This conforms with the thermodynamics of relaxation for dispersion A as substantiated by the following considerations:

(i) For both the nitrocelluloses the entropy of activation is approximately the same due to counterbalancing effects. As the degree of nitration approaches 3 and the binding of the molecules becomes tighter and more orderly, the entropy of activation for breaking an interchain bond diminishes. At the same time, the number of bonds increases. The first effect tends to reduce and the second to increase the entropy of activation for the dielectric relaxation process.

(ii) Because the bonds between the molecules of the trinitrate are tighter and more numerous than those in the other sample, it has the higher enthalpy of activation for the relaxation process. These statements about entropy and enthalpy will hold whether the relaxation is a rotation of nitrate groups or of segments of the nitrocellulose chain.

Dispersions A and B for both papers occurred at lower temperatures than did those for the nitrocellulose film with 0.7% acetone, and slopes of their log ($1/2\pi f$) versus $1/T$ curves are less steep (Fig. 56, curves 2, 3). The largest factor in these differences is probably the freedom from sorbed acetone of the paper dielectric. A second factor may be the heterogeneous nature of the paper dielectric. However, it was not possible from the results of these researches to calculate dielectric values of nitrocellulose from those of the papers, so this factor is an unknown and will be neglected in further discussions. Future measurements should be made as is recommended for cellulose papers in the next section. The influence of acetone on dispersions A and B will be discussed again in a later section.

At high frequency and very low temperature another absorption region was evident (Fig. 53, e.g. at 2000 Kc, t_m = -125°C). This will be designated dispersion E. As will subsequently be discussed it may be related to dispersion D.

5. Cellulose Papers

(a) General

Results obtained with nitrocellulose were presented and discussed in the preceding four sections. This section will deal with work done on the parent compound, cellulose. Measurements were made on cellulose papers dried at 90°C and at 174°C., with frequencies ranging from 0.1 to 4000 Kc. The first paper revealed an important dispersion when measured at temperatures from 90° down to -140°C. Corrections for the dissipation factor of leads were discussed. In their absence extraneous absorption effects were observed.

Formulae to convert ϵ'_m, ϵ''_m, $(\epsilon'_m)_n$, ϵ''_m to ϵ', ϵ'' were presented in Theoretical Development. The mechanics of this conversion and the merits of the formulae are discussed in this section. These formulae were the basis of new semi-empirical formulae which were developed to convert ϵ'_m, ϵ''_m, alone, to ϵ', ϵ''. This conversion was made for results on the first paper.

A secondary peak in the ϵ'' - t curves was shown to be due to electrical leakage in the temperature bath. The primary peaks involved a dielectric dispersion which was shown to be the principle dispersion from the frequencies of its occurrence up to those of light.

Measurements on the paper dried at 174°C showed a second dispersion at high temperatures and low frequencies. Its characteristics suggest that it is caused largely by free rotation of segments of cellulose molecules, although there is probably a contribution from interfacial polarization.

(b) Low Temperature Dispersion of Cellulose Paper Dried at 90°C

Dielectric measurements were made on dry cellulose paper from 90 to -140°C and from 0.1 to 4000 Kc (Experimental). Results for dielectric constant and loss ϵ'_m, ϵ''_m are shown in Tables LIV to LVII. They reveal the same dielectric dispersion which Seidman measured over narrower ranges of frequency and temperature (41). From ϵ'_m, ϵ''_m values of dielectric constant ϵ', ϵ'' for the cellulose in the paper were calculated. The method of calculation will be given later in this section and will be followed by a discussion of this dispersion in terms of homogeneous cellulose.

In Table LV ϵ''_m values were corrected for the dissipation factor of leads from the capacitance bridges to the plates of the dielectric cell. A typical plot of ϵ''_m - f is illustrated by curve 1 in Fig. 57. Curve 2 illustrates a similar plot for values of ϵ''_m which were not corrected for the dissipation factor of the leads. For curve 1, $\epsilon''_m = C_m \epsilon'_m$; for curve 2, $\epsilon''_m = C_{XP} \epsilon'_m$ (Experimental). Values of $C_m \epsilon'_m$ and $C_{XP} \epsilon'_m$ are given in Table LX.

The break in curve 2 was due to a change of capacitance bridges and a corresponding change in leads and lead impedances. This break was eliminated when lead corrections were applied (curve 1). However, there was a sharp increase in ϵ''_m at the highest frequencies. Since similar increases in curve 2 were due to the absence of lead corrections, it is reasonable to suppose that the increase in curve 1 is due to insufficient correction for lead errors.

It was not until considerable experimentation had been completed that the great importance of lead corrections was realized. Measurements of this correction for cellulose nitrate were inadequate, so that only uncorrected values of ϵ'_m are given.

Seidman (41) did not use the right method to correct for the dissipation factor of leads so her values of ϵ''_m do not bear scrutiny as functions of frequency. This fact she realized to some extent and thus restricted her considerations to curves of ϵ', ϵ'' vs. t rather than vs. log f. The latter indicate (a) a false dispersion peak which corresponds to the cusp in curve 2, Fig. 57, and (b) a "false high frequency dispersion" which seems to peak beyond the range of measurement. This second apparent dispersion can also be seen in the graphs of this thesis. Deiser and coworkers (31) observed a similar phenomenon for cellulose nitrate and other cellulose esters.

The author believes that the "false high frequency dispersion" is indeed illusory and is due to insufficient lead corrections. If there were a Debye dispersion at these high frequencies, it would shift to lower frequencies at lower temperatures. Measurements in this investigation have been made as low as -155°C, yet this high frequency dispersion still persists with no indication of its imminent resolution into distinct absorption peaks. At the same time, temperature scanning at constant frequency has revealed low temperature dispersions D and E which are independent of this high frequency dispersion. Finally, correction figures of the magnitude necessary for high frequencies are not known with sufficient accuracy to give significant values for corrected ϵ''_m. There can be little doubt that the high frequency loss under discussion is spurious.

(c) Formulae for dielectric constant and loss of cellulose from Those for Cellulose Paper

Dry paper has been called a composite dielectric being composed of cellulose and air. In Theoretical Development, formulae were derived which related the dielectric constant and loss of paper (ϵ'_m, ϵ''_m) to those of the cellulose in the paper (ϵ', ϵ''). The validity of some of these formulae will be checked in the following paragraphs, and further formulae for the limited results of this investigation will be presented.

(i) Sheets and fibres parallel to dielectric plates

The most straightforward check is that for a paper sheet in which the fibres lie in the plane of the sheet while it lies between two dielectric plates. In this way the electric field of force between the plates is normal to axes of the fibres and equation 30 or 32 applies.

Brown measured H' for the cellulose of linen paper by the method of mixtures (42) and found it to be 5.27 at 300 Kc and 25°C. This paper was dried under vacuum at 25°C. He also measured H'_m for the paper in air, and found it to be 1.363 under the following conditions: weight of the paper sample was 17.82 gm; it was confined in the cell to a volume of 45.10 cc. Using the value of 1.55 gm./cc. for the density of cellulose, the partial volume of cellulose in the paper, $\bar{V}_2$, was 0.255.

In the present investigation equation 30 for cylindrical fibres yielded a value of 6.0 for H'. This represents 14%

error, against Brown's figure, but compares favorably with 55% error for Argue and Maass' formula. Their formula is similar in form to equation 33 but has no allowance for anisotropy. Equation 32 gave a value of 5.82 for H' which means only 10% error. This indicates that equation 32 for fibres of square cross-section is the better one; it will be used throughout the remainder of this discussion.

When Brown's experimentally established value H' = 5.27 is used to calculate values for H'_m by equations 33, 30 and 32, the margin of error shrinks notably. As compared with Brown's experimental result $H'_m = 1.363$, the three equations above give 2.290, 1.342 and 1.350 respectively. The last is only 1% out.

The calculations show that H' is very sensitive to small changes in H'_m. A 1% experimental error in the determination of H'_m makes a 10% error in the calculated value of H'.

(ii) Fibres oriented by angle θ from plane of sheet

Orientation of fibres can cause major changes in the observed dielectric constant ϵ'_m of paper. Two factors are involved; one is due to geometry, the other to anisotropy. The geometrical formulae change in form from that of 32 to that of 33 as the orientation of the fibres changes from being parallel to being normal to the dielectric plates. At the same time the mean dielectric constant of a fibre changes from H' through to V'.

With the formulae in hand it is necessary to measure ϵ'_m and $(\epsilon'_m)_n$ under conditions which are in all other respects similar. It is also necessary to make these two measurements under one set of conditions for which H' and V' are known so that θ can be determined. This will be seen from the formulae:

$$H'_m = 1 - (\bar{V})^{\frac{1}{2}} + H'/\ H'\ [(\bar{V}_2)^{-\frac{1}{2}} - 1] + 1 \quad \ldots\ \underline{32}$$

$$V'_m = 1 + (V' - 1)\ \bar{V}_2 \quad \ldots\ \underline{33}$$

$$\epsilon'_m = V'_m \sin^2\theta + H'_m \cos^2\theta$$

$$= (V'_m - H'_m) \sin^2\theta + H'_m \quad \ldots\ \underline{41}$$

$$(\epsilon'_m)_n = (V'_m - H'_m)(\cos^2\theta)/2 + H_m \quad \ldots\ \underline{42}$$

When H', V' are known, H'_m and V'_m can be readily calculated. Hence θ can be obtained from either <u>41</u> or <u>42</u> and ϵ'_m or $(\epsilon'_m)_n$ respectively; a check for θ is thus provided.

Once θ is known, determinations of ϵ'_m and $(\epsilon'_m)_n$ can be made for any conditions of frequency and temperature. H'_m and V'_m are two unknowns for the two equations <u>41</u> and <u>42</u>. H' and V' follow from equations <u>41</u> and <u>42</u> respectively. If the mean dielectric constant ϵ' is then desired, it can be obtained from

$$\epsilon' = V' \sin^2\theta + H' \cos^2\theta \quad \ldots\ \underline{40}$$

(iii) <u>Calculations of dielectric constant of cellulose from determinations of ϵ'_m without determinations of $(\epsilon'_m)_n$</u>

Because no measurements with the sample sheet normal to the dielectric plates were made in the present study, it was necessary to devise some compromise in the application to the equations just discussed.

By the method described above using equations 32, 33 and 31, θ was determined from values $V_2 = 0.293$ and $\epsilon'_m = 1.588$ at 300 Kc, 25°C, and 3×10^{-4} mm. Hg (Experimental). It was at this frequency and this temperature that Brown found $H' = 5.27$ and $V' = 7.19$ for dry paper. Hence $H'_m = 1.422$, $V'_m = 2.812$ and $\theta = 20° \, 15'$ for the present sample.

Some of this orientation is due to the presence of cotton in the paper (25% cotton, 75% bast fibre by microscope (41); fibrils in cotton spiral around the cotton fibre thus effecting an orientation of crystalline regions with respect to the fibre direction. As the sheet used was a piece of filter paper, most of the orientation is probably that of the fibres from the plane of the sheet.

At other frequencies and temperatures, H' could not be determined. The compromise to get around this stalemate was to use the following semi-empirical formulae for the mean dielectric constant ϵ':

$$\epsilon'_m = v'_m \chi \sin^2 \theta + h'_m \xi \cos^2 \theta \qquad \ldots\ldots 73$$

$$h'_m = 1 - (V_2)^{\frac{1}{2}} + \epsilon'/\epsilon' [(V_2)^{-\frac{1}{2}} - 1] + 1 \qquad \ldots\ldots 74$$

$$v'_m = 1 + (\epsilon' - 1)V_2 \qquad \ldots\ldots 75$$

where v'_m, h'_m are defined by equations 74, and 75 and χ and ξ are constants. On comparing equations 75 and 42 it is seen that v'_m is smaller in magnitude than V'_m --since ϵ' is smaller than V'. Similarly, by equations 74 and 33, h'_m is greater than H'_m--since ϵ' is greater than H'. ξ and χ are therefore selected such that:

$$h'_m \xi = H'_m \qquad \qquad .... \underline{76}$$
$$v'_m \chi = V'_m$$

Then equation 73 is valid--from equation 41--whenever equation 76 is valid.

For the results of Brown and the author at 300 Kc and 25°C, the values of H', V', θ, V_2 are known. ϵ' is given by

$$\epsilon' = V' \sin^2 \theta + H' \cos^2 \theta \qquad \qquad .... \underline{40}$$

to be $\epsilon' = 5.50$.

From equations 74, 75, h'_m and v'_m were found to be 1.962 and 2.319 respectively. Since H'_m and V'_m are 1.422 and 2.812, the values of ξ and χ are respectively 0.994 and 1.212.

It is very unlikely that ξ and χ will be truly constant for conditions other than 300 Kc and 25°C but they probably change slowly enough that their use is temporarily permissable. Tentative values of ϵ' have been calculated for the results on cellulose paper up to 90°C.

ϵ'_m was calculated for some specific values of ϵ' and a plot was made (Fig. 58). Values of ϵ' corresponding to all experimental values of ϵ'_m were then read off the graph.

(iv) Dielectric loss of cellulose from determinations of both ϵ''_m and $(\epsilon''_m)_n$

If, in the future, measurements are made of dielectric losses of paper ϵ''_m and $(\epsilon''_m)_n$, they will doubtlessly be made in conjunction with measurements of dielectric constants ϵ'_m and $(\epsilon'_m)_n$. From the latter, as was previously shown in this section, values of H', V', H'_m, V'_m and θ will have been determined. Hence values of H''_m, V''_m and of H", V" can be calculated from the equations derived in Theoretical development:

$$\frac{1}{\sqrt{(H'')^2+(H')^2}} = \frac{1}{\sqrt{(H''_m)^2 + (H'_m)^2 + (\bar{V}_2)^{\frac{1}{2}}-1}} - [(\bar{V}_2)^{-\frac{1}{2}} - 1] \quad \dots\dots \underline{44}$$

$$V''_m = V'' \sqrt{\bar{V}_2 \; (V'_m/V')} \quad \dots\dots \underline{46}$$

$$\epsilon''_m = V''_m \sin^2\theta + H''_m \cos^2\theta = (V''_m - H''_m) \sin^2\theta + H''_m \quad \dots\dots \underline{49}$$

$$(\epsilon''_m)_n = (V''_m - H''_m)(\cos^2\theta) / 2 + H''_m \quad \dots\dots \underline{50}$$

H''_m and V''_m are two unknowns for the two equations 49 and 50 and can therefore be found. From H''_m and V''_m, equations 44 and 46 yield values for H" and V" respectively. The mean dielectric loss of the cellulose may then be obtained from

$$\epsilon'' = V'' \sin^2 \theta + H'' \cos^2 \theta \quad \dots\dots \underline{48}$$

(v) Dielectric loss of cellulose from determinations of ϵ''_m without determinations of $(\epsilon''_m)_n$.

Measurements on dielectric loss ϵ''_m of paper lying parallel to the dielectric plates were made in the present investigation along with measurements on dielectric constant ϵ'_m. As previously shown in this section, compromise formulae 73 to 76 led to tentative values for the mean dielectric constant of cellulose ϵ' and for h'_m, v'_m which are defined by equations 74, 75 respectively.

Terms h''_m, v''_m are now defined by the following equations in terms of the mean dielectric loss ϵ'' of cellulose in the paper:

$$\frac{1}{\sqrt{(\epsilon'')^2+(\epsilon')^2}} = \frac{1}{\sqrt{(h''_m)^2+(h'_m)^2} + (\bar{V}_2)^{\frac{1}{2}}-1} - [(\bar{V}_2)^{-\frac{1}{2}} - 1] \quad .. \ \underline{77}$$

$$v''_m = \epsilon''\sqrt{\bar{V}_2 \ (v'_m/\epsilon')} \quad .... \ \underline{78}$$

It is presumed by analogy that

$$\epsilon''_m = v''_m \, \chi \sin^2\theta + h''_m \, \xi \cos^2\theta \quad .... \ \underline{79}$$

This gives three equations for the three unknowns v''_m, h''_m and ϵ''_m.

A family of curves of $\epsilon'' - \epsilon''_m$ was prepared (Fig. 59) for different values of ϵ'. This was done by selecting values of ϵ', ϵ'' and calculating the corresponding values of h''_m and v''_m from equations 77 and 78; finally, h''_m and v''_m were substituted in equation 79 to obtain ϵ''_m.

The mean dielectric loss ϵ'' of cellulose in paper was then found from values of ϵ' and ϵ''_m, and by interpolation from Fig. 59.

(d) Low Temperature Dispersion of the Cellulose Component of Dry Paper

Results for dielectric constant and loss for dry paper are given in Tables LIV, LV. The preceding section outlines a method for converting these into values for dielectric constant and loss ϵ', ϵ'' of the cellulose in the paper. The converted values are given in Tables LVI, LVII.

Plots of ϵ' - t, ϵ'' - t are shown in Fig. 60 and Fig. 61. The principal dispersion region is clearly visible in both sets of curves. It will be discussed later.

A secondary absorption peak was detected at low frequencies and in the neighbourhood of 0°C (see curve for 0.2 Kc, Fig. 61). This was found to be due to leakage via the bath as was demonstrated by the following experiment. The cell was emptied of paper, cleaned, evacuated, and immersed in an alcohol bath. Since alcohol has a higher conductance than toluene, the regular bath liquid, leakage effects were more pronounced than in ordinary experimentation. The capacitance C_{XP} and dissipation factor D_X of the empty cell were measured (Tables LVIII, LIX). Plots of C_{XP} - t and D_X - t showed that both $C_{X\rho}$ and D_X had maxima around 0°C, (Fig. 62). The maxima were not evident at frequencies over 100 Kc; they became more pronounced as the frequency was lowered. These characteristics were identical to those of the secondary peak for ϵ'' - t in Fig. 61. At 0°C and low frequencies there was even an increase in the value of ϵ' over that expected from smoothed curves of ϵ' - t (Fig. 60). This spurious effect was presumably magnified by a bare lead which passed through the bath from the outside of the cell to the grounded post of the capacitance bridge. Measurements on nitrocellulose were performed with the Balsbaugh and film cells which were free of electrical connections through the bath, so results on nitrocellulose were probably free of this distortion.

The principal dispersion of cellulose in the present measurements will be termed the low temperature dispersion; a dispersion at higher temperatures will be discussed later on. The low temperature dispersion was previously mentioned and is illustrated by plots of ϵ' - t, ϵ'' - t (Fig. 60, 61). It may also be illustrated by plotting ϵ', ϵ'' as functions of frequency (Fig. 63, 64). The latter plot is masked to a certain extent by the high frequency losses referred to earlier in this section. In spite of this, there is fair agreement between the temperature-frequency characteristics of the dispersion as taken from curves of ϵ'' - t and ϵ'' - f. Values of t_m and f_m corresponding to peak values of ϵ'' are recorded in Table LXI and curves of log (1/2πf) vs. $1/T_m$ and of log $(1/2\pi f_m)$ vs. 1/T were drawn (Fig. 65). The two curves are not coincident but they are linear, parallel and close together, indicating that the temperature-frequency characteristics of the dispersion are essentially similar for the two ways of detecting them.

Seidman and Mason (44) determined the log (1/2πf) vs. $1/T_m$ characteristics of this dispersion for cellulose paper dried at 25°C. The present results show that this dispersion is undoubtedly the one which Muus (45) termed a "high frequency dispersion." He was not able to span the absorption peak using frequencies up to 100 Kc and temperatures down to 21°C. This failure is understandable, for extrapolation to 21°C in Fig. 65 shows that the absorption peak occurs at $f_m = 400$ Kc. Within the temperature and frequency range of Muus' measurements, Muus and the writer each found a single dispersion; the former termed it a "high frequency dispersion" while the latter labelled it a "low temperature dispersion." Evidently both names apply to the same dispersion.

Thermodynamic parameters were found for the relaxation mechanism of this dispersion; their values as determined by Seidman and Mason (41), Muus, and the writer are compared in Table LXII. Muus, of course, had to estimate his values. This was done by employing the distribution function for relaxation times proposed by Fuoss and Kirkwood (73) and by fitting theoretical and experimental curves $\epsilon'' - f$ at different temperatures. The values are in fair agreement. Those from curves of log $(1/2\pi f)$ vs. $1/T_m$ are most free of error, although curves of log $(1/2\pi f_m)$ vs. $1/T_m$ are theoretically better. f_m, unlike t_m, is obtained at a constant temperature. This is advantageous in that cellulose does not change its physical properties during the determination of f_m (Introduction, Part 3). Consequently the thermodynamic parameters derived from t_m are more accurate than the others.

Thermodynamic parameters of this low temperature dispersion for cellulose resemble those for dispersion A of nitrocellulose papers (Table LXII). The likelihood that they both are due to the same mode of relaxation will be discussed further in the General Discussion.

The dielectric constants determined for cellulose are very interesting, particularly when plotted against frequency (Fig. 63). At 90°C the low temperature dispersion of ϵ' is insignificant below 300 Kc. At lower temperatures it shifts to lower frequencies. At -115°C ϵ' is almost constant at frequencies above 300 Kc. The limit of the dispersion is most readily estimated (74) from a Cole-Cole plot (Fig. 71). The limit at 25°C is 3.5. This value may be appropriately compared with the values of the optical dielectric constant.

The refractive indices of ramie and flax in the axial and normal directions of the fibre are 1.596 and 1.528 respectively (75). These correspond to optical dielectric constants of $(1.596)^2 = 2.55$ and $(1.528)^2 = 2.33$. These figures indicate that there is at least one more dispersion at frequencies higher than those of the "low temperature dispersion" of this section. However, it cannot be the same as the "false" dispersion discussed previously. The latter was due to leakage because observed ϵ''_m indicated that the false dispersion would have much higher loss peaks than did the "low temperature dispersion"; hence dispersion of ϵ' would be larger for the former than the latter. Such is not the case, for the "low temperature dispersion" increases ϵ' from 3.5 to 5.9--an increase of 2.4; the residual dispersion of ϵ' is from 2.3 or 2.5 to 3.5--an increase of only 1.1.

In conclusion, as far as the derived values of ϵ' hold, the "low temperature dispersion" of cellulose is the major one which occurs at room temperature between the frequencies of its occurrence and optical frequencies.

(e) High Temperature Dispersion of Cellulose Paper

Indications of a second dispersionfor cellulose were observed at low frequencies with high temperatures. At 0.2 Kc a distinct increase in ϵ'' occurred as the temperature was raised from 20°C to 90°C (Fig. 61). Further measurements were made up to 175°C and 264°C. Because of differences in degree of dryness at different times during the experimentation, the sample was referred to as cellulose paper (b) and cellulose paper (c) for the two sets of results.

Measurements of ϵ'_m, ϵ''_m for cellulose paper (b)(Table LXIII) are useful when compared with those on cellulose paper (c)(Table LXIV, LXV) to show the moderate change in properties due to preliminary drying at 90 and 174°C respectively.

Plots of ϵ'_m - log f (Fig. 66) reveal a sharp increase in ϵ'_m at low frequencies and temperatures over 174°C. At the same time, values of ϵ''_m increase with lower frequencies and higher temperatures. Plots of log ϵ''_m - log f (Fig. 67) are linear over a large range of frequencies. They show signs of peaking at frequencies lower than the limits of measurement (0.05 Kc) for temperatures over 200°C. The absorption moves to higher frequencies at higher temperatures and is of much greater magnitude than that of the "low temperature dispersion."

From Fig. 67 it appears that the dispersion has been spanned as a function of temperature at 0.05 Kc. This is probably deceiving for drying of the paper occurred about 224°C, as is seen from the smaller rate of increase in ϵ_m'' with temperatures above 224°C regardless of the operating frequency.

Drying is not the reason for curvature at low frequencies of the 224, 249 and 264°C curves. Measurements were made at each of these temperatures with respectively increasing, decreasing and increasing frequencies. Spanning of the peak is therefore imminent. The author estimates that peaking of the 264°C absorption curve occurs at nearly 5 c.p.s. An estimate was also made of the enthalpy of activation for the dispersion. On the assumption that the frequency-temperature dependence of $\epsilon_m'' = 0.05$ was the same as the frequency-temperature dependence of the dispersion peak, frequencies f_m were taken from Fig. 67 such that $\epsilon_m'' = 0.05$ for the curves at different temperatures. (Table LXV1). From a plot of log $(1/2\pi f_m)$ vs. $1/T$, a slope and its corresponding ΔH^* was determined; $\Delta H^* = 24.4$ Kcals/mole. Accordingly, the peak would occur at 3.3×10^{-7} c.p.s. at 25°C; hence ΔF^* at 25°C = 25.2 Kcals/mole, and $\Delta S^* = -3$ e.u.

Muus made measurements on cellophane up to 70°C and witnessed the same dispersion. With sufficient sorbed water, curves of $\log \epsilon_m''$ - $\log f$ were also linear. Assuming a Fuoss-Kirkwood distribution of relaxation times for this dispersion, and after a process of curve fitting, he arrived at the following thermodynamic parameters of relaxation:

$\Delta F^* = 17.00$ Kcal./mole, $\Delta H^* = 20.50$ Kcal./mole, $\Delta S^* = 11.8$ e.u.

These figures are far from accurate, for calculation from them gives f_m = 0.34 c.p.s. at 25°C and 2.8×10^9 c.p.s. at 250°C. Muus attributed the dispersion to rearrangement of hydroxyl groups in crystalline regions of cellophane. He suggested that the extra dielectric losses found with 2-4% sorbed water were due to interfacial polarization of the Maxwell-Wagner mechanism. The present results indicate that such may be the principal mechanism for the dispersion of even dry cellulose; however, another possibility is that this is a dispersion which, as in ice, occurs at temperatures just below the melting point.

A curious phenomenon stems from consideration of values of $'_m$ which are constant over an interval of frequency between the high and low temperature dispersions. These plateau values (ϵ_{pl}) of ϵ'_m can be found by extrapolation to $\epsilon''_m = 0$ on a Cole-Cole plot of ϵ''_m vs. ϵ'_m (Fig. 68). ϵ_{pl} was determined for temperatures 90 - 264°C (Table LXVII) and a plot of ϵ_{pl} vs. t was made (Fig. 69). It exhibits a cusp peaking at 211°C, the low temperature curve being festooned and the high temperature curve being arched. The sample when at 226 and 249°C released volatiles which condensed into clear aqueous droplets on those walls of the cell which extended above the temperature bath.

At 264°C the condensate was tarry from strong decomposition. However, the 226°C value of ϵ'_m has been only slightly affected by the loss of volatiles. The affect can be estimated from the fact that cellulose paper (b) appeared to produce at least as much condensate at 175°C as did cellulose paper (a) at 226°C. Comparing ϵ_{pl} of cellulose (b) at 91°C before loss of of volatiles with cellulose (c) at 91°C after loss of volatiles, their values are 1.656, 1.670 respectively--a difference of 0.016. As a continuation of the festooned curve, ϵ_{pl} at 226°C should have been 0.08 higher than the observed value--a loss too high to be caused by decomposition alone. The dashed curve in Fig. 69 is estimated for a case where there is no decomposition.

The sharp rise followed by a small change in dielectric constant (Fig. 69) is characteristic of molecular rotation in crystals near a melting point (77). The melting point occurs at the point of the cusp or at higher temperatures as in the case of di-isopropyl ketone (76). In line with this concept, the melting point of cellulose was given by Zechmeister and Toth to be somewhat higher than 270°C. This melting point is indicative although it was a vague decomposition point. A further complicating factor is that the degree of order varies throughout cellulose. Probably, melting really occurs over an interval of temperatures as it does with glass, and that previous to this melting, rotation occurs.

Partington (77) states that "a relatively symmetrical gravimetric and volumetric distribution of atoms around the centre of gravity of the molecule facilitates its rotation in the crystal." Cellulose is such a molecule. Probably the high temperature dispersion of cellulose is due to rotation of cellulose molecules or molecular segments.

ϵ_{pl}, however, is not influenced by the mechanism for high temperature dispersion. It is affected by the low temperature dispersion. Relaxation of hydroxyls could not conceivably be responsible for the festooned portion of Fig. 69. However, rotation of segments of the cellulose molecule could well be the effective mechanism.

Mechanisms of dielectric relaxation for both the high and low temperature dispersions will be further discussed in the General Discussion which follows.

6. General Discussions

(a) General

In the preceding sections of Results and Discussions the existence of anomalous dielectric dispersion in nitrocellulose was clearly demonstrated. It is true that spurious effects were encountered, but at least four and possibly five dispersion regions were identified. The following effects have already been discussed: measurements on solutions in acetone, solvate formation with camphor, small changes in degree of nitration, and mixed solution and solvate effects on sorption of acetone.

In this section the five dispersions will be discussed in the order of their alphabetical designations, A, B, C, D, and E. Similarities between two of the dispersions for nitrocellulose, A and C, and the two dispersions for cellulose, low and high temperature, will be commented on. Finally some remarks will be made about the dynamic mechanical properties of cellulose and its derivatives.

(b) Dielectric Dispersions

(i) Low temperature dispersion for cellulose and dispersion A for nitrocellulose

(1) Comparison of modified Cole - Cole plots at 0.2 Kc for the low temperatuve dispersion of cellulose and for nitrocellulose film no. 1 indicates that the dispersions are remarkably similar (Fig. 70). Extrapolation of the curves $\epsilon'' \equiv 0$ gives values of $\epsilon'' = 3.2$ for both materials. Their refractive indices are nearly equal, the principal one for nitrocellulose being 1.514 (64). The corresponding optical dielectric constant is $(1.514)^2 = 2.3$. Therefore, just as the low temperature dispersion of cellulose was shown to be the principal one (except for the high temperature dispersion) up to optical frequencies, the same line of reasoning indicates that dispersion A for nitrocellulose is the main dispersion between the frequencies of its occurrence and those of light.

(2) As plasticization progresses, the radius of the Cole - Cole plot shortens and the curve itself is more sharply arched. This effect was observed under two sets of conditions:
(i) At constant frequency, the plots being for different concentrations of acetone sorbed by nitrocellulose (Fig. 70).
(ii) At constant temperatures, the plots being for cellulose at different temperatures (Fig. 71).

A more direct comparison with (i) can be made from Seidman and Mason's results with the sorbents water, methanol and ethanol. Their values of ϵ''_T increased markedly with sorption, illustrating the same trend as (i).

(3) Thermodynamic parameters are also significant. In the last section they were shown to be nearly the same for dry papers of cellulose and nitrocellulose (Table LXll). For both materials H* and S* increased with sorption of volatiles up to the maximum values given in Table LXVlll. The values are higher for water than for methanol or ethanol sorbed on cellulose. They are still higher for acetone sorbed on nitrocellulose. Nevertheless the trend with sorbates is similar for the dispersions of both cellulose and nitrocellulose.

These three points of similarity are good evidence that the same basic mechanism is responsible for both the "low temperature" dispersion for cellulose and dispersion A for nitrocellulose.

Stoops (42) and Jatkar (34) were in essential agreement with this thesis. Working with derivatives of cellulose in solution, they considered that one main dispersion occurred between megacycle and optical frequencies, and that the dipole relaxation responsible for dispersion was the same for all the derivatives and cellulose itself. Jatkar backed these concepts with the results of Sakurada and Lee (32) in which similar specific polarizations were found for trisubstituted derivatives. Stoops based his conclusions on his detection of a dispersion in cellulose triacetate which was similar, though less marked, to that of cellulose. Dieser and coworkers (31) found dispersion peaks for cellulose propionate and acetate but apparently did not attribute any mechanism to them. At 25°C the peaks occurred at 70 and 1000 Kc respectively. From curves for the propionate of loss factor versus frequency the data in Table LXIX was derived. These thermodynamic parameters may be badly in error, but as they stand they are in fair agreement with the same parameters for cellulose and nitrocellulose. All in all, the evidence indicates that dispersion A is common to cellulose and its derivatives. This will be assumed in further discussion.

Three mechanisms have been suggested for the dispersion:
(a) relaxation of restricted hydroxyls for cellulose,
(b) rotation of anhydroglucose units for cellulose and derivatives.
(c) rotation of cellobiose units for cellulose and derivatives.

The counterpart of mechanism (a) for derivatives of cellulose is relaxation of restricted substituent groups. Lee and Sakurada found an increase in dipole moment with temperature for some derivatives in solution. This dispersion with acetates of cellulose, cellobiose and glucose (33) and of ethyl and benzyl cellulose (34) was attributed to the relaxation being a hindered rotation of substituent groups.

In view of the effect which impurities have been found to make in the present work on solutions, it is conceivable that some of Lee and Sakurada's materials may have been subject to the same effects. Indeed, the writer believes that there is as much reason to attribute their observed dispersion to impurities as there is to attribute it specifically to rotation of the substituent groups.

Arguing in favour of mechanism (a), Brown (42) asserted that rotation of anhydroglucose units was not compatible with the anisotropy of cellulose. The dielectric constant in the direction of the fibre axis was 7.19, but only 5.27 in the direction normal to the axis. He pointed out that rotation of the glucose anhydride rings in the chain direction is highly improbable. The greater polarization in the axial rather than the transverse direction therefore suggested to him that rotation of the glucose anhydride ring is not responsible for dispersion A.

However, it is quite possible that orientation of glucose or cellobiose units is caused by forces which pass along the molecule. The two factors (1) and (2) given below could understandably combine to effect a larger polarization in the axial rather than the transverse direction of the fibre.

(1) Theoretical Development and the preceeding section of Results and Discussions combine to show that contribution to dielectric constant of paper is much greater when fibres are in the field direction rather than normal to the field. It is conceivable when linear molecules in homogeneous cellulose are substituted for fibres in paper that the same effect will hold. A greater density of lines of force should pass lengthwise through the molecule rather than through the inter-molecular spaces and the polarization would be larger.

(2) When a cellulose molecule is in the direction of a field it is improbable that the molecule is under a tensile stress; these stresses may be subject to

relaxation by the rotation of a glucose or cellobiose unit. An example of how easily this could occur is given by a strand of string passing through an eccetric hole in a button; when the string is snapped taut the button rotates. When a macromolecule lies in an alternating field, there must be rapid rearrangement of the molecular field and it is probable that there are frequent rearrangements which are favourable to rotations of glucose or cellobiose units.

An argument against mechanism (a) is that relaxation of hydroxyl groups in cellulose is subject to different basic moments than relaxation of ester or ether groups. Also, the intermolecular restrictive forces are dissimilar, as was stressed by Spurlin (4). If mechanism (a) is the true explanation, the similarities found between the dispersions of cellulose nitrate and its parent compound would be entirely fortuitous.

Meyer (78) considered that mechanisms (b) and (c) were possible both in cellulose and in its derivatives. He said, "Chains which are not associated to form crystallites need not retain a stretched form, for, although the framework of the glucose rings must be assumed to be fairly rigid, rotation or vibration "about the bridging COC - linkages" appears entirely possible."

In Discussions on Cellulose Paper, a cusp was observed in ϵ_{pl}-t (Fig. 69). The sharp increase in this curve at temperatures approaching 211°C also indicates that dispersion A is due to rotation of molecules or possibly of monomeric or dimeric, etc. units.

Lee and Sakurada calculated dipole moments of cellulose derivatives on the basis of a glucose unit. This is the way that dipole moments should be calculated if Stoops' mechanism (b) is effective. As was mentioned in the Introduction dipole moments calculated in this way are nearly identical for cellulose trinitrate, triacetate and starch triacetate. This much conforms with Stoops' theory, but the dipole moment for disubstituted cellulose acetate was also the same as that of the trisubstituted materials. Jatkar reasoned that the discrepancy vanishes if cellobiose is the base unit. He assumed that the dipole moment of the cellulose unit was the resultant of the dipole groups in the unit. Further assuming that there was considerable freedom of rotation of substituent groups, he reasoned that the contributions to the resultant would cancel out if the unit were symetrically substituted as in the case of mono-, di-, and tri-substituted glucose units. He believed that this was true for the substituents being in the positions 6, 6', 3, 3', according to the theory of Haworth (Fig. 1).

Using a modified Debye-Classius-Mossotti equation, and combining his results on nitrocellulose with Lee and Sakurada's, Jatkar gave both experimental and theoretical evidence to indicate that evenly substituted cellobiose units had a dipole moment of 2.0 D, while the oddly substituted units had a dipole moment of 7.7 D. Experimental discrepancies for the tetra-substituted units were attributed to a lack of homogeniety in degree of nitration.

The chemical evidence of Haworth and the X-ray evidence of Meyer and Mark support the theory that the cellobiose unit is the base unit of cellulose. The optical activity of cellulose and its esters provides further evidence in support of this theory.

According to Haworth esterifications proceed in the order 6, 6', 3, 3', 2, 2' (Fig. 1), however Spurlin believed that substituents are attached to esters according to a preferred distribution instead of selectivity (79)--for example, in a dinitrate, the 6 positions would be mostly substituted, the 3 position more than half substituted and the 2 position somewhat less. A selectively substituted 3, 6 dinitrate has recently been prepared by Falconer (80) according to a modification of the method of Segall and Purves (81). A trinitrate was partially de-esterified with pyridine in the presence of O-methyl Hydroxylamine.

The selective substitution was identified with the help of a chromatographic method; the dinitrate was hydrolyzed to substituted glucoses and the glucoses were separated and identified. By the same method, the distribution of substituents on any cellulose nitrate may be determined at least on the basis of the glucose unit.

This tool is available for future workers on the dielectrics of nitrocellulose. Dielectric work with different nitrates, especially the dinitrate, trinitrate and an intermediate nitrate promises to clarify the present status on the dipole rotor in cellulose nitrate and cellulose.

In the meantime Dyson's method (72) can be used to estimate (a) the mean number, $\bar{n}$, of glucose units involved in rotations and (b) the mean number, $\bar{r}$, of alternative configurations possible in the activated state. The entropy of activation is given by

$$\Delta S^{*} = R \ln (\overline{r^{n}}) \qquad \ldots\ldots 80$$

where R is the gas constant. Meyer's value of the molar cohesion between cellulose chains is 6200 cal. per mole (82). If the relaxation mechanism involves $\bar{n}$ monomer units in co-operative motion, the heat of activation will be of the order of 6200 $\bar{n}$ cal. per mole. The value of $\bar{r}$ is derived from

$$\Delta H^{*}/ \Delta S^{*} = 6200\ \bar{n}\ (R\bar{n}.\ \ln\ \bar{r}) = 6200/ (R \ln \bar{r}.) \ldots.\ 81$$

From the data in Table <u>LX11</u> $\Delta H^{*}/\Delta S^{*} = 2160^{o}K$, $\bar{r} = 4.2$ and $\bar{n} = 1.5$. This last value implies that one and a half glucose units comprise a dipole rotor. Since this is impossible, there must be both glucose and cellobiose rotations. There may also be rotations of larger chain lengths, but the majority must be glucose and cellobiose units. This is in accord with an average of only four possible configurations in a rotation.

Such a complex system of dipoles would explain an apparent discrepancy in Jatkar's theory. The dipole moment of cellulose and of starch triacetate was found by Lee and Sakurada to be the same. Jatkar recognized that the base unit of starch is glucose and that Lee and Sakurada's findings were inconsistent with his cellobiose theory for cellulose. He attributed the discrepancy to incomplete substitution of one or both derivatives. However, if one, two, three or more glucose units were involved in dipolar orientation of both starch and cellulose, then it is evident that a smoothened dipole moment will result. It could lie between the values expected for rotation of glucose or cellobiose units. Similarly a disubstituted cellulose would have a dipole moment which was a little different from trisubstituted or other ordinarily substituted materials. The dipole moment for unsubstituted cellulose would be lower according to the principle of vectorial summation by induction of moments within the rotor. However, this deficit might be compensated by a greater increment to the moment from induction of neighbouring chains and units.

Dipole rotors of one, two or more glucose units may be subject to unusual solvent effects. This may explain an anomalous effect by solvents on the dipole moments of nitrocellulose. Dipole moments were determined by Jatkar and coworkers using butyl and isoamyl acetates as solvents (Table LXX). The differences in moment for the two solvents was highest for cellulose nitrate of D.S. about 2. Jatkar attributed the high moments to mixtures of nitrates of D.S. 1.5 and 2.5, each of which have high moments according to his cellobiose rotor theory. Although he was aware of the discrepancy with different solvents, he did not attempt to explain them. It is possible that the ratio of cellobiose to glucose rotors differs in different solvents.

Results presented in this paper and the foregoing considerations indicate that the probable mechanism for Dispersion A is that of rotation of glucose, cellobiose, cellotriose, etc. units such that the overall effect is of a unit half way in size between a glucose and cellobiose unit. A future investigation will be helped by (a) realization of some of the limitations of the present experiments and results and (b) suggestions that have been made to overcome them. Determinations which are devoid of spurious frequency effects will be extremely helpful in either disproving or confirming the above hypothesis..

(ii) Dispersion B

This dispersion was observed as a set of secondary absorption peaks for nitrocellulose films and papers (Figs. 45, 47, 52, 53). Dispersion B is not caused by spurious bath effects such as were responsible for the secondary peak at 0.2 Kc in the absorption curve for cellulose paper "a" (Fig. 61). Accompanying the spurious peak was a hump in the ϵ' - t curve (Fig. 60). However no such hump accompanies dispersion B (Figs. 54, 55.)

Dispersion B was most prominent in nitrocellulose papers, becoming less prominent in films as the acetone concentration increased. It merges with dispersion A when there was 10% or more sorbed acetone and when, as in celluloids, nitrocellulose was plasticized with camphor.

From values of H , S for dispersion B with nitrate papers, the number of glucose units involved in a relaxation are $\bar{n} = 7.7$, and the number of possible configurations for a chain of this length is $\bar{r} = 100$. These values of H S may not be correct because of interference with the values of t_m from dispersion A.

In the amorphous part of nitrocellulose there are points of attachment (hindrances) between pairs of molecules. Dispersion B may be caused by 'evaporation' of segments of molecules from such points. It is reasonable that an average of 7.7 glucose units should be involved in the mechanism. It is also reasonable that with upwards of 10% sorbed acetone there should be few hindrances between unsolvated nitrocellulose chains, and thus that dispersion B should disappear.

(iii) Dispersion C.

The high temperature dispersion for cellulose paper was discussed previously. It displayed a sharp increase in dielectric loss with decreasing frequencies. (Fig. 59, 61). The absorption curves moved to higher frequencies with increase both of temperature and of sorbed water.

Dispersion C for cellulose nitrate films had essentially the same characteristics: there was a sharp increase in loss versus frequency; absorption curves moved to higher frequencies with increases in temperature or sorbed acetone. Because of these similarities and the fact that both dispersions appear at the low frequency and high temperature limits of experimentation, it seems reasonable to conclude that both dispersions are due to the same basic phenomenon.

Estimates were made by Muus and by the author of thermodynamic parameters of the relaxation process for cellulose papers. The estimates disagreed. In part 5 of this section it was shown that there was a considerable possibility of error in Muus' figures. Although the basis for estimating the author's figures was not rigorous, they are probably more accurate than Muus'.

Values of zero or slightly negative values of the entropy have been found for several substances (27) including highly plasticized polyvinyl chloride (10). This is interpreted by Eyring as indicating that the molecules are rotating freely in the normal state. Presumably this could also indicate free rotation of segments of molecules, the segments being in the normal state. Since the molecules of cellulose and nitrocellulose are relatively stiff, it is probable that segments of them undergo this type of rotation. This mechanism may be responsible for dispersion C for it was found to have a slightly negative entropy of activation.

There is little doubt that dispersion C is partially caused by interfacial polarization. This is not the principal contributor, for experimentally, the temperature coefficient of relaxation time is apparently negative and for interfacial polarization it should be positive (83). This being the case, the explanation suggested in the preceding paragraph seems to be a more adequate mechanism for dispersion C.

(iv) Dispersion D and E

Dispersion D was discovered in dry celluloids and was shown to be a Debye type dispersion. It occurred at temperatures below -40°C even at the highest working frequency, 300 Kc.

Dispersion E appeared in nitrocellulose papers at even lower temperatures and higher frequencies. (Fig. 53, e.g. at 2000 Kc, $t_m = -125^oC$). Curves of $\epsilon' - T$ do not show a distinct extra dispersion in this region, but dispersion E is believed to be of the Debye type because values of t_m moved to higher temperatures at higher frequencies.

Dispersion A was attributed to rotation of glucose, cellobiose, cellotriose etc. units on the basis that there was relatively free rotation of nitrate groups. Dispersion E may be due to restricted but 'relatively free' rotation of nitrate groups. Dispersion D occurs at higher temperatures and therefore is more restricted than E, but is probably caused by the same mechanism. The restriction may be due to camphor for it forms a solvate with nitrocellulose through those hydrogens which are on the same carbons as the nitrate groups.

(c) Mechanical Properties and Dielectric Dispersions A, B, C

Theoretical considerations seemed to indicate that there should be good co-ordination between mechanical and electrical properties of polar polymers. Experimental work in this field has provided only partial substantiation for this expectation. Fuoss and coworkers met with some success in comparing dispersions of Young's modulus with that of dielectric constant (84), (85). Nolle found that there was incomplete coordination for rubber, a weakly polar polymer (1). Tuckett (86), Funt (87) and Dyson (26) have attempted to relate dielectric dispersion with such properties as brittle points and second order transition temperatures. No known efforts in this direction have yet been made for cellulose.

A spectrum of Young's modulus against frequency has been proposed (82) in which two dispersions are indicated: a large one at 0.3 cps. and a smaller one at 10^6 cps. The latter is seemingly confirmed from "cold points" which are defined by deflection of dynamic modulus. They occur at -20 and -30°C for cellulose acetate and ethylcellulose respectively. They have not yet been detected for crystalline cellulosic materials such as fibres, but presumably would be at elevated temperatures (82).

This cold point is reminiscent of dispersion B in that it has not been found for cellulose fibres. Also, as the temperature below the "cold point" is increased the chain length between hindrances becomes longer and there is less order in the material. The order disappeared from dispersion B with 10% or more sorbed acetone. Hermans, Kratky and Mark (88) have shown from crystallite order versus elongation curves that dry cellulosic materials have many hindrances. As samples take up solvent the number of hindrances diminishes towards zero.

The dispersion at 0.3 c.p.s. is confirmed by creep curves of acetate, viscose and cotton at 65% R.H. and 70°F; they exhibited inflections in the vicinity of 10 seconds (82). Immediately a correlation with dispersion C is suspected because of the long relaxation times. In creep the secondary forces between chain molecoles must be overcome for flow to occur. Hindrances will disengage and reform, chains and crystallites will orient into the direction of stress, but free rotation of chain segments does not seem to have much bearing on the creep phenomena. Correlations between dispersions A and B and creep might be possible in some future work.

Wakeham (82) has pointed out a second-order transition range of temperature and/or solvation condition at which some low-order crystallites which restrict chain movement are "melting out". For wet cellulose acetate and textile rayons the transition temperature lies between 25 and 75 °C. Completely dry viscose rayon, wet cotton and wet ramie fibres show no evidence of such a transition at temperatures below 90°C. A critical temperature of 211°C was found in the present investigation. It occurred at a cusp in the curve ϵ_{pl} - t (Fig. 69). It is probable that there is a correlation between the temperature of such cusps and the above transition temperatures, but this again, is a problem for future investigation.

The dynamic mechanical properties of cellulose nitrate will parallel those of cellulose and other derivatives. They will be subject to unpredictable low frequency relaxations and "melting out". At high frequencies the Young's modulus will probably pass through two dispersion regions which will correspond to dielectric dispersions A and B.

Of course, many of the concepts contained in this thesis are tentative, but have been postulated in the hope of presenting a unified physical picture of the mechanisms in dielectric relaxation of cellulose and its derivatives, in particular of cellulose nitrates.

SUGGESTIONS FOR FUTURE WORK

1. In any future work the use of guard circuits and guard cells is strongly recommended; these are necessary below 10 Mc in order to remove the effects of surface conductivity and polarization.
2. The investigation of solutions of nitrocellulose may be fruitful if performed with nitrocellulose purified by boiling in distilled water. The dispersion should be investigated at low temperature, perhaps in solution of ethyl acetate instead of acetone.
3. It would be well that the investigations on celluloid be repeated with more concentrations of camphor and that measurements be carried to higher temperatures or frequencies. This is necessary in order to complete the study on kinetics of dielectric relaxation for the camphor-nitrocellulose complex.
4. Future measurements on cellulose or nitrocellulose sheets should be made with the sheet perpendicular as well as parallel to the dielectric plates, and the formulae derived in theoretical development should be tested for their validity.
5. It is recommended that the effect of degree of substitution be studied with sheet specimens provided that the formulae in (4) are valid. They can readily be prepared free of occluded solvent, unlike films, and they are more easily dried of atmospheric moisture. If it is necessary to use films, the acetone may be

leached out with water; this can most readily be done at elevated temperatures. Alternatively, it may be possible to eliminate acetone by evacuating the sample at final temperatures of 60 - 90°C. The results will be more meaningful on samples in which the substitution is selective and identified.

6. Dispersion C of cellulose should be investigated more thoroughly and under more favourable conditions. A transient current method should be used to permit scanning at lower frequencies. Oxygen should be eliminated from the dielectric cell; trickle flushing of the cell with dry preheated nitrogen would provide adequate thermal contact between bath and sample and would remove trace moisture which accelerates decomposition of cellulose.

7. Dispersion C of cellulose nitrate should be followed by the same method as in (6). Fibres would decompose more slowly than films as moisture in the interior of the sample would be removed more easily.

8. Dynamic mechanical and sonic measurements over wide frequency and temperature ranges would be extremely interesting.

CLAIMS TO ORIGINAL WORK AND CONTRIBUTION TO KNOWLEDGE

1. Theoretical techniques were developed for calculating dielectric constant and dielectric loss factor of a hetergeneous material from the dielectric constant and loss of its components - provided that the material can be divided into identical repeating cells, such that the components are symetrically distributed between the upper and lower faces of such cells.

2. Formulae were derived relating the dielectric constant and dielectric loss factor of paper to those of the fibre material. Because of the anisotropic nature of fibres, these formulae were based on measurements being made with the sheet in two directions to the dielectric plates - normal and parallel. The formulae yield the angle of average orientation of fibres to the plane of the sheet and values of dielectric constant and loss of fibres in the axial, radial and mean direction. The mean direction is that for a fibre of average orientation to the plane of the sheet - that is, when the sheet is parallel to the dielectric plates.

3. Semi-empirical formulae were developed relating values of dielectric constant and dielectric loss factor when taken only with the sheets parallel to the dielectric plates. The formulae yield the angle of average orientation of fibres to the plane of the sheet and values of dielectric constant and loss of a fibre in the mean direction.

4. An immersion dielectric cell and techniques were devised for homogeneous sheets and films. Gold or silver dielectric plates were condensed in vacuo on the specimens; the plates were made of such thickness that they provided complete electrical contact to the specimen and, at the same time, were permeable to such vapours as water and acetone. The cell permitted conditioning with the volatiles of the specimen in situ.

5. Values of dielectric constant and dielectric loss factor were determined for cellulose nitrate and cellulose. The cellulose nitrate was investigated as follows: in solution with acetone, as homogeneous sheet plasticized with camphor, as film prepared from solution in acetone and as a paper- that is, a hetergeneous sheet comprised of fibres and air. Cellulose was studied only as a paper; values for the paper were converted into ones for cellulose fibres in the mean direction.

6. From the temperatures of maxima in the loss curves, relaxation times were evaluated. From plots of log $(1/2\pi f)$ versus $1/T_m$, calculations were made at 298° K of the free energy, enthalpy and entropy of activation for dielectric relaxation.

7. Four dielectric dispersion regions of solid nitrocellulose were identified and designated A, B, C, D. Dispersion E, a fifth, was probably the same as dispersion D. They were Debye-type dispersions, modified by a distribution of relaxation times. Most measurements were performed from 0.2 to 300 Kc and from -70 to 25°C.

8. Two dielectric dispersion regions of cellulose were examined and identified with ones found by previous workers. Their findings were consolidated from 0.1 to 4000 Kc and from -115 to 90°C. The high temperature dispersion was studied up to 264°C.

9. The thermodynamic parameters of solid nitrocellulose's dispersion A were considered as functions of camphor and acetone content and of degree of substitution. They exhibited peak values at a camphor content corresponding to a camphor-nitrocellulose solvate; solvate formation, solid solution and changes in degree of crystalline order were considered as functions of acetone content and degree of substitution.

10. Between the regions of dispersion A and C of cellulose, the dielectric constant was constant over a range of frequencies. This plateau value of dielectric constant was plotted against temperature, a curve with a discontinuity resulting. It was compared to similar curves of static dielectric constant against temperature, curves which indicate free rotation of dipolar molecules.

11. Cole - Cole plots of dispersion A for cellulose and cellulose nitrate were drawn. The flatness of the circular arc plots indicated a broad distribution of relaxation times.

12. Of the two dispersion regions of cellulose, the one occurring at lower temperatures and higher frequencies was similar to dispersion A of nitrocellulose, the other to dispersion C.

13. It was established that the dispersions discussed account for the major contribution to dielectric constant of cellulose and nitrocellulose over that calculated from the refractive index of light on the basis of Maxwell's theory.

14. Tentative mechanisms were attributed to the various dispersions; dispersion A was considered to be due to rotation of segments of cellulose or nitrocellulose molecules, the segments averaging one and a half glucose units in length; dispersion B was attributed to 'evaporation' of portions of chains from points of attachment between pairs of molecules in the amorphous parts of nitrocellulose; dispersion C probably was caused partially by interfacial polarization and principally by relatively free rotation of molecules or long segments of molecules; dispersions D and E of nitrocellulose were attributed to 'relatively free" rotation of nitrate groups. These dispersions were discussed re the physical properties of cellulose and derivatives.

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APPENDIX

OF

TABLES AND FIGURES

TABLES

TABLE I

Frequency Range	50 c.p.s. - 20 Kc	35 Kc	100 - 300 Kc	0.55 - 10 Mc
Oscillator	Hewlett Packard, Model 200A		Clough Brengle, Model 110A	
Preamplifier	None			Built to Specifications*
Bridge	General Radio Type, 716-C Capacitance Bridge			General Radio Type 821-A Twin-T Impedance Measuring Circuit
Detector	(a) General Radio Type 1231-B Amplifier (and Null Detector)	(a) RCA Type TE-2368 Radio Receiver (MI-22102 Power unit and MI-2212 Receiver unit)		(a) Halicrafter S-40 Radio Receiver
	(b) General Radio Type 1231-P5 Filter	(b) Earphones or Sylvania Electric Type 112 Cathode-Ray Oscilloscope		(b) Earphones
	(c) Sylvania Electric Type 112 Cathode-Ray Oscilloscope			

* See Funt (28)

TABLE II

APPARENT DIELECTRIC CONSTANT OF CELLULOID IN FILM CELL WHEN USING METALLIZED COATINGS FOR ELECTRODES

Specimen Number	Electrode Metal	Conditions of Drying: Initial Temperature °C	Conditions of Drying: Final Temperature °C	Conditions of Drying: Final Pressure mm. Hg	Apparent Dielectric Constant at 10 Kc and 25°C
G 7	Gold	25	25	0.0003	4.35
G 12	Gold	25	24	0.0003	4.37
G 13	Gold	25	22	0.0003	4.32
G 14	Gold	25	17	0.0003	4.37
G 17	Gold	25	20	0.0003	4.40
G 19	Gold	25	22	0.0003	4.37
S 3	Silver	25	25	0.005	4.70
S 6	Silver	25	25	0.0003	4.46

TABLE III

ϵ'_m, ϵ''_m AT 24.4°C FOR SOLUTION #1 OF 3.09 GRAMS CELLULOSE NITRATE (D.S. 2.32) PER 100 cc. OF SOLUTION WITH ACETONE

f (Kc)	ϵ'_m	ϵ''_m
175	26.03	47.3
200	25.47	41.0
235	24.73	34.4
275	23.54	28.7
300	22.99	26.0

TABLE IV

ϵ'_m, ϵ''_m AT 26.0°C FOR SOLUTION #2 OF 3.00 GRAMS CELLULOSE NITRATE (D.S. 2.32) PER 100 cc. OF SOLUTION WITH ACETONE

f (Kc)	ϵ'_m	ϵ''_m
100	20.10	38.3
115	20.04	33.4
130	19.91	29.8
150	19.92	25.7
175	19.89	22.0
200	19.83	19.2
3,000	19.84	1.30
10,000	19.78	-

TABLE V

ϵ'_m, ϵ''_m AT 100 Kc FOR SOLUTION #2

t°C	Time (hr.:min.)	ϵ'_m	ϵ''_m
26.0	0:00	20.92	36.7
19.6	0:15	21.62	34.5
5.3	0:26	22.57	31.4
-27.1	0:55	26.66	20.3
-40.8	1:03	28.32	16.6
-70.2	1:24	32.06	10.0
-43.4	2:00	28.67	16.0
11.2	11:00	21.94	33.2
25.7	11:25	20.17	39.0
40.9	12:05	18.55	44.8
49.8	12:30	17.72	48.0

TABLE VI

ϵ'_m, ϵ''_m AT 21.9°C FOR SOLUTION #3 OF 17 GRAMS CELLULOSE NITRATE (D.S. 2.32) PER 100 cc. OF SOLUTION WITH ACETONE

f (Kc)	ϵ'_m	ϵ''_m
115	20.04	54.7
130	19.87	48.5
150	19.80	42.1
175	19.65	36.2
200	19.66	31.6
230	19.60	27.4
245	19.61	25.7
3,000	19.71	2.16
10,000	19.48	0.91

TABLE VII

ϵ'_m, ϵ''_m AT 23.4°C FOR SOLUTION #3

f (Mc)	ϵ'_m	ϵ''_m
1.8	19.76	3.61
2.0	19.79	3.23
3.0	19.78	2.14
4.5	19.50	1.53
8	19.43	1.01
10	19.32	0.93
12	19.15	0.86
14	19.15	0.82
16	18.93	0.83
18	18.73	0.88

TABLE VIII

ϵ'_m, ϵ''_m AT 45.4°C FOR SOLUTION #3

f (Mc)	ϵ'_m	ϵ''_m
1.5	17.52	-----
2	17.51	-----
3	17.50	-----
4	17.48	2.32
5	17.44	1.83
7	17.34	-----
8	17.40	1.276
10	17.29	1.086
12	17.23	0.986
14	17.10	0.915
16	16.93	0.874
18	16.70	0.867

TABLE IX

ϵ'_m, ϵ''_m AT -75°C FOR SOLUTION #3

f (Kc)	ϵ'_m	ϵ''_m
100	30.05	11.43
115	30.01	10.02
130	29.95	9.00
150	29.91	7.91
175	29.84	6.86
200	29.79	6.05
245	29.75	5.05
1,000	29.59	1.495
3,000	29.23	0.720
10,000	28.60	0.704
14,000	28.12	0.827

TABLE X

ϵ'_m, ϵ''_m AT 130 Kc FOR SOLUTION #3

t°C	ϵ'_m	ϵ''_m
-63.3	28.92	12.23
-58.4	28.38	14.08
-54.0	27.84	16.09
-49.1	27.32	18.22
-44.6	26.89	20.5
-39.3	26.38	23.1
-33.9	25.80	25.8
-28.7	25.18	28.8
-23.8	24.76	30.9
-19.4	24.33	33.2
-14.6	23.79	35.9
-10.0	23.27	38.8
- 5.1	22.72	41.7
0.0	22.14	44.6
4.7	21.63	47.4
9.6	21.17	50.4
14.4	20.58	53.5
19.5	20.19	56.9
24.7	19.54	59.9

TABLE XI

ϵ'_m AT 16 Mc FOR SOLUTION #3

Cooling		Heating	
t°C	ϵ'_m	t°C	ϵ'_m
18.3	19.31	-54.8	26.27
12.7	19.71	-50.6	25.78
8.0	20.18	-46.2	25.37
3.2	20.60	-41.0	24.89
-2.2	21.11	-35.3	24.35
-8.0	21.67	-30.1	23.86
-15.6	22.30	-25.3	23.42
-20.7	22.81	-20.3	22.97
-26.5	23.35	-15.3	22.50
-31.2	23.82	-10.6	22.05
-35.9	24.28	- 5.5	21.58
-40.7	24.72	- 0.7	21.18
-44.7	25.09	4.1	20.69
-50.3	25.64	9.0	20.22
-55.2	26.17	14.3	19.76
-60.9	26.63	19.5	19.24

TABLE XII

ϵ''_m CORRECTED FOR D.C. RESISTANCE FOR SOLUTIONS 2, 3

Frequency	Solution			
(Mc)	#2 at 26.0°C	#3 at 21.9°C	#3 at 23.4°C	#3 at -75°C
0.100	0.0	-	-	0.00
0.115	0.1	0.0	-	0.08
0.130	0.3	0.1	-	0.10
0.150	0.2	0.1	-	0.28
0.175	0.1	0.2	-	0.32
0.200	0.1	0.1	-	0.33
0.230	-	0.0	-	-
0.245	-	0.0	-	0.38
1.0	-	-	-	0.352
1.8	-	-	0.06	-
2.0	-	-	0.03	-
3.0	-	0.06	0.01	0.339
4.5	-	-	0.11	-
8	-	-	0.21	-
10	-	0.28	0.29	0.555
12	-	-	0.33	-
14	-	-	0.36	0.745
16	-	-	0.43	-
18	-	-	0.52	-

TABLE XIII

PORTION OF ϵ_m'' FOR ACETONE DUE TO DISPERSION OF ACETONE

(ϵ_m'' For Acetone Corrected For D.C. Resistance)

f (Mc)	ϵ_m''
1	0.00
3	0.014
10	0.205
14	0.341
18	0.459

TABLE XIV

ϵ'_m, ϵ''_m FOR CELLULOID OF 40% CAMPHOR *

Frequency = 1000 Kc			Frequency = 100 Kc			Frequency = 10 Kc		
t°C	ϵ'_m	ϵ''_m	t°C	ϵ'_m	ϵ''_m	t°C	ϵ'_m	ϵ''_m
94.0	2.767	.0811	43.6	2.663	.0554	47.5	2.717	.0192
84.4	2.726	.0834	35.9	2.625	.0596	40.1	2.691	.0213
73.4	2.676	.0851	28.0	2.586	.0640	32.3	2.661	.0234
63.4	2.611	.0856	20.1	2.546	.0668	24.5	2.624	.0256
54.9	2.570	.0856	11.7	2.493	.0659	17.2	2.589	.0285
43.0	2.517	.0848	4.1	2.446	.0627	9.2	2.546	.0295
31.4	2.455	.0817	- 3.0	2.399	.0581	1.5	2.498	.0302
22.1	2.411	.0781	-10.9	2.358	.0522	- 7.2	2.443	.0283
12.3	2.373	.0726	-18.6	2.318	.0478	-13.7	2.402	.0264
3.5	2.331	.0678	-26.6	2.278	.0426	-21.5	2.358	.0240
- 3.7	2.302	.0633	-34.2	2.248	.0378	-30.1	2.312	.0199
-10.9	2.272	.0588	-43.0	2.218	.0331	-37.2	2.280	.0181
-19.6	2.228	.0530	-53.5	2.188	.0285	-45.0	2.249	.0163
-25.9	2.222	.0498	-60.8	2.172	.0250	-52.5	2.222	.0144
-33.7	2.197	.0453	-69.4	2.150	.0232	-60.1	2.197	.0122
-43.1	2.172	.0408				-69.6	2.174	.0110
-51.5	2.147	.0369				-78.2	2.157	.0097
-62.8	2.129	.0330						
-74.6	2.112	.0291						
-196	2.041	.0141						

* Preliminary values, water sorbed at atmospheric humidity and at 25°C. Measurements in closed system with Mason-Seidman cell.

TABLE XV

ϵ' FOR CELLULOID OF 40% CAMPHOR

Frequency	Temperature °C									
Kc	25.0	14.6	4.2	- 6.2	-17.7	-26.9	-37.3	-47.1	-58.1	-68.5
.2	4.661	4.537	4.403	4.269	4.145	4.003	3.895	3.823	3.753	3.698
.5	4.600	4.469	4.336	4.202	4.086	3.946	3.848	3.777	3.717	3.665
1	4.551	4.420	4.287	4.153	4.041	3.906	3.813	3.747	3.692	3.646
2	4.502	4.367	4.238	4.107	3.999	3.876	3.783	3.720	3.669	3.623
5	4.417	4.284	4.156	4.035	3.938	3.822	3.735	3.678	3.635	3.596
10	4.347	4.229	4.105	3.982	3.898	3.790	3.709	3.655	3.618	3.578
20	4.294	4.169	4.050	3.944	3.859	3.754	3.680	3.634	3.593	3.556
100	4.134	4.023	3.927	3.838	3.766	3.672	3.614	3.572	3.537	3.497
200	4.079	3.976	3.886	3.806	3.737	3.644	3.578	3.549	3.513	3.480
300	4.048	3.955	3.867	3.787	3.722	3.632	3.578	3.541	3.503	3.468

TABLE XVI

ϵ'' FOR CELLULOID OF 40% CAMPHOR

Frequency	Temperature °C									
Kc	25.0	14.6	4.2	- 6.2	-17.7	-26.9	-37.3	-47.7	-58.1	-68.5
.2	.0978	.1030	.1079	.1063	.1024	.0929	.0837	.0757	.0634	.0571
.5	.1076	.1135	.1149	.1101	.1021	.0911	.0800	.0691	.0595	.0508
1	.1174	.1211	.1192	.1130	.1022	.0894	.0782	.0667	.0572	.0505
2	.1270	.1275	.1237	.1142	.1020	.0876	.0757	.0645	.0558	.0507
5	.1352	.1324	.1243	.1114	.0969	.0818	.0702	.0601	.0491	.0484
10	.1413	.1345	.1232	.1083	.0935	.0781	.0669	.0585	.0525	.0487
20	.1460	.1347	.1211	.1041	.0891	.0751	.0653	.0583	.0507	.0505
100	.1509	.1279	.1162	.0994	.0870	.0756	.0692	.0646	.0621	.0586
200	.1542	.1352	.1185	.1039	.0919	.0820	.0766	.0720	.0734	.0654
300	.1583	.1515	.1307	.1098	.0994	.0908	.0841	.0797	.0781	.0721

TABLE XVII

ϵ' FOR CELLULOID OF 35.3% CAMPHOR

Frequency	Temperature °C									
Kc	26.3	14.6	4.2	- 6.2	-16.5	-26.8	-37.3	-47.6	-58.1	-68.0
.2	5.030	4.944	4.867	4.773	4.697	4.619	4.557	4.495	4.435	4.372
.5	4.832	4.756	4.686	4.609	4.507	4.477	4.426	4.371	4.313	4.251
1	4.693	4.626	4.563	4.492	4.435	4.379	4.334	4.281	4.226	4.161
2	4.568	4.508	4.450	4.388	4.335	4.285	4.242	4.191	4.138	4.049
5	4.397	4.343	4.289	4.238	4.189	4.147	4.109	4.065	4.010	3.921
10	4.290	4.242	4.192	4.149	4.107	4.067	4.030	3.982	3.929	3.824
20	4.195	4.149	4.105	4.064	4.026	3.988	3.953	3.909	3.852	3.725
100	3.963	3.925	3.890	3.860	3.827	3.792	3.757	3.713	3.627	3.494
200	3.865	3.838	3.804	3.774	3.743	3.709	3.676	3.626	3.526	3.425
300	3.806	3.777	3.743	3.717	3.686	3.657	3.624	3.572	3.465	3.360

TABLE XVIII

ϵ'' FOR CELLULOID OF 35.3% CAMPHOR

Frequency	Temperature °C									
Kc	26.3	14.6	4.2	- 6.2	-16.5	-26.8	-37.3	-47.6	-58.1	-68.0
.2	0.322	0.310	0.298	0.279	0.258	0.238	0.213	0.178	0.196	0.191
.5	0.313	0.299	0.286	0.268	0.248	0.229	0.213	0.190	0.197	0.200
1	0.305	0.290	0.274	0.257	0.241	0.225	0.212	0.204	0.200	0.208
2	0.290	0.276	0.265	0.247	0.233	0.221	0.212	0.205	0.204	0.212
5	0.265	0.251	0.239	0.227	0.213	0.207	0.203	0.198	0.202	0.227
10	0.255	0.243	0.231	0.221	0.212	0.205	0.201	0.197	0.204	0.234
20	0.256	0.245	0.236	0.226	0.218	0.213	0.210	0.209	0.221	0.257
100	0.349	0.337	0.327	0.319	0.311	0.307	0.302	0.304	0.324	0.297
200	0.484	0.470	0.453	0.448	0.432	0.431	0.423	0.472	0.433	0.385
300	0.620	0.600	0.582	0.571	0.559	0.550	0.541	0.542	0.532	0.478

TABLE XIX

ϵ' FOR CELLULOID OF 29.8% CAMPHOR

Frequency	Temperature °C									
Kc	25.0	14.6	4.4	- 6.1	-16.6	-26.8	-37.2	-47.5	-58.0	-68.2
.2	4.318	4.275	4.225	4.176	4.126	4.072	4.018	3.959	3.901	3.843
.5	4.241	4.193	4.148	4.095	4.047	3.996	3.940	3.890	3.835	3.778
1	4.182	4.137	4.089	4.036	3.989	3.941	3.894	3.842	3.790	3.729
2	4.124	4.077	4.031	3.980	3.935	3.889	3.826	3.796	3.752	3.680
5	4.032	3.986	3.939	3.891	3.849	3.808	3.752	3.721	3.676	3.598
10	3.969	3.925	3.878	3.833	3.797	3.760	3.719	3.675	3.625	3.541
20	3.908	3.865	3.822	3.782	3.746	3.710	3.668	3.629	3.579	3.483
100	3.754	3.719	3.683	3.651	3.619	3.587	3.551	3.518	3.440	3.357
200	3.693	3.660	3.624	3.595	3.566	3.539	3.501	3.455	3.380	3.314
300	3.657	3.625	3.596	3.564	3.533	3.514	3.471	3.424	3.347	3.293

TABLE XX

ϵ'' FOR CELLULOID OF 29.8% CAMPHOR

Frequency	Temperature °C									
Kc	25.0	14.6	4.4	- 6.1	-16.6	-26.8	-37.2	-47.5	-58.0	-68.2
.2	.1291	.1308	.1331	.1324	.1304	.1266	.1210	.1150	.1092	.1091
.5	.1336	.1354	.1352	.1339	.1340	.1255	.1195	.1130	.1089	.1118
1	.1388	.1394	.1386	.1352	.1312	.1257	.1195	.1130	.1103	.1175
2	.1435	.1439	.1415	.1369	.1318	.1260	.1205	.1140	.1126	.1244
5	.1496	.1475	.1430	.1370	.1312	.1257	.1190	.1165	.1176	.1331
10	.1540	.1503	.1458	.1395	.1336	.1282	.1240	.1185	.1247	.1370
20	.1610	.1554	.1494	.1441	.1382	.1336	.1295	.1290	.1353	.1390
100	.235	.225	.217	.210	.203	.1987	.1955	.1970	.205	.1799
200	.327	.315	.304	.298	.288	.283	.278	.282	.279	.248
300	.419	.404	.389	.383	.374	.366	.362	.363	.351	.317

TABLE XXI

ϵ' FOR CELLULOID OF 27.2% CAMPHOR

Frequency Kc	Temperature °C 25.0	14.7	4.2	- 6.0	-16.5	-26.9	-37.2	-47.7	-58.1	-68.4
.2	4.161	4.121	4.083	4.043	3.995	3.958	3.894	3.838	3.785	3.727
.5	4.111	4.073	4.032	3.989	3.941	3.903	3.843	3.792	3.743	3.682
1	4.077	4.037	3.995	3.948	3.904	3.866	3.805	3.758	3.709	3.649
2	4.041	3.999	3.958	3.913	3.869	3.833	3.777	3.729	3.684	3.622
5	3.981	3.939	3.896	3.860	3.804*	3.781	3.730	3.686	3.644	3.576
10	3.942	3.884	3.856	3.819	3.771*	3.748	3.700	3.661	3.616	3.544
20	3.899	3.844	3.819	3.780	3.741	3.716	3.668	3.633	3.584	3.514
100	3.793	3.759	3.723	3.688	3.656	3.625	3.592	3.558	3.497	3.448
200	3.755	3.721	3.690	3.655	3.626	3.607	3.564	3.527	3.466	3.424
300	3.736	3.705	3.672	3.641	3.612	3.593	3.551	3.512	3.451	3.413

* These measurements at -17.7°C

TABLE XXII

ϵ'' FOR CELLULOID OF 27.2% CAMPHOR

Frequency	Temperature °C									
Kc	25.0	14.7	4.2	- 6.0	-16.5	-26.9	-37.2	-47.7	-58.1	-68.4
.2	.0770	.0795	-----	.0853	.0879	.0887	.0857	.0814	.0757	.0738
.5	.0818	.0839	.0879	.0889	.0891	.0863	.0822	.0770	.0711	.0729
1	.0864	.0892	.0911	.0912	.0890	.0854	.0795	.0737	.0690	.0766
2	.0909	.0928	.0930	.0916	.0878	.0832	.0774	.0716	.0681	.0750
5	.0952	.0953	.0935	.0900	.0841*	.0794	.0719	.0697	.0692	.0733
10	.0993	.0971	.0941	.0897	.0837*	.0787	.0740	.0703	.0730	.0726
20	.1025	.0988	.0951	.0903	.0849	.0803	.0759	.0763	.0785	.0720
100	.1217	.1169	.1113	.1066	.1024	.0978	.0952	.0961	.0983	.0817
200	.1476	.1410	.1354	.1297	.1262	.1219	.1201	.1224	.1182	.1068
300	.1748	.1667	.1608	.1551	.1506	.1473	.1463	.1486	.1387	.1307

* These measurements at -17.7°C

TABLE XXIII

ϵ'_m FOR CELLULOID OF 40% CAMPHOR WITH 4.1% SORBED ACETONE

Frequency Kc	Temperature °C 25.1	14.7	4.2	- 6.2	-16.5	-26.9	-37.3	-47.8	-58.1	-68.5
.2	6.131	6.014	5.868	5.907	5.496	5.141	4.806	4.502	4.371	4.105
.5	6.069	5.931	5.766	5.666	5.343	5.080	4.672	4.396	4.293	4.046
1	6.014	5.867	5.679	5.560	5.235	4.880	4.583	4.324	4.173	4.005
2	5.961	5.791	5.589	5.454	5.126	4.785	4.502	4.264	4.094	3.969
5	5.857	5.664	5.441	5.286	4.959	4.644	4.385	4.177	4.928	3.922
10	5.772	5.588	5.322	5.173	4.855	4.551	4.315	4.124	3.992	3.899
20	5.659	5.456	5.214	5.061	4.751	4.462	4.252	4.075	3.956	3.869
100	5.405	5.169	4.923	4.778	4.504	4.273	4.294	3.971	3.874	3.799
200	5.292	5.054	4.819	4.664	4.423	4.215	4.062	3.937	3.846	3.753
300	5.228	4.988	4.763	4.630	4.387	4.188	4.041	3.920	3.835	3.765

TABLE XXIV

ϵ'' FOR CELLULOID OF 40% CAMPHOR WITH 4.1% SORBED ACETONE

Frequency	Temperature °C									
Kc	25.1	14.7	4.2	- 6.2	-16.5	-26.9	-37.3	-47.8	-58.1	-68.5
.2	.1048	.1098	.1672	.210	.232	.236	.217	.1796	.1354	.1026
.5	.1226	.1536	.1908	.229	.246	.240	.207	.1648	.1233	.0947
1	.1377	.1725	.208	.243	.252	.234	.1971	.1548	.1177	.0885
2	.1538	.1870	.229	.255	.257	.231	.1873	.1445	.1093	.0829
5	.1821	.217	.250	.264	.256	.216	.1719	.1282	.0967	.0745
10	.205	.236	.255	.266	.247	.202	.1596	.1184	.0906	.0715
20	.228	.253	.263	.267	----	.1896	.1518	.1137	.0878	.0724
100	.262	.278	.268	.254	.208	.1560	.1327	.0969	.0790	.0689
200	.291	.291	.271	.250	.205	.1517	.1263	.1000	.0831	.0736
300	.301	.298	.274	.250	.205	.1587	.1293	.1007	.0882	.0836

TABLE XXV

t_m (°C) FOR CELLULOIDS AT DIFFERENT FREQUENCIES

Composition	Frequency (Kc)									
	0.2	0.5	1	2	5	10	20	100	200	300
Celluloid, 40% camphor	½	7	13	19	--	--	--	---	---	---
Celluloid 35.3% camphor	>25	---	---	---	--	--	--	---	---	---
Celluloid, 29.8% camphor	1	11	16	19	--	--	--	---	---	---
Celluloid, 27.2% camphor	-24	-10	-1½	7	20	--	--	---	---	---
Celluloid, 40% camphor to which has been added 4.1% acetone	-22½	-19	-14½	-12	-8	-5	1	12	20	23½

TABLE XXVI

THERMODYNAMIC PARAMETERS OF ACTIVATION FOR DIELECTRIC RELAXATION IN CELLULOIDS

Composition	ΔF^* at 25°C (K cals./mole)	ΔH^* (K cals./mole)	ΔS^* (e.u./mole)
Celluloid, 40% camphor	11.4	18.9	25.1
Celluloid, 35.3% camphor	13.4	19.(?)	25.1(?)
Celluloid, 29.8% camphor	11.6	18.5	23.0
Celluloid, 27.2% camphor	11.1	10.3	2.7
Celluloid, 40% camphor to which has been added 4.1% acetone	7.8	24.9	57.3

TABLE XXVII

ϵ' FOR NITROCELLULOSE FILM #1 (D.S. 2.33) DRIED AT 25°C

Frequency	Temperature °C									
Kc	25.0	14.6	4.3	- 6.2	-16.5	-26.9	-37.3	-47.6	-58.0	-68.5
.2	5.204	5.032	4.907	4.743	4.605	4.465	4.338	4.228	4.119	4.022
.5	5.110	4.962	4.832	4.675	4.540	4.399	4.283	4.170	4.069	3.969
1	5.084	4.931	4.777	4.618	4.488	4.352	4.259	4.128	4.022	3.925
2	5.030	4.879	4.722	4.568	4.441	4.305	4.194	4.086	3.980	3.888
5	4.941	4.790	4.639	4.490	4.365	4.234	4.121	4.010	3.917	3.825
10	4.884	4.730	4.584	4.430	4.307	4.179	4.066	3.965	3.870	3.783
20	4.827	4.670	4.521	4.372	4.247	4.122	4.011	3.910	3.820	3.735
100	4.647	4.488	4.339	4.203	4.080	3.965	3.862	3.771	3.688	3.622
200	4.569	4.410	4.266	4.127	4.012	3.897	3.807	3.721	3.649	3.586
300	4.525	4.360	4.227	4.088	3.975	3.863	3.778	3.703	3.651	3.567

TABLE XXVIII

ϵ'' FOR NITROCELLULOSE FILM #1 (D.S. 2.33) DRIED AT 25°C

Frequency Kc	Temperature °C 25.0	14.6	4.3	- 6.2	-16.5	-26.9	-37.3	-47.6	-58.0	-68.5
.2	.1134	.1218	.1241	.1224	.1165	.1085	.1019	.0968	.0923	.0877
.5	.1206	.1250	.1266	.1225	.1171	.1095	.1045	.1009	.0964	.0937
1	.1266	.1292	.1290	.1242	.1194	.1140	.1098	.1073	.1022	.0981
2	.1333	.1337	.1317	.1288	.1243	.1188	.1170	.1120	.1075	.1007
5	.1383	.1384	.1373	.1333	.1301	.1257	.1220	.1163	.1101	.1014
10	.1455	.1452	.1444	.1413	.1387	.1329	.1281	.1197	.1115	.1014
20	.1554	.1550	.1542	.1517	.1474	.1406	.1328	.1228	.1123	.1012
100	.1910	.1903	.1890	.1795	.1697	.1558	.1417	.1278	.1121	.0982
200	.217	.213	.206	.1948	.1817	.1632	.1466	.1302	.1149	.1000
300	.236	.228	.220	.204	.1880	.1707	.1511	.1344	.1176	.1024

TABLE XXIX

ϵ' FOR NITROCELLULOSE FILM #2 (D.S. 2.33) DRIED AT 45°C

Frequency Kc	Temperature °C 46.0	35.6	25.2	14.6	4.3	- 6.0	-16.3	-26.7
.2	5.307	5.199	5.056	4.926	4.785	4.646	4.519	4.368
.5	5.281	5.142	4.988	4.861	4.722	4.591	4.467	4.318
1	5.210	5.092	4.944	4.814	4.678	4.547	4.425	4.282
2	5.166	5.045	4.900	4.769	4.634	4.505	4.386	4.242
5	5.099	4.975	4.827	4.699	4.563	4.437	4.318	4.174
10	5.052	4.926	4.775	4.655	4.516	4.388	4.268	4.125
20	5.000	4.874	4.725	4.595	4.461	4.328	4.208	4.059
100	4.852	4.720	4.572	4.431	4.292	4.166	4.038	3.900
200	4.790	4.655	4.499	4.358	4.222	4.093	3.973	3.834
300	4.753	4.616	4.457	4.316	4.182	4.054	3.931	3.803

TABLE XXX

ϵ'' FOR NITROCELLULOSE FILM #2 (D.S. 2.33) DRIED AT 45°C

Frequency	Temperature °C							
Kc	46.0	35.6	25.2	14.6	4.3	- 6.0	-16.3	-26.7
.2	.0961	.0993	.0981	.1042	.1053	.1013	.0958	.0917
.5	.0998	.1044	.1067	.1084	.1058	.1024	.0992	.0950
1	.1042	.1095	.1107	.1102	.1085	.1055	.1031	.1010
2	.1105	.1150	.1151	.1149	.1140	.1113	.1105	.1090
5	.1157	.1189	.1192	.1193	.1191	.1193	.1200	.1181
10	.1207	.1241	.1251	.1266	.1278	.1277	.1280	.1258
20	.1280	.1331	.1347	.1383	.1405	.1402	.1397	.1364
100	.1669	.1727	.1765	.1799	.1785	.1754	.1692	.1579
200	.1964	.203	.2056	.204	.1993	.1940	.1824	.1672
300	.221	.225	.2260	.224	.216	.2067	.1897	.1727

TABLE XXXI

VALUE OF t_m (°C) FOR DISPERSIONS A, B OF NITROCELLULOSE FILMS

Film No. *	1	2	2	3	4	5	6	7
Dispersion	A & B	A	B	A & B	A	A	A	A
f (Kc)								
0.2	4	---	8	-42	---	-41	-66	---
0.5	6	---	17	-47	---	-33	-58	---
1	10	---	22	-46	---	-30	-53	---
2	19	---	23	-43	-26	-24	-48	-65
5	20	-14	26	-39	-19	-19	-41	-58
10	20	- 6	---	-32	-14	-16	-35	-51
20	15	---	---	-23	- 9	---	---	-44
35	--	---	---	---	---	- 6	-22	-37
100	15	12	---	1	6	6	- 7½	-25
200	--	24	---	17	19	17	½	-15
300	--	27	---	---	---	24	5	- 6

* See Table XXXVI for description of film according to film number

TABLE XXXII

ϵ' FOR NITROCELLULOSE FILM #3 (D.S. 2.33) HAZED WITH MOISTURE AND DRIED AT 25°C

Frequency	Temperature °C									
Kc	25.0	14.6	4.2	- 6.2	-17.7	-26.9	-37.3	-47.7	-57.9	-68.5
.2	4.790	4.719	4.640	4.561	4.494	4.414	4.337	4.257	4.180	4.097
.5	4.752	4.684	4.602	4.520	4.450	4.376	4.294	4.213	4.139	4.056
1	4.725	4.651	4.570	4.490	4.420	4.346	4.261	4.181	4.100	4.023
2	4.695	4.624	4.537	4.460	4.390	4.308	4.288	4.145	4.068	3.987
5	4.646	4.573	4.488	4.411	4.338	4.256	4.176	4.093	4.013	3.935
10	4.611	4.537	4.453	4.376	4.303	4.221	4.135	4.052	3.975	3.900
20	4.576	4.497	4.418	4.333	4.256	4.177	4.094	4.011	3.934	3.862
100	4.467	4.388	4.298	4.213	4.137	4.054	3.980	3.905	3.835	3.768
200	4.416	4.334	4.247	4.161	4.088	4.003	3.933	3.864	3.800	3.741
300	4.391	4.310	4.209	4.134	4.061	3.981	3.909	3.842	3.781	3.727

TABLE XXXIII

ϵ'' FOR NITROCELLULOSE FILM #3 (D.S. 2.33) HAZED WITH MOISTURE AND DRIED AT 25°C

Frequency	Temperature °C									
Kc	25.0	14.6	4.2	- 6.2	-17.7	-26.9	-37.3	-47.7	-57.9	-68.5
.2	.0642	.0694	.0719	.0743	.0741	.0741	.0755	.0753	.0748	.0725
.5	.0698	.0731	.0745	.0750	.0761	.0770	.0777	.0784	.0774	.0754
1	.0746	.0767	.0772	.0777	.0796	.0804	.0818	.0824	.0812	.0796
2	.0789	.0805	.0812	.0821	.0834	.0857	.0867	.0870	.0854	.0829
5	.0827	.0851	.0866	.0904	.0911	.0923	.0927	.0925	.0895	.0850
10	.0881	.0903	.0935	.0950	.0977	.0988	.0988	.0964	.0918	.0862
20	.0961	.0990	.1025	.1040	.1064	.1069	.1044	.1007	.0944	.0857
100	.1313	.1333	.1362	.1357	.1336	.1285	.1198	.1128	.1001	.0897
200	.1625	.1607	.1618	.1577	.1517	.1429	.1310	.1206	.1087	.0980
300	.1849	.1810	.1789	.1732	.1665	.1553	.1450	.1325	.1195	.1070

TABLE XXXIV

ϵ' FOR NITROCELLULOSE FILM #4 (D.S. 2.46) DRIED AT 25°C

Frequency	Temperature °C									
Kc	25.1	14.6	4.2	- 6.2	-17.7	-26.9	-37.3	-47.7	-58.1	-68.5
.2	5.524	5.417	5.304	5.193	5.081	4.961	4.874	4.736	4.696	4.529
.5	5.498	5.357	5.244	5.126	5.014	4.897	4.782	4.671	4.561	4.464
1	5.424	5.309	5.198	5.078	4.966	4.844	4.734	4.623	4.516	4.418
2	5.386	5.264	5.153	5.032	4.916	4.801	4.686	4.573	4.467	4.372
5	5.323	5.195	5.069	4.953	4.842	4.721	4.607	4.496	4.380	4.299
10	5.261	5.142	5.024	4.903	4.786	4.668	4.551	4.440	4.340	4.253
20	5.209	5.082	4.964	4.842	4.724	4.604	4.515	4.385	4.287	4.200
100	5.049	4.917	4.906	4.668	4.553	4.436	4.359	4.238	4.154	4.084
200	4.977	4.846	4.718	4.598	4.484	4.371	4.299	4.185	4.106	4.038
300	4.937	4.795	4.679	4.558	4.446	4.337	4.256	4.159	4.108	4.017

TABLE XXXV

ϵ'' FOR NITROCELLULOSE FILM #4 (D.S. 2.46) DRIED AT 25°C

Frequency	Temperature °C									
Kc	25.1	14.6	4.2	- 6.2	-17.7	-26.9	-37.3	-47.7	-58.1	-68.5
.2	-----	.0948	.1024	.1049	.1092	.1096	.1106	.1089	.1087	.0942
.5	.0979	.1034	.1112	.1112	.1133	.1131	.1128	.1121	.1099	.1058
1	.1047	.1094	.1138	.1158	.1172	.1172	.1169	.1156	.1129	.1091
2	.1120	.1158	.1201	.1213	.1224	.1234	.1223	.1203	.1166	.1119
5	.1214	.1241	.1272	.1283	.1298	.1293	.1262	.1245	.1198	.1131
10	.1299	.1332	.1366	.1383	.1393	.1377	.1347	.1296	.1228	.1140
20	.1412	.1433	.1479	.1482	.1483	.1455	.1400	.1320	.1230	.1130
100	.1787	.1814	.1854	.1797	.1721	.1619	.1508	.1377	.1246	.1119
200	.2026	.2026	.1982	.1972	.1834	.1713	.1560	.1431	.1293	.1151
300	.2227	.2215	.2120	.2083	.1947	.1765	.1639	.1468	.1343	.1201

TABLE XXXVI

THERMODYNAMIC PARAMETERS OF ACTIVATION FOR DIELECTRIC DISPERSIONS A, B OF NITROCELLULOSE FILMS

Film No.	Degree of Substitution Nitrocellulose (D.S.)	Drying Temperature (°C)	Grams Acetone per gram 'bone-dry' Nitrocellulose (% wt./wt.)	ΔF^* (Kcals/mole)	ΔH^* (Kcals/mole)	ΔS^* (e.u.)
			DISPERSION A			
2	2.33	45	0.7	8.92	16.15	24.3
3*	2.33	25	---	8.77	8.06	- 2.4
4	2.46	25	2.4	8.42	15.90	25.1
5	2.33	25	4.3	8.18	17.70	32.0
6	2.33	25	9.9	7.93	11.54	12.1
7	2.33	25	16.0	7.71	8.79	3.6
			DISPERSION B			
1	2.33	25	**			

* Moisture hazed film

** Some water as well as acetone retained in film

TABLE XXXVII

RESIDUAL ACETONE IN FILMS

Nitrogen Content of Nitrocellulose (% N)	Degree of Substitution (D.S.)	Residual Acetone in grams per 100 grams bone-dry Nitrocellulose (% wt./wt.)
9.7	1.64	0.0
10.95	1.96	0.4
11.6	2.15	1.7
12.2	2.33	2.5
12.6	2.46	2.4
13.6	2.80	1.5

TABLE XXXVIII

SORPTION ISOTHERM AT 25°C ACETONE-NITROCELLULOSE FILM (D.S. 2.33)

Vapour Pressure mm. of Hg	Grams Acetone Sorbed per 100 grams Nitrocellulose
4.7	0.043
24.9	0.099
71	0.188
124	0.289
185	0.540

TABLE XXXIX

CONCENTRATIONS OF ACETONE IN FILMS OF NITROCELLULOSE (D.S. 2.33)

Grams Acetone per gram 'bone-dry' Nitrocellulose	Moles Acetone per Anhydroglucose Unit	Moles Acetone per Nitrate Group
0.7	0.03	0.07
4.3	0.20	0.46
9.9	0.45	1.04
16.0	0.73	1.69

TABLE XL

ϵ' FOR NITROCELLULOSE FILM #5 (D.S. 2.33) WITH 4.3% SORBED ACETONE

Frequency	Temperature °C									
Kc	25.1	14.8	4.4	- 6.2	-16.5	-26.9	-37.2	-47.6	-58.1	-68.3
.2	5.399	5.313	5.218	5.097	4.993	4.860	4.728	4.603	4.473	4.341
.5	5.357	5.257	5.157	5.034	4.918	4.788	4.656	4.531	4.399	4.269
1	5.322	5.213	5.111	4.983	4.865	4.735	4.601	4.498	4.345	4.218
2	5.285	5.176	5.067	4.937	4.814	4.684	4.549	4.427	4.301	4.174
5	5.220	5.104	4.986	4.856	4.730	4.580	4.466	4.345	4.220	4.102
10	5.171	5.053	4.930	4.800	4.670	4.547	4.408	4.290	4.164	4.058
35	5.060	4.939	4.814	4.675	4.545	4.422	4.285	4.199	4.062	3.963
100	4.962	4.830	4.700	4.566	4.429	4.297	4.188	4.081	3.976	3.884
200	4.893	4.761	4.624	4.491	4.357	4.243	4.123	4.027	3.928	3.844
300	4.851	4.721	4.580	4.450	4.320	4.208	4.090	4.002	3.907	3.823

TABLE XLI

ϵ'' FOR NITROCELLULOSE FILM #5 (D.S. 2.33) WITH 4.3% SORBED ACETONE

Frequency	Temperature °C									
Kc	25.1	14.8	4.4	- 6.2	-16.5	-26.9	-37.2	-47.6	-58.1	-68.3
.2	.0734	.0808	.0976	.1045	.1108	.1166	.1191	.1178	.1158	.1072
.5	.0809	.0915	.1026	.1128	.1200	.1221	.1220	.1205	.1170	.1101
1	.0910	.1011	.1114	.1201	.1250	.1264	.1261	.1228	.1186	.1118
2	.0999	.1108	.1206	.1264	.1305	.1316	.1296	.1262	.1213	.1127
5	.1127	.1215	.1296	.1345	.1376	.1365	.1335	.1290	.1215	.1132
10	.1246	.1334	.1405	.1445	.1457	.1446	.1402	.1343	.1249	.1136
35	.1523	.1585	.1642	.1650	.1636	.1592	.1504	.1398	.1279	.1149
100	.1826	.1869	.1898	.1863	.1785	.1693	.1558	.1436	.1276	.1130
200	.214	.216	.212	.206	.1939	.1820	.1657	.1506	.1339	.1192
300	.239	.237	.233	.222	.207	.1923	.1755	.1581	.1410	.1262

TABLE XLII

ϵ' ON COOLING FOR NITROCELLULOSE FILM #6 (D.S. 2.33) WITH 9.9% SORBED ACETONE

Frequency Kc	Temperature °C 25.0	14.7	4.3	- 6.2	-16.4	-26.7	-37.4	-47.7	-57.9	-68.1
.2	6.124	6.044	5.955	5.856	5.747	5.656	5.529	5.350	5.155	4.909
.5	6.083	5.999	5.900	5.795	5.670	5.563	5.433	5.241	5.039	4.793
1	6.046	5.958	5.856	5.740	5.610	5.391	5.355	5.164	4.951	4.712
2	6.011	5.914	5.812	5.684	5.547	5.417	5.280	5.083	4.867	4.640
5	5.948	5.842	5.726	5.587	5.433	5.297	5.148	4.946	4.740	4.529
10	5.900	5.788	5.670	5.512	5.375	5.206	5.055	4.858	4.659	4.459
35	5.788	5.656	5.512	5.343	5.171	5.020	4.879	4.693	4.508	4.329
100	5.672	5.524	5.366	5.183	5.016	4.860	4.733	4.561	4.392	4.232
200	5.589	5.429	5.264	5.081	4.911	4.768	4.647	4.485	4.322	4.181
300	5.538	5.371	5.206	5.027	4.856	4.707	4.598	4.452	4.290	4.157

TABLE XLIII

ϵ'' ON COOLING FOR NITROCELLULOSE FILM #6 (D.S. 2.33) WITH 9.9% SORBED ACETONE

Frequency	Temperature °C									
Kc	25.0	14.7	4.3	- 6.2	-16.4	-26.7	-37.4	-47.7	-57.9	-68.1
.2	.0753	.0798	.0899	.1042	.1195	.1367	.1576	.1658	.1768	.1787
.5	.0809	.0900	.1032	.1188	.1344	.1524	.1673	.1819	.1874	.1816
1	.0895	.1007	.1159	.1326	.1498	.1680	.1821	.1931	.1941	.1800
2	.1004	.1130	.1302	.1483	.1653	.1831	.1959	.202	.1961	.1772
5	.1148	.1303	.1500	.1687	.1870	.201	.209	.207	.1920	.1689
10	.1304	.1482	.1690	.1874	.204	.214	.217	.207	.1878	.1632
35	.1649	.1810	.209	.220	.233	.233	.226	.206	.1803	.1541
100	.214	.233	.249	.257	.253	.242	.228	.203	.1761	.1498
200	.264	.279	.288	.286	.274	.261	.239	.210	.1811	.1547
300	.298	.308	.312	.306	.289	.268	.247	.219	.1892	.1625

TABLE XLIV

ϵ', ϵ'' FOR NITROCELLULOSE FILM #6 (D.S. 2.33) WITH 9.9% SORBED ACETONE ON HEATING AFTER COOLING TO -68.1°C

Frequency	ϵ'					ϵ''				
	Temperature °C									
Kc	-16.6	- 6.2	4.3	14.6	25.0	-16.6	- 6.2	4.3	14.6	25.0
.2	5.955	6.113	6.248	6.324	6.357	.1256	.1100	.0993	.0904	.0807
.5	5.881	6.048	6.185	6.278	6.306	.1394	.1227	.1082	.0960	.0876
1	5.819	5.993	6.139	6.236	6.264	.1530	.1580	.1215	.1066	.0940
2	5.756	5.916	6.090	6.199	6.227	.1698	.1497	.1340	.1178	.1027
5	5.645	5.842	6.004	6.125	6.162	.1925	.1729	.1543	.1354	.1158
10	5.559	5.767	5.935	6.071	6.115	.2135	.1953	.1751	.1542	.1333
35	5.368	5.589	5.781	5.936	5.997	.2495	.2414	.2226	.2012	.1679
100	5.194	5.389	5.621	5.800	5.872	.2732	.2797	.2732	.2540	.2272
200	5.085	5.278	5.510	5.698	5.781	.2970	.3125	.3146	.3054	.2798
300	5.025	5.236	5.445	5.638	5.728	.3125	.3341	.3440	.3411	.3156

TABLE XLV

ϵ', ϵ'' FOR NITROCELLULOSE FILM #6 (D.S. 2.33) WITH 9.9% SORBED ACETONE
SHOWING EFFECTS OF COOLING-HEATING CYCLE
MEASUREMENTS AT FREQUENCY OF 10 Kc

Cooling from 25°C			Heating Back to 25°C		
Temperature °C	ϵ'	ϵ''	Temperature °C	ϵ'	ϵ''
25.3	5.897	.1285	24.9	6.032	.1393
14.5	5.784	.1440	14.6	5.925	.1523
4.3	5.651	.1627	4.2	5.791	.1714
- 6.7	5.542	.1829	- 6.2	5.635	.1893
-17.0	5.334	.1990	-16.8	5.452	.2050
-26.9	5.201	.2101	-26.7	5.269	.2129
-37.2	5.039	.2126	-36.6	5.065	.2127
-47.5	4.839	.2052	-47.5	4.844	.2034
-57.9	4.631	.1852			
-67.1	4.440	.1629			

TABLE XLVI

ϵ' FOR NITROCELLULOSE FILM #7 (D.S. 2.33) WITH 16.0% SORBED ACETONE

Frequency	Temperature °C									
Kc	25.0	14.6	4.2	- 6.2	-17.7	-26.9	-37.3	-47.7	-58.1	-68.4
.116	6.890	6.733	6.605	6.459	6.278	6.120	5.953	5.761	5.552	5.327
.2	6.886	6.705	6.579	6.436	6.243	6.090	5.914	5.719	5.501	5.266
.5	6.800	6.654	6.528	6.378	6.189	6.018	5.832	5.621	5.389	5.150
1	6.758	6.614	6.489	6.334	6.136	5.958	5.791	5.545	5.301	5.055
2	6.723	6.579	6.450	6.289	6.088	5.904	5.698	5.466	5.211	4.960
5	6.665	6.517	6.380	6.208	5.997	5.816	5.575	5.322	5.060	4.814
10	6.621	6.470	6.327	6.141	5.897	5.712	5.477	5.218	4.953	4.707
20	6.575	6.417	6.262	6.071	5.837	5.617	5.371	5.109	4.844	4.612
35	6.521	6.354	6.194	5.993	5.747	5.512	5.264	5.000	4.794	4.519
100	6.422	6.245	6.055	5.835	5.566	5.322	5.067	4.821	4.580	4.375
200	6.350	6.164	5.953	5.716	5.445	5.197	4.951	4.712	4.487	4.297
300	6.308	6.102	5.893	5.647	5.371	5.125	4.886	4.659	4.438	4.266

TABLE XLVII

ϵ'' FOR NITROCELLULOSE FILM #7 (D.S. 2.33) WITH 16.0% SORBED ACETONE

Frequency	Temperature °C									
Kc	25.0	14.6	4.2	- 6.2	-17.7	-26.9	-37.3	-47.7	-58.1	-68.4
.116	.217	.1212	.0933	.0911	.0967	.1089	.1226	.1423	.1582	.1694
.2	.1673	.1086	.0968	.0946	.1043	.1169	.1331	.1510	.1672	.1854
.5	.1219	.0978	.0957	.1040	.1157	.1306	.1499	.1703	.1902	.206
1	.1081	.0985	.1028	.1140	.1276	.1460	.1674	.1880	.210	.220
2	.1049	.1039	.1129	.1264	.1437	.1629	.1869	.208	.226	.231
5	.1086	.1153	.1289	.1484	.1679	.1919	.215	.234	.241	.235
10	.1192	.1307	.1487	.1707	.1916	.217	.238	.249	.247	.231
20	.1354	.1508	.1735	.1979	.222	.244	.260	.262	.249	.227
35	.1545	.1735	.1994	.226	.248	.267	.275	.266	.252	.220
100	.207	.232	.263	.289	.302	.306	.297	.274	.242	.208
200	.272	.300	.326	.343	.347	.338	.316	.285	.249	.211
300	.325	.350	.374	.383	.376	.358	.329	.294	.255	.220

TABLE XLVIII

ϵ'_m FOR NITROCELLULOSE PAPER (D.S. 2.16)

Frequency	Temperature °C										
Kc	14.8	6.0	- 4.0	-14.0	-24.0	-34.0	-44.0	-54.0	-64.0	-74.0	-84.0
.2	1.438	1.433	1.427	1.419	1.410	1.401	1.391	1.383	1.375	1.365	1.356
.5	1.436	1.430	1.424	1.416	1.406	1.397	1.388	1.379	1.371	1.362	1.353
1	1.433	1.427	1.421	1.411	1.401	1.392	1.383	1.377	1.368	1.357	1.348
2	1.431	1.424	1.416	1.408	1.398	1.389	1.379	1.371	1.363	1.354	1.345
5	1.428	1.419	1.410	1.405	1.391	1.383	1.373	1.365	1.361	1.349	1.340
10	1.425	1.416	1.406	1.397	1.388	1.379	1.370	1.361	1.354	1.347	1.337
20	1.421	1.412	1.401	1.393	1.383	1.375	1.364	1.356	1.349	1.341	1.334
35	1.416	1.408	1.397	1.388	1.378	1.370	1.361	1.353	1.345	1.339	1.332
100	1.409	1.400	1.389	1.379	1.371	1.363	1.354	1.346	1.340	1.333	1.327
200	1.404	1.395	1.385	1.374	1.366	1.358	1.350	1.342	1.336	1.332	1.325
300	1.402	1.393	1.382	1.373	1.364	1.357	1.350	1.342	1.335	1.330	1.324
550	1.398	1.389	1.378	1.370	1.361	1.352		1.340		1.327	
1000	1.393	1.383	1.373	1.365	1.356	1.350		1.336		1.327	
2000	1.387	1.379	1.369	1.359	1.353	1.347		1.333	1.32	1.325	
4000	1.386	1.362	1.356	1.348	1.341	1.346		1.336		1.327	

TABLE XLIX

ϵ''_m FOR NITROCELLULOSE PAPER (D.S. 2.16)

Frequency	Temperature °C										
Kc	14.8	6.0	- 4.0	-14.0	-24.0	-34.0	-44.0	-54.0	-64.0	-74.0	-84.0
.2	.0044	.0047	.0060	.0067	.0080	.0078	.0075	.0081	.0082	.0079	.0081
.5	.0054	.0058	.0074	.0085	.0092	.0085	.0089	.0091	.0095	.0087	.0082
1	.0061	.0064	.0086	.0095	.0096	.0093	.0094	.0095	.0096	.0087	.0083
2	.0070	.0075	.0098	.0101	.0101	.0098	.0099	.0100	.0099	.0088	.0078
5	.0074	.0079	.0098	.0102	.0101	.0098	.0098	.0096	.0093	.0082	.0073
10	.0083	.0088	.0101	.0105	.0103	.0102	.0099	.0095	.0092	.0081	.0072
20	.0093	.0099	.0109	.0111	.0109	.0107	.0102	.0098	.0091	.0079	.0068
35	.0099	.0104	.0113	.0112	.0110	.0107	.0102	.0094	.0086	.0075	.0065
100	.0114	.0116	.0118	.0117	.0112	.0106	.0098	.0088	.0078	.0067	.0057
200	.0125	.0123	.0124	.0120	.0115	.0106	.0095	.0085	.0075	.0066	.0058
300	.0131	-----	.0130	.0120	.0119	.0105	.0095	.0083	.0071	.0064	.0056
550	.0138	.0134	.0130	.0120	.0111	.0103		.0076		.0054	
1000	.0149	.0140	.0134	.0134	.0114	.0102		.0079		.0061	
2000	.0165	.0157	.0148	.0133	.0124	.0112		.0088		.0074	
4000	.0202	.0190	.0180	.0163	.0158	.0148		.0127		.0108	

TABLE L(a)

ϵ'_m FOR CELLULOSE TRINITRATE PAPER (D.S. 3.00)

Frequency	Temperature °C					
Kc	15	5	-5	-15	-25	-35
.2	1.607	1.598	1.590	1.581	1.571	1.563
.5	1.603	1.595	1.585	1.577	1.566	1.558
1	1.600	1.591	1.581	1.573	1.562	1.554
2	1.598	1.587	1.578	1.569	1.558	1.551
5	1.593	1.582	1.572	1.563	1.552	1.545
10	1.590	1.578	1.569	1.559	1.548	1.541
20	1.586	1.574	1.564	1.554	1.544	1.536
35	1.582	1.569	1.559	1.549	1.539	1.534
100	1.575	1.561	1.552	1.542	1.531	1.525
200	1.570	1.557	1.547	1.537	1.527	1.521
300	1.567	1.554	1.544	1.535	1.525	1.519
550	1.561	1.548	1.539	1.529		1.517
1000	1.556	1.543	1.535	1.525		1.512
2000	1.545	1.534	1.525	1.515		1.503
4000	1.537	1.525	1.518	1.510		1.499

TABLE L(b)

ϵ'_m FOR CELLULOSE TRINITRATE PAPER (D.S. 3.00)

Frequency Kc	Temperature °C						
	-45	-55	-64	-75	-95.1	-115.4	-155
.2	1.554	1.544	1.535	1.526	1.509	1.497	1.478
.5	1.549	1.539	1.530	1.521	1.505	1.493	1.477
1	1.545	1.535	1.527	1.517	1.502	1.490	1.475
2	1.542	1.531	1.523	1.514	1.499	1.489	1.474
5	1.535	1.526	1.517	1.509	1.496	1.486	1.474
10	1.532	1.522	1.514	1.506	1.493	1.482	1.473
20	1.527	1.518	1.510	1.503	1.491	1.482	1.472
35	1.524	1.514	1.508	1.500	1.489	1.481	1.471
100	1.517	1.508	1.502	1.495	1.485	1.479	1.470
200	1.513	1.505	1.499	1.493	1.483	1.477	1.470
300	1.511	1.503	1.497	1.492	1.483	1.477	1.469
550		1.501		1.491	1.483	1.477	1.471
1000		1.499		1.489	1.482	1.477	1.470
2000		1.492		1.482	1.476	1.472	1.465
4000		1.489		1.481	1.475	1.471	1.465

TABLE LI(a)

ϵ''_m FOR CELLULOSE TRINITRATE PAPER (D.S. 3.00)

Frequency	Temperature °C					
Kc	15	4.7	-5.2	-15	-25	-35
.2	.0064	.0071	.0078	.0084	.0091	.0089
.5	.0066	.0076	.0082	.0087	.0092	.0089
1	.0069	.0080	.0086	.0091	.0091	.0090
2	.0075	.0089	.0093	.0096	.0095	.0094
5	.0081	.0093	.0095	.0097	.0096	.0096
10	.0089	.0099	.0101	.0102	.0103	.0101
20	.0100	.0105	.0107	.0107	.0106	.0103
35	.0111	.0111	.0112	.0112	.0109	.0108
100	.0120	.0122	.0121	.0115	.0111	.0103
200	.0131	.0131	.0128	.0121	.0113	.0101
300	.0140	.0137	.0132	.0125	.0114	.0097
550	.0150	.0144	.0136	.0125		.0106
1000	.0163	.0156	.0146	.0134		.0109
2000	.0192	.0179	.0166	.0153		.0123
4000	.0259	.0245	.0231	.0217		.0190

TABLE LI(b)

ϵ''_m FOR CELLULOSE TRINITRATE PAPER (D.S. 3.00)

Frequency	Temperature °C						
Kc	-45	-55	-64	-75	-95.1	-115.4	-155
.2	.0089	.0090	.0089	.0085	.0075	.0062	.0030
.5	.0089	.0088	.0088	.0083	.0071	-----	.0031
1	.0090	.0090	.0087	.0082	.0068	.0052	.0026
2	.0094	.0091	.0088	.0082	.0067	.0050	.0025
5	.0094	.0090	.0086	.0079	.0061	.0043	.0020
10	.0098	.0092	.0087	.0078	.0058	.0041	.0020
20	.0100	.0096	.0086	.0077	.0057	.0041	.00193
35	.0099	.0090	.0083	.0072	.0051	.0034	.00165
100	.0094	.0083	.0073	.0063	.0042	.0027	.00123
200	.0091	.0079	.0067	.0056	.0037	.0023	.00095
300	.0088	.0074	.0060	.0052	.0035	.0023	.00076
550		.0079		.0057	.0041	.0029	.00181
1000		.0081		.0062	.0048	.0038	.0027
2000		.0103		.0081	.0065	.0062	.0053
4000		.0168		.0151	.0142	.0135	.0125

TABLE LII

TEMPERATURES t_m OF DIELECTRIC ABSORPTION PEAKS FOR NITROCELLULOSE PAPERS (°C)

D. S. of Nitrocellulose	Dispersion Term	Frequency (Kc)											
		.116	.2	.5	1	2	5	10	20	35	100	200	300
2.16	A	-75	-69	-62	-60	-56	-52	---	-42	---	---	0	12
2.16	B	-28	-28	-23	-20	-16	-17	-16	-11	-9	-5	---	---
3.00	A	---	-55	-52	-47	-38	-27	-21	-13	---	---	---	---
3.00	B	---	-25	-23	-19	-17	---	---	-13	-7	---	---	---

TABLE LIII

THERMODYNAMIC PARAMETERS FOR DIELECTRIC RELAXATION OF NITROCELLULOSE PAPERS AT 25°C

Dispersions	ΔF^* (Kcal./mole)	ΔH^* (Kcal./mole)	ΔS^* (e.u.)
Dispersion A of Nitrocellulose of D.S. 2.16	8.61	9.35	2.2
Dispersion A of Nitrocellulose of D.S. 3.00	9.07	9.80	2.2
Dispersion B of Nitrocelluloses of D.S. 2.16 and 3.00	5.36	36.8	105

TABLE LIV(a)

ϵ'_m FOR CELLULOSE PAPER (a)

Frequency Kc	Temperature °C 91.1	70.5	50.4	35.1	25.1	14.7	4.3	6.0	-16.3	-27.0
.116	1.668	1.656	1.636	1.630	1.626	1.620	1.621	1.610	1.601	1.599
.2	1.666	1.652	1.638	1.629	1.625	1.617	1.621	1.610	1.601	1.590
.5	1.661	1.650	1.634	1.626	1.620	1.617	1.615	1.606	1.599	1.586
1	1.660	1.648	1.636	1.624	1.618	1.614	1.613	1.601	1.595	1.584
2	1.660	1.648	1.631	1.622	1.618	1.612	1.610	1.599	1.592	1.580
5	1.657	1.646	1.631	1.622	1.615	1.610	1.604	1.593	1.581	1.569
10	1.657	1.644	1.629	1.617	1.614	1.607	1.600	1.588	1.575	1.558
20	1.657	1.643	1.628	1.617	1.611	1.603	1.596	1.581	1.567	1.550
35	1.655	1.643	1.626	1.614	1.606	1.597	1.591	1.570	1.554	1.540
100	1.654	1.640	1.621	1.610	1.598	1.586	1.577	1.555	1.540	1.520
200	1.653	1.640	1.618	1.603	1.592	1.578	1.571	1.542	1.527	1.509
300	1.653	1.639	1.616	1.601	1.588	1.574	1.561	1.538	1.521	1.503
550	1.651	1.639	1.613	1.596	1.583	1.568	1.551	1.532	1.512	1.496
1000	1.650	1.631	1.610	1.586	1.573	1.556	1.538	1.520	1.503	1.485
2000	1.642	1.619	1.594	1.571	1.557	1.539	1.522	1.504	1.490	1.475
4000	1.630	1.610	1.579	1.554	1.539	1.523	1.509	1.493	1.481	1.464

TABLE L1V (b)

ϵ'_m FOR CELLULOSE PAPER (a)

Frequency Kcs.	Temperature °C -37.2	-47.6	-57.9	-64.1	-68.8	-74.0	-84.1	-94.1	-104.2	-114.4
.116	1.588	1.581	1.563	1.556	1.548	1.538	1.520	1.494	1.473	1.455
.2	1.585	1.574	1.460	1.548	1.542	1.530	1.510	1.490	1.468	1.450
.5	1.577	1.569	1.549	1.537	1.530	1.515	1.498	1.480	1.458	1.441
1	1.571	1.558	1.539	1.529	1.520	1.506	1.489	1.468	1.450	1.437
2	1.565	1.550	1.530	1.517	1.509	1.495	1.480	1.460	1.443	1.431
5	1.552	1.534	1.513	1.500	1.494	1.482	1.466	1.450	1.438	1.425
10	1.541	1.523	1.501	1.490	1.484	1.472	1.459	1.442	1.432	1.422
20	1.529	1.513	1.493	1.480	1.472	1.464	1.450	1.437	1.427	1.417
35	1.512	1.500	1.481	1.470	1.462	1.455	1.444	1.431	1.421	1.410
100	1.499	1.484	1.465	1.456	1.451	1.442	1.435	1.422	1.417	1.408
200	1.490	1.475	1.457	1.449	1.444	1.438	1.431	1.419	1.411	1.406
300	1.484	1.472	1.455	1.448	1.440	1.437	1.430	1.420	1.413	1.406
550	1.480	1.468	1.451	1.442	1.439	1.434	1.430	1.420	1.415	1.410
1000	1.472	1.460	1.447	1.439	1.436	1.430	1.428	1.418	1.417	1.410
2000	1.459	1.450	1.438	1.430	1.429	1.425	1.421	1.413	1.410	
4000	1.453	1.444	1.433	1.426	1.430	1.416	1.420	1.413	1.406	

TABLE LV (a)

ϵ''_m FOR CELLULOSE PAPER (a)

Frequency	Temperature °C									
Kcs.	91.1	70.5	50.4	35.1	25.1	14.7	4.3	6.0	-16.3	-27.0
.116	.0070	.0033	.029	.029	.031	.0024	.0045	.0058	.0056	.0062
.2	.0050	.0030	.026	.023	.023	.0026	.0047	.0069	.0072	.0078
.5	.0035	.0025	.023	.023	.024	.0037	.0053	.0066	.0081	.0101
1	.0028	.0021	.023	.026	.029	.0039	.0060	.0076	.0100	.0127
2	.0023	.0020	.026	.027	.034	.0048	.0072	.0085	.0119	.0166
5	.0025	.0023	.029	.040	.053	.0067	.0086	.0123	.0155	.0188
10	.0023	.0026	.037	--	.068	.0087	.0108	.0152	.0186	.0215
20	.0030	.0034	.049	.071	.087	.0113	.0151	.0187	.0221	.0248
35	.0033	.0043	.065	.090	.114	.0143	.0178	.0215	.0241	.0259
100	.0051	.0074	.103	.143	.170	.0204	.0240	.0267	.0283	.0281
200	.0078	.0105	.148	.195	.220	.0221	.0278	.0304	.0302	.0285
300	.0109	.0147	.187	.220	.258	.0282	.0305	.0325	.0314	.0290
550	.0119		.235	.284	.309	.0324	.0335	.0334	.0324	.0291
1000	.0204		.301	.340	.353	.0361	.0362	.0348	.0318	.0288
2000	.0317	.0361	.398	.411	.413	.0408	.0388	.0357	.0328	.0292
4000	.0479	.0494	.503	.511	.495	.0476	.0445	.0409	.0363	.0328

TABLE LV (b)

ϵ''_m FOR CELLULOSE PAPER (a)

Frequency Kcs.	Temperature °C									
	-37.2	-47.6	-57.9	-64.1	-68.8	-74.0	-84.1	-94.1	-104.2	-114.4
.116	.0097	.0122	.0167	.0184	.0195	.0215	.0217	.0209	.0190	.0157
.2	.0108	.0135	.0178	.0200	.0202	.0217	.0219	.0206	.0179	.0145
.5	.0131	.0165	.0195	.0212	.0211	.0220	.0212	.0188	.0159	.0124
1	.0160	.0193	.0216	.0226	.0228	.0226	.0212	.0182	.0148	.0115
2	.0186	.0212	.0234	.0234	.0234	.0224	.0204	.0170	.0137	.0104
5	.0217	.0236	.0238	.0233	.0226	.0215	.0186	.0154	.0122	.0097
10	.0240	.0250	.0239	.0228	.0217	.0200	.0170	.0141	.0112	.0086
20	.0257	.0260	.0239	.0223	.0214	.0189	.0162	.0126	.0104	.0079
35	.0266	.0256	.0231	.0212	.0202	.0182	.0156	.0123	.0098	.0078
100	.0268	.0245	.0214	.0192	.0179	.0162	.0139	.0108	.0089	.0070
200	.0267	.0240	.0205	.0181	.0170	.0152	.0135	.0104	.0086	.0065
300	.0270	.0238	.0202	.0177	.0177	.0151	.0129	.0097	.0079	.0068
550	.0262	.0225	.0196	.0176	.0161	.0145	.0126	.0106	.0079	.0069
1000	.0248	.0219	.0188	.0160	.0152	.0138	.0120	.0095	.0083	.0075
2000	.0271	.0225	.0188	----	.0163	.0150	.0128	.0104	.0087	.0078
4000	.0296	.0250	.0228	.0212	.0223	.0187	.0182	.0148	.0130	.0118

TABLE LV1 (a)

ϵ' FOR CELLULOSE FROM DIELECTRIC VALUES FOR CELLULOSE PAPER (2)

Frequency Kcs.	Temperature °C 91.1	70.5	50.4	35.1	25.1	14.7	4.3	6.0	-16.3	-27.0
.116	6.70	6.52	6.12	6.13	6.06	5.97	5.98	5.82	5.69	5.66
.2	6.67	6.46	6.25	6.11	6.05	5.93	5.98	5.82	5.69	5.53
.5	6.59	6.43	6.18	6.06	5.97	5.93	5.90	5.75	5.67	5.48
1	6.57	6.40	6.21	6.02	5.94	5.88	5.87	5.68	5.60	5.45
2	6.57	6.40	6.14	6.00	5.94	5.85	5.82	5.65	5.57	5.39
5	6.53	6.36	6.14	6.00	5.90	5.83	5.73	5.58	5.41	5.25
10	6.53	6.34	6.11	5.93	5.88	5.77	5.67	5.51	5.33	5.08
20	6.53	6.32	6.10	5.93	5.84	5.72	5.62	5.41	5.22	4.98
35	6.50	6.32	6.06	5.88	5.76	5.63	5.54	5.26	5.04	4.85
100	6.49	6.27	5.99	5.82	5.64	5.48	5.35	5.05	4.85	4.60
200	6.47	6.27	5.94	5.72	5.56	5.36	5.27	4.88	4.70	4.46
300	6.47	6.27	5.91	5.69	5.50	5.31	5.13	4.82	4.62	4.38
550	6.44	6.26	5.87	5.62	5.43	5.22	5.00	4.75	4.50	4.30
1000	6.43	6.14	5.82	5.48	5.30	5.06	4.83	4.60	4.38	4.17
2000	6.30	5.96	5.58	5.27	5.08	4.84	4.62	4.39	4.23	4.06
4000	6.12	5.82	5.38	5.04	4.84	4.63	4.47	4.27	4.12	3.93

TABLE LV1 (b)

ϵ' FOR CELLULOSE FROM DIELECTRIC VALUES FOR CELLULOSE PAPER (a)

Frequency	Temperature °C									
Kcs.	-37.2	-47.6	-57.9	-64.1	-68.8	-74.0	-84.1	-94.1	-104.2	-114.4
.116	5.50	5.41	5.16	5.06	4.96	4.83	4.60	4.28	4.03	3.83
.2	5.47	5.31	5.12	4.96	4.88	4.72	4.48	4.23	3.98	3.78
.5	5.38	5.24	4.98	4.82	4.72	4.54	4.33	4.11	3.86	3.69
1	5.27	5.09	4.84	4.71	4.60	4.42	4.22	3.97	3.78	3.64
2	5.19	4.99	4.72	4.56	4.47	4.34	4.11	3.89	3.70	3.58
5	5.01	4.77	4.51	4.35	4.28	4.14	3.95	3.78	3.65	3.52
10	4.87	4.63	4.37	4.23	4.16	4.02	3.87	3.69	3.59	3.49
20	4.71	4.51	4.27	4.11	4.02	3.93	3.78	3.64	3.54	3.44
35	4.50	4.35	4.13	4.00	3.91	3.83	3.72	3.58	3.48	3.37
100	4.34	4.16	3.94	3.84	3.79	3.69	3.62	3.49	3.44	3.35
200	4.23	4.05	3.85	3.77	3.71	3.65	3.58	3.46	3.38	3.33
300	4.16	4.02	3.83	3.76	3.67	3.64	3.57	3.47	3.40	3.33
550	4.11	3.98	3.79	3.69	3.66	3.61	3.57	3.47	3.42	3.37
1000	4.02	3.89	3.75	3.66	3.63	3.57	3.55	3.45	3.44	3.37
2000	3.88	3.78	3.65	3.57	3.56	3.52	3.48	3.40	3.37	3.29
4000	3.81	3.72	3.60	3.53	3.57	3.43	3.47	3.40	3.33	3.30

TABLE LV11 (a)

ϵ'' FOR CELLULOSE FROM DIELECTRIC VALUES FOR CELLULOSE PAPER (a)

Frequency	Temperature °C									
Kcs.	91.1	70.5	50.4	35.1	25.1	14.7	4.3	-6.0	-16.3	-27.0
.116	0.063	0.029	0.025	0.025	0.026	0.020	0.036	0.047	0.045	0.049
.2	0.045	0.026	0.022	0.020	0.020	0.022	0.039	0.055	0.057	0.060
.5	0.032	0.021	0.020	0.020	0.021	0.030	0.042	0.052	0.064	0.078
1	0.025	0.018	0.020	0.022	0.024	0.032	0.049	0.060	0.078	0.098
2	0.021	0.017	0.022	0.023	0.028	0.039	0.059	0.067	0.093	0.127
5	0.022	0.021	0.024	0.033	0.043	0.056	0.069	0.097	0.119	0.140
10	0.021	0.022	0.031	----	0.055	0.070	0.086	0.116	0.141	0.157
20	0.026	0.030	0.041	0.058	0.071	0.091	0.118	0.142	0.163	0.178
35	0.029	0.038	0.054	0.074	0.092	0.113	0.138	0.161	0.174	0.180
100	0.045	0.063	0.086	0.112	0.134	0.157	0.180	0.194	0.199	0.186
200	0.069	0.089	0.122	0.155	0.171	0.169	0.207	0.217	0.204	0.186
300	0.095	0.126	0.154	0.174	0.199	0.210	0.222	0.230	0.214	0.186
550	0.105	-----	0.196	0.221	0.233	0.239	0.242	0.230	0.210	0.183
1000	0.178	-----	0.246	0.261	0.284	0.261	0.252	0.229	0.203	0.174
2000	0.255	0.297	0.310	0.306	0.299	0.287	0.258	0.228	0.201	0.173
4000	0.401	0.402	0.382	0.370	0.348	0.315	0.289	0.251	0.218	0.190

TABLE LV11 (b)

ϵ'' FOR CELLULOSE FROM DIELECTRIC VALUES FOR CELLULOSE PAPER (a)

Frequency Kcs.	Temperature °C -37.2	-47.6	-57.9	-64.1	-68-8	-74.0	-84.1	-94.1	-104.2	-114.4
.116	0.074	0.093	0.123	0.133	0.140	0.152	0.142	0.129	0.113	0.088
.2	0.083	1.101	0.130	0.144	0.142	0.149	0.136	0.126	0.106	0.081
.5	0.100	0.123	0.140	0.150	0.146	0.145	0.133	0.113	0.090	0.068
1	0.120	0.140	0.152	0.158	0.152	0.146	0.130	0.108	0.082	0.062
2	0.137	0.153	0.159	0.155	0.152	0.141	0.122	0.098	0.074	0.055
5	0.156	0.163	0.156	0.149	0.141	0.130	0.109	0.086	0.066	0.050
10	0.170	0.168	0.153	0.142	0.131	0.118	0.098	0.077	0.060	0.044
20	0.174	0.168	0.148	0.135	0.126	0.109	0.090	0.069	0.055	0.041
35	0.173	0.163	0.138	0.125	0.118	0.103	0.085	0.066	0.051	0.039
100	0.168	0.148	0.126	0.110	0.101	0.088	0.074	0.056	0.046	0.035
200	0.165	0.142	0.116	0.100	0.093	0.082	0.072	0.054	0.044	0.032
300	0.162	0.140	0.115	0.098	0.095	0.082	0.069	0.050	0.040	0.034
550	0.158	0.132	0.110	0.097	0.088	0.077	0.066	0.055	0.040	0.035
1000	0.146	0.127	0.105	0.087	0.081	0.072	0.063	0.049	0.043	0.038
2000	0.158	0.126	0.101	-----	0.087	0.078	0.066	0.053	0.044	0.039
4000	0.167	0.137	0.121	0.107	0.117	0.095	0.094	0.075	0.066	0.059

TABLE LV111

C_{XP} FOR EMPTY SEIDMAN CELL USING ALCOHOL BATH

Frequency Kcs	Temperature °C									
	25.0	14.6	4.2	-6.2	-16.2	-26.9	-37.1	-47.5	-58.2	-68.2
.2	74.1	76.0	76.7	76.6	76.1	75.0	74.4	74.0	73.8	73.9
.5	73.8	75.2	75.7	75.7	75.3	74.4	74.1	73.8	73.7	73.8
1	73.8	74.7	75.3	75.1	74.8	74.1	73.9	73.8	73.7	73.8
2	73.8	74.2	74.7	74.5	74.4	74.0	73.9	73.7	73.7	73.8
5	73.6	73.8	74.1	74.0	74.0	73.8	73.8	73.6	73.6	73.7
10	73.6	73.7	73.9	73.9	73.7	73.6	73.8	73.5	73.6	73.6
35	73.5	73.6	73.5	73.6	73.5	73.3	73.6	73.4	73.4	73.4
100	73.4	73.4	73.4	73.7	73.4	73.5	73.5	73.5	73.4	73.5
200	73.5	73.5	73.5	73.7	73.5	73.5	73.6	73.5	73.5	73.5
300	73.5	73.6	73.6	73.6	73.6	73.6	73.7	73.5	73.6	73.5

TABLE LIX

D_X FOR EMPTY SEIDMAN CELL USING ALCOHOL BATH

Frequency Kcs.	Temperature °C									
	25.0	14.6	4.2	-6.2	-16.2	-26.9	-37.1	-47.5	-58.2	-68.2
.2	.0078	.0183	.0187	.0192	.0183	.0154	.0096	.0056	.0027	.0027
.5	.0043	.0171	.0181	.0183	.0165	.0120	.0060	.0038	.0020	.0020
1	.0031	.0136	.0165	.0162	.0140	.0089	.0042	.0027	.0019	.0019
2	.0019	.0107	.0141	.0136	.0113	.0065	.0030	.0022	.0016	.0016
5	.0015	.0066	.0103	.0093	.0073	.0040	.0022	.0015	.0013	.0012
10	.0014	.0047	.0077	.0067	.0051	.0030	.0020	.0011	.0011	.0011
35	.0019	.0028	.0048	.0043	.0034	.0024	.0024	.0016	.0018	.0016
100	.0035	.0035	.0043	.0039	.0038	.0032	.0035	.0030	.0031	.0028
200	.0060	.0057	.0060	.0054	.0057	.0054	.0059	.0049	.0057	.0054
300	.0081	.0081	.0089	.0085	.0085	.0081	.0081	.0081	.0081	.0081

TABLE LX

VALUES OF ϵ_m'', (a) UNCORRECTED ($C_{XP}\epsilon_m'$ AND (b) CORRECTED ($C_m\epsilon_m'$) FOR DISSIPATION FACTOR OF LEADS

FOR CELLULOSE PAPER (a) AT - 57.9° C.

f (Kc)	$C_{XP}\epsilon_m'$	$C_m\epsilon_m'$
0.116	0.0158	0.0167
0.2	.0172	.0178
0.5	.0191	.0195
1	.0209	.0216
2	.0228	.0234
5	.0230	.0238
10	.0233	.0239
20	.0233	.0239
35	.0231	.0231
100	.0228	.0214
200	.0243	.0205
300	.0269	.0202
550	.0207	.0196
1000	.0229	.0188
2000	.0290	.0188
4000	.0406	.0228

TABLE LX1

VALUES OF t_m AND f_m FOR LOW TEMPERATURE DISPERSION OF CELLULOSE

f (kc)	t_m (°C)	t (°C)	f_m (Kc)
0.116	- 78	- 27.0	140
0.2	- 76	- 37.2	71
0.5	- 69	- 47.6	12.6
1	- 64½	- 57.9	7.1
2	- 57	- 68.8	3.0
5	- 48½		
10	- 43		
20	- 35		
35	- 28		
100	- 14		
200	- 5½		
300	- 2½		
550	+ 11		
1000	+ 22½		
2000	+ 44		
4000	+ 72		

TABLE LX11

THERMODYNAMIC PARAMETERS OF ' LOW TEMPERATURE DISPERSION ' FOR CELLULOSE AND OF DISPERSION 'A' FOR NITROCELLULOSE PAPERS

MATERIAL	ΔF^* (Kcal/mole)	ΔH^* (Kcal/mole)	ΔS^* e.u.
Cellulose from values of paper, (Fig. R5-8)			
(a) from log $1/2\pi f$ vs $1/T_m$ plot	8.1	9.3	4.3
(b) from log $1/2\pi f_m$ vs $1/T$ plot	7.2	9.3	7.2
Cellulose paper, Seidman and Mason (S-3/			
from log $1/2\pi f$ vs $1/T_m$ plot	7.7	8.8	3.9
Cellophane, Muus (M-2/	9.1	11.0	6.6
Nitrocellulose (D.S. 2.16) papers	6.3	9.3	2.2
Nitrocellulose (D.S. 3.00) papers	6.6	9.8	2.2

TABLE LX111

$\epsilon'_m, \epsilon''_m$ FOR CELLULOSE PAPER (b)

	ϵ'_m			ϵ''_m		
	Temperature °C					
Frequency Kcs	124.6	149.1	174.4	124.6	149.1	174.4
.116	1.715	1.770	1.899	.0232	.0532	.1615
.2	1.710	1.758	1.877	.0167	.0442	.1187
.5	1.702	1.741	1.814	.0116	.0261	.0712
1	1.699	1.731	1.799	.0080	.0185	.0488
2	1.696	1.727	1.783	.0061	.0133	.0330
5	1.693	1.735	1.769	.0044	.0081	.0202
10	1.690	1.722	1.762	.0037	.0065	.0141
20	1.692	1.719	1.760	.0037	.0051	.0107

TABLE LXIV

ϵ'_m FOR CELLULOSE PAPER (c)

Frequency Kcs.	Temperature °C 90.9	110.8	129.1	149.1	174.3	199.2	224.2	249.2	264.
.05	----	-----	1.744	-----	1.951	2.378	3.054	3.75	3.836
.116	1.677	1.702	1.729	1.770	1.878	2.138	2.689	3.065	3.116
.2	1.679	1.698	1.719	1.757	1.842	2.051	2.421	2.742	2.819
.5	1.676	1.694	1.711	1.741	1.798	1.928	2.135	2.290	2.328
1	1.673	1.691	1.708	1.732	1.780	1.881	2.026	2.109	2.107
2	1.671	1.689	1.707	1.726	1.769	1.854	1.956	1.997	1.953
5	1.670	1.686	1.702	1.722	1.761	1.826	1.889	1.892	1.832
10	1.667	1.685	1.702	1.719	1.751	1.813	1.864	1.854	1.786
20	1.667	1.682	1.699	1.716	1.748	1.805	1.850	1.831	1.760
35			1.698	1.714	1.745	1.800	1.835	1.814	1.729
100			1.695	1.712	1.741	1.791	1.826	1.801	1.717
200			1.694	1.712	1.741	1.791	1.822	1.797	1.708
300			1.695	1.713	1.742	1.789	1.822	1.797	1.710

TABLE LXV

ϵ'' FOR CELLULOSE PAPER (c)

Frequency Kcs.	Temperature °C 90.9	110.8	129.1	149.1	174.3	199.2	224.2	249.2	264.
.05	----	-----	.045	0.094	0.248	0.680	1.460	1.556	1.465
.116	.0085	.0162	.0296	0.0619	0.1576	0.453	0.976	1.180	1.094
.2	.0067	.0122	.0232	0.0460	0.1164	0.310	0.726	0.976	0.925
.5	.0044	.0078	.0139	0.0279	0.0683	0.185	0.420	0.616	0.617
1	.0039	.0059	.0101	0.0187	0.0463	0.1226	0.283	0.430	0.442
2	.0028	.0044	.0070	0.0131	0.0313	0.0801	0.1858	0.286	0.297
5	.0032	.0037	.0051	0.0084	0.0183	0.0436	0.1041	0.1640	0.1706
10	.0032	.0034	.0042	0.0062	0.0130	0.0310	0.0665	0.1070	0.1102
20	.0038	.0034	.0042	0.0051	0.0093	0.0209	0.0435	0.0681	0.0707
35			.0039	0.0046	0.0077	0.0155	0.0314	0.0484	0.0493
100			.0051	0.0048	0.0061	0.0104	0.0186	0.0268	0.0290
200			.0071	0.0068	0.0068	0.0098	0.0153	0.0203	0.0224
400			.0095	0.0082	0.0077	0.0107	0.0151	0.0190	

TABLE LXVI

FREQUENCIES f" FOR WHICH $\epsilon''_m = 0.05$; FOR CELLULOSE PAPER (C) ABOVE 90° C

t°C	f" (Kc)
129	0.042
149	0.16
174	0.87
199	4.0
224	16

TABLE LXV11

ϵ_{pl}, PLATEAU VALUES OF ϵ_m' FROM ARGAND DIAGRAMS

t°C	ϵ_{pl}
91	1.670
111	1.685
129	1.698
149	1.715
174	1.742
199	1.787
226	1.811
249	1.783
264	1.690

TABLE LXV111

MAXIMUM VALUES OF ΔH^*, ΔS^*, AND CORRESPONDING VALUES OF ΔF^* FOR CELLULOSE-SORBENT AND NITROCELLULOSE-ACETONE

('LOW TEMPERATURE' AND 'A' DISPERSIONS)

System	ΔF^* (Kcal/mole)	ΔH^* (Kcal/mole)	ΔS^* (e.u.)	Source
(a) Cellulose paper - water	6.4	12	18	S-2
(b) Cellulose paper - methanol	6.9	10.3	11.6	S-2
(c) Cellulose paper - ethanol	6.9	10.2	10.8	S-2
(d) Nitrocellulose (D"S" 2.33) film-acetone	9	18	33	this work

TABLE LXIX

DISPERSION OF DRY UNPLASTICIZED CELLULOSE PROPIONATE

FROM DATA OF DEISER ET AL (31)

(a)

t(^{o}C)	$\log_{10} f_m$ ($\log_{10}$c.p.s.)
80	6.5
25	4.7
-40	3.4

(b)

ΔF^* (Kcals / mole)	ΔH^* (Kcals / mole)	ΔS^* (e.u.)
9.3	8.3	- 3

TABLE LXX

DIPOLE MOMENTS OF NITROCELLULOSES IN BUTYL AND ISOAMYL ACETATE ESTIMATED AT 35°C FROM JATKAR'S RESULTS (34) USING HIS NEW EQUATION FOR A CELLOBIOSE UNIT

Percent Nitrogen Content of Nitrocellulose	Degree of Substitution (D.S.)	μ (Debye units) In Butyl Acetate	μ (Debye units) In Isoamyl Acetate
8.4	1.33	5.0	6.0
10.0	1.72	6.1	4.7
10.7	1.89	<3.3	6.2
11.1	2.00	3.5	5.9
11.5	2.12	<3	6.1
13.1	2.62	7.0	6.3

FIGURE 1, 2

FIGURE 1

Schematic structure of cellulose

(illustrated in Introduction, Part 2)

FIGURE 2

Schematic structure of nitrocellulose monomer

(illustrated in Introduction, Part 2)

FIGURE 3a,3b

FIGURE 3a,3b

Illustrations of force tube between interface of two dielectrics and dielectric plate

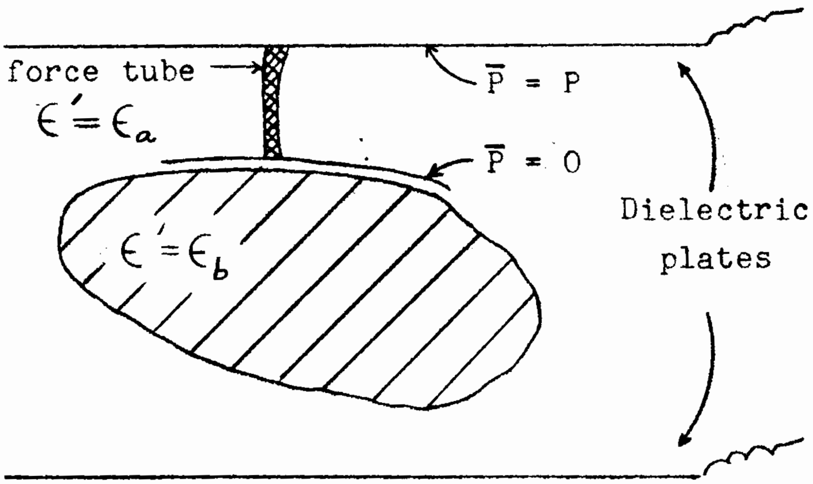


FIGURE 3a

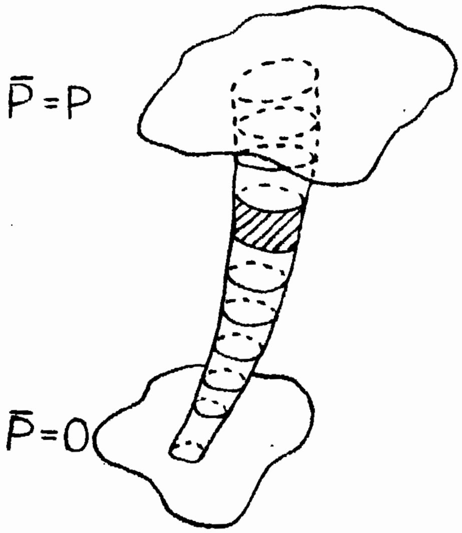


FIGURE 3b

FIGURES 4 & 5

FIGURE 4

Possible paths taken by tubes of force in a heterogeneous dielectric

FIGURE 5

Illustration of heterogeneous dielectric and surfaces of integration

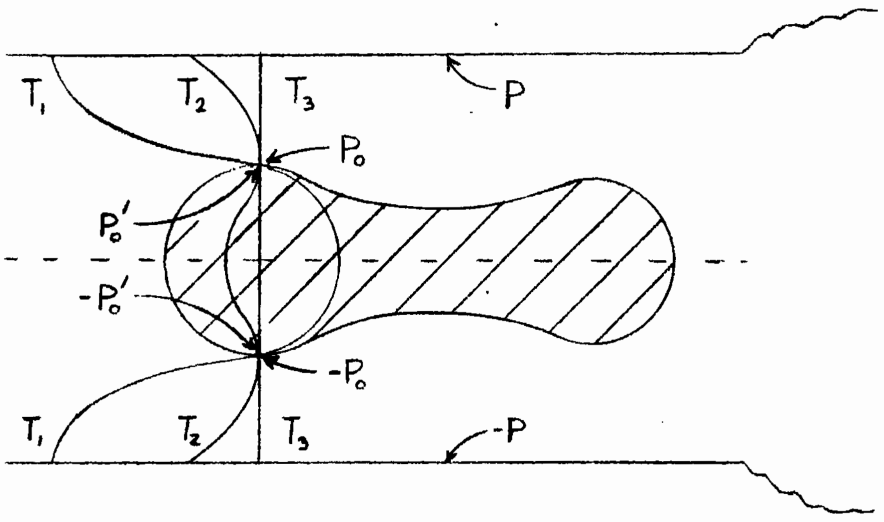


FIGURE 4

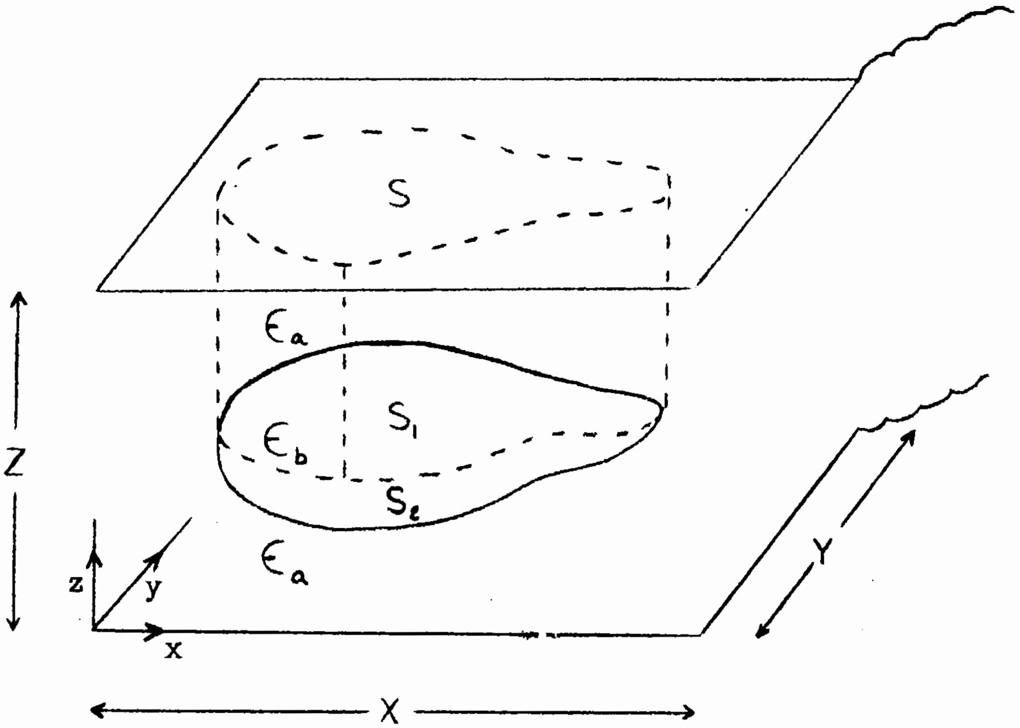


FIGURE 5

Figure 6a, 6b

FIGURE 6a, 6b

Illustrations of model (a) for cellulose paper

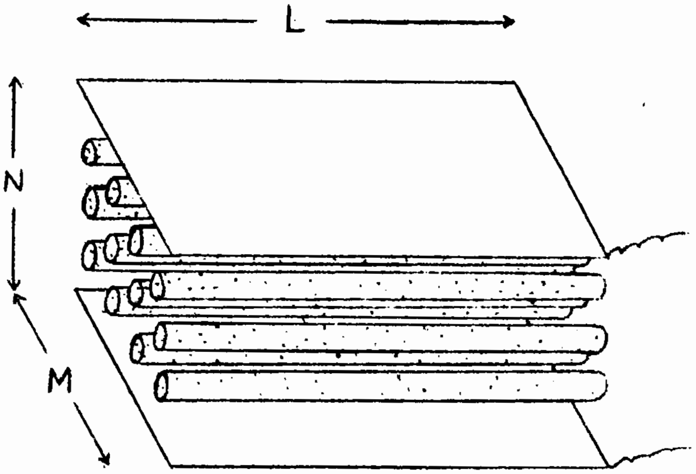


FIGURE 6a

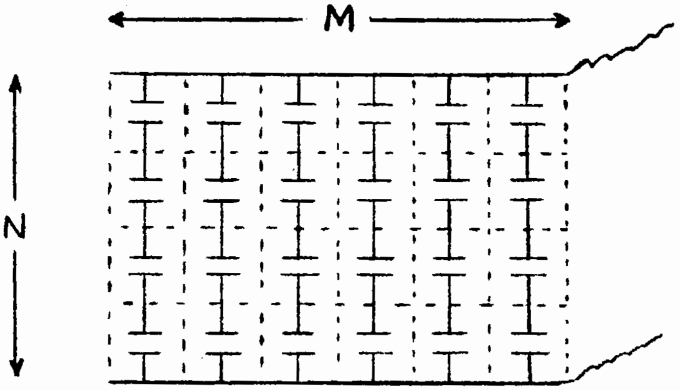


FIGURE 6b

FIGURE 7

FIGURE 7

Imaginary unit condenser of model (a) for cellulose paper

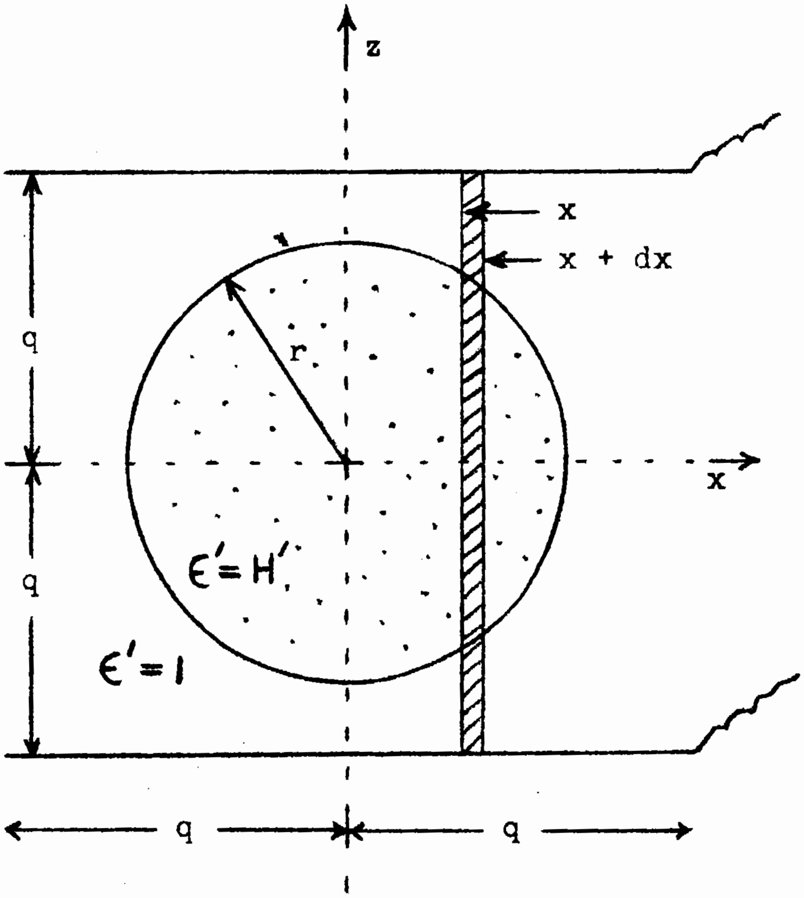

z
x
x + dx
r
q
q
ϵ′ = H′
ϵ′ = 1
x
q
q

FIGURE 8a, 8b

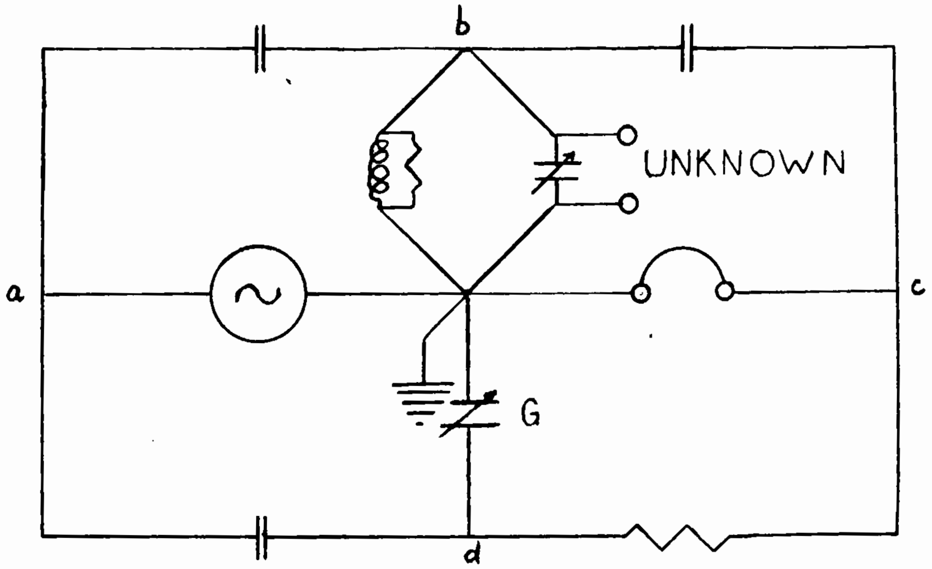
FIGURE 8a

Twin-T circuit

FIGURE 8b

Schering bridge circuit - modification for substitution method

(a)



(b)

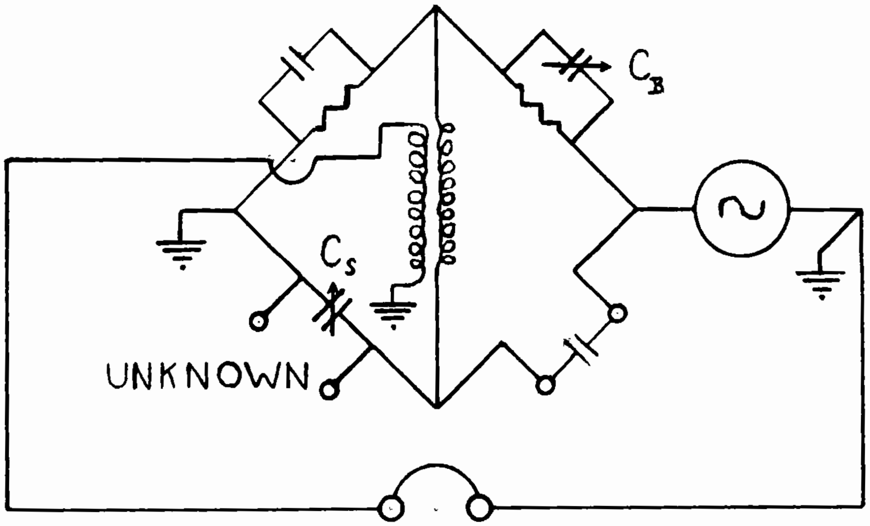


FIGURE 9

FIGURE 9

Balsbaugh liquid dielectric cell

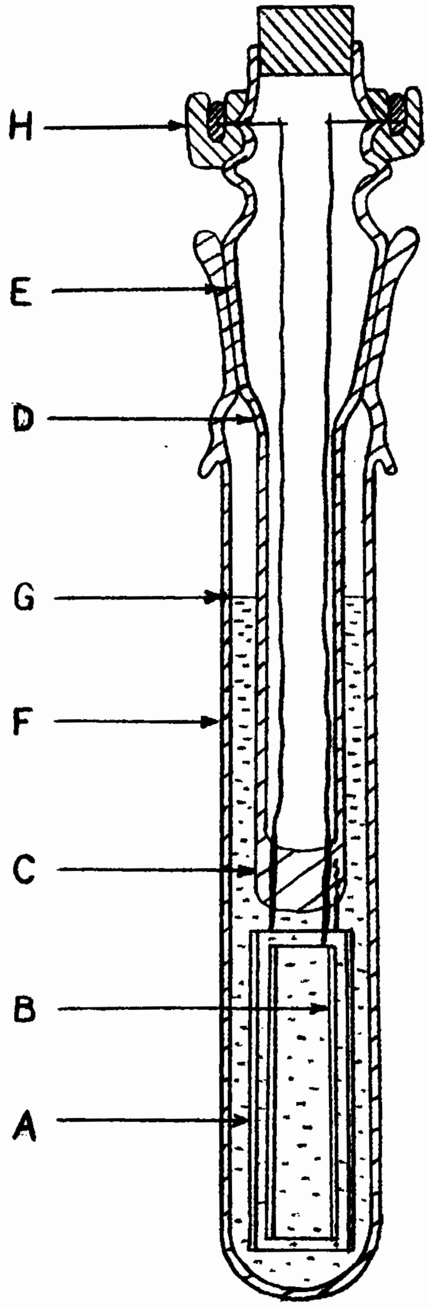

H
E
D
G
F
C
B
A

FIGURE 10

FIGURE 10

Film dielectric cell

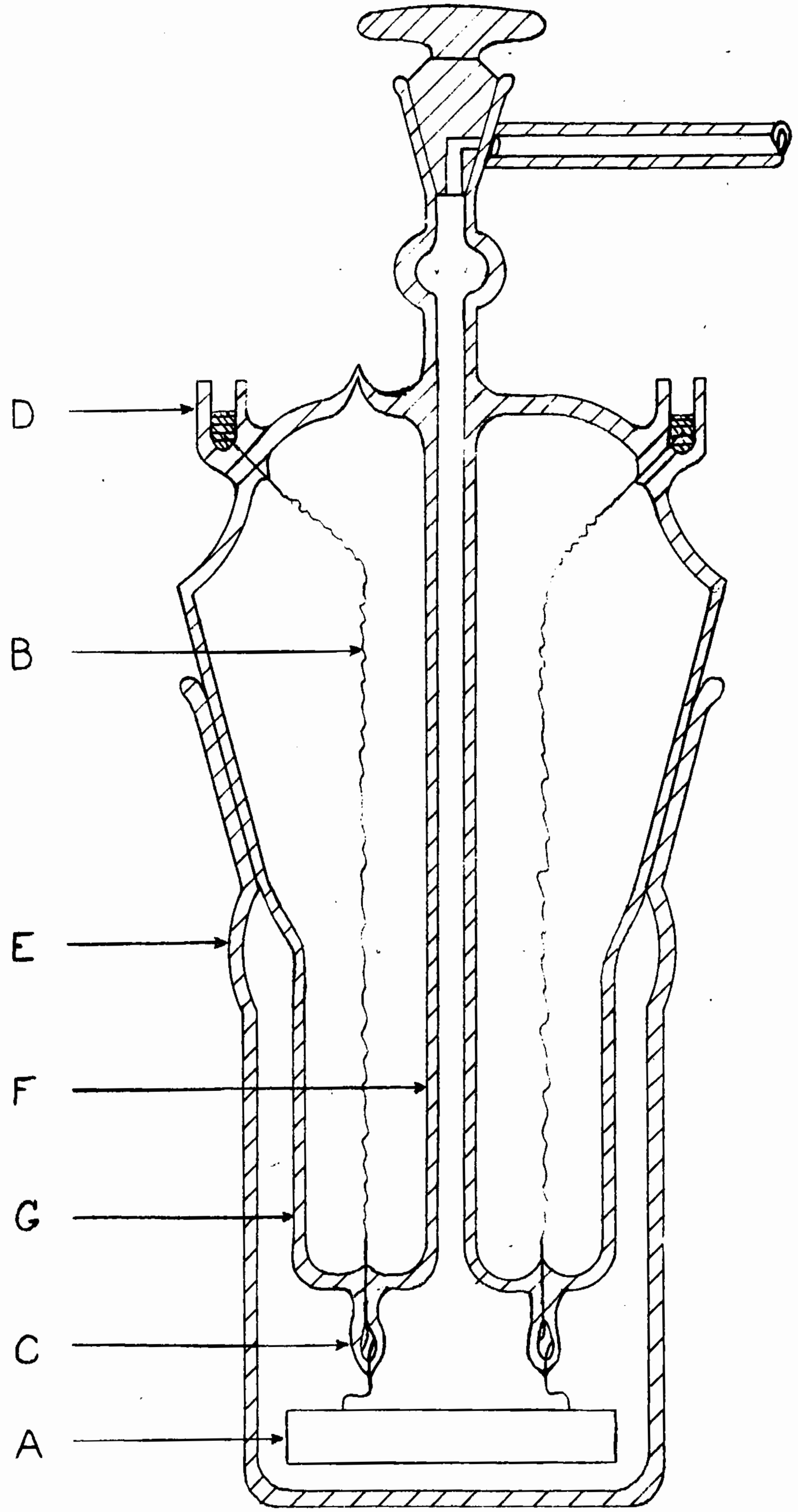

D
B
E
F
G
C
A

FIGURE 11

FIGURE 11

Shields for metallizing film specimens

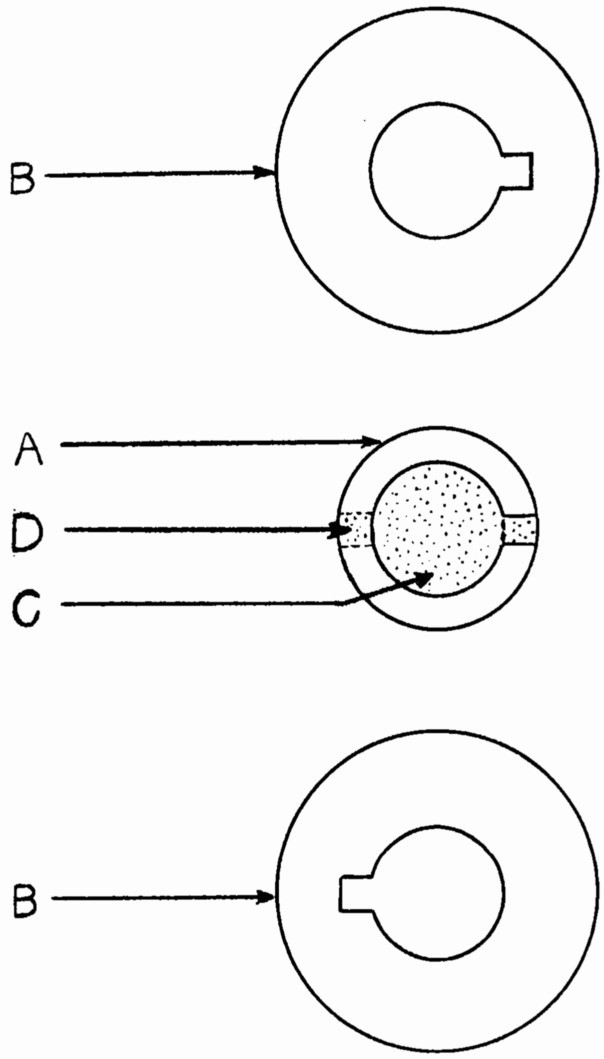

B
A
D
C
B

FIGURE 12

FIGURE 12

Vacuum equipment for metallizing film

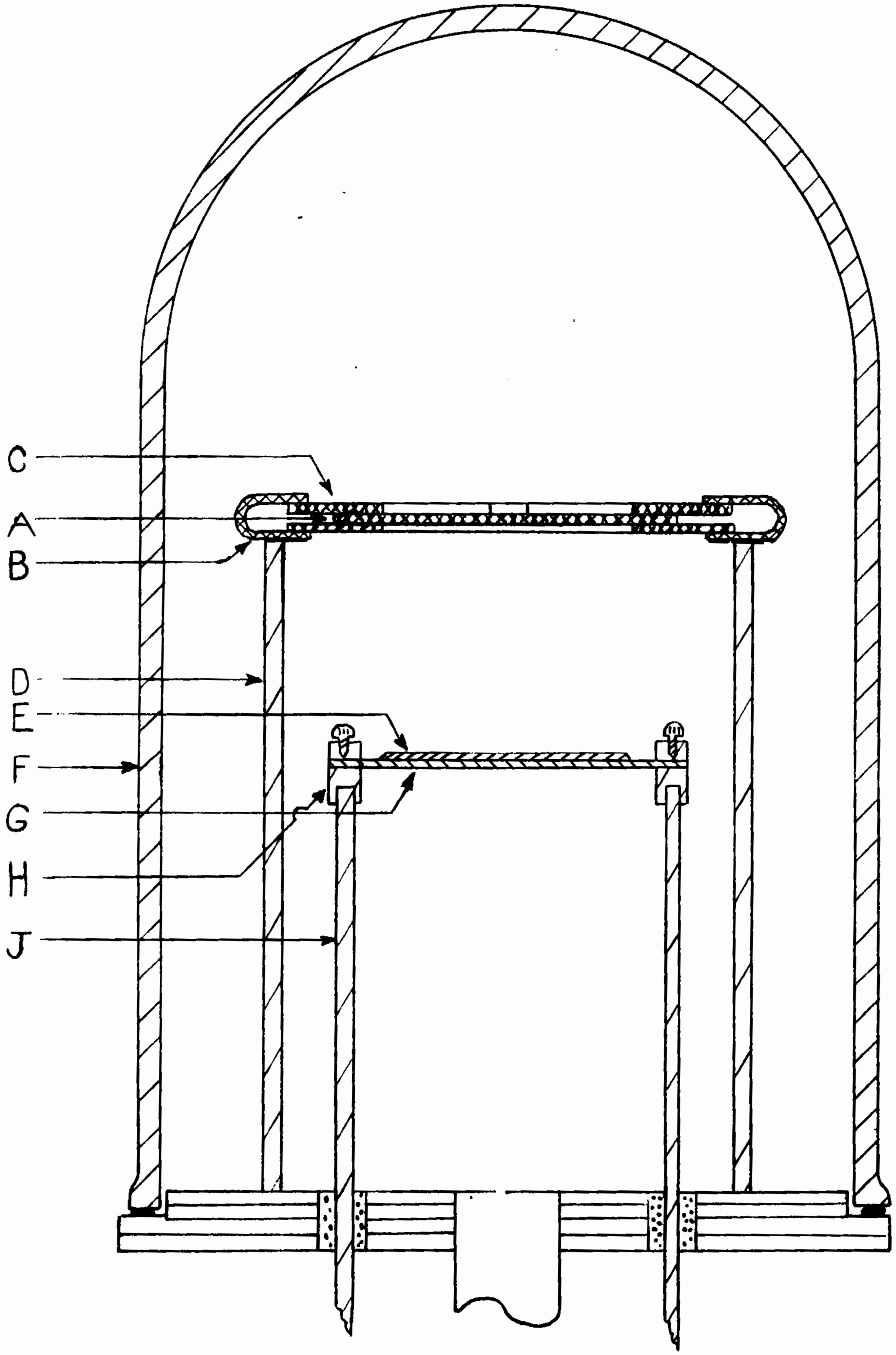

C
A
B
D
E
F
G
H
J

FIGURE 13

FIGURE 13

Condenser for film dielectric cell

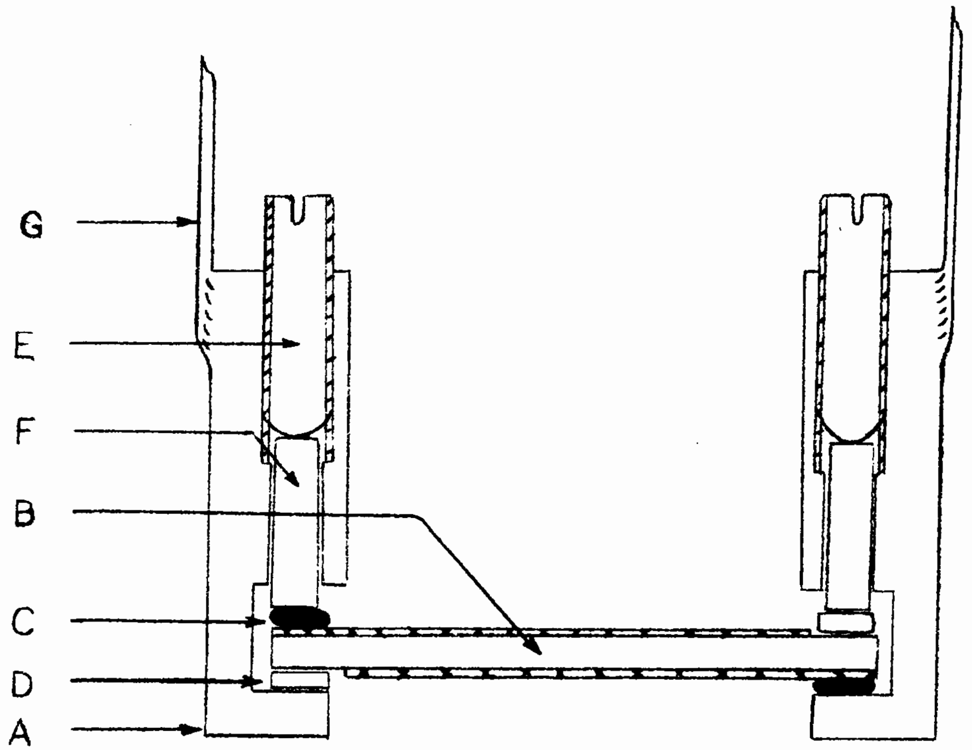

G
E
F
B
C
D
A

FIGURE 14

FIGURE 14

Condenser for film dielectric cell modified to receive paper samples.

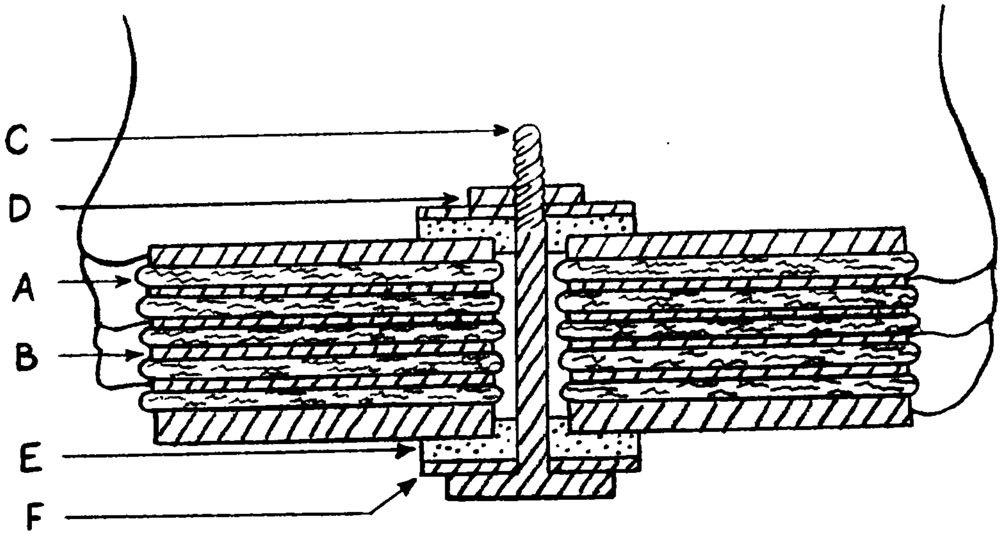

C
D
A
B
E
F

FIGURE 15

FIGURE 15

Vessel for preparation of film samples from solutions.

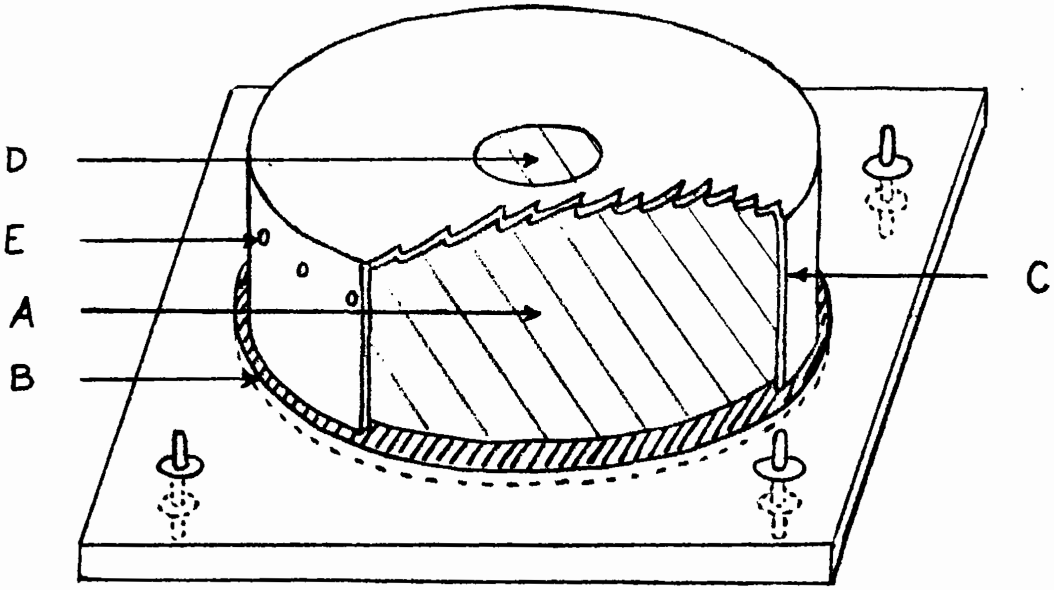

D
E
A
B
C

FIGURE 16

FIGURE 16

Thermoregulator for temperature from 25 to -65° C.

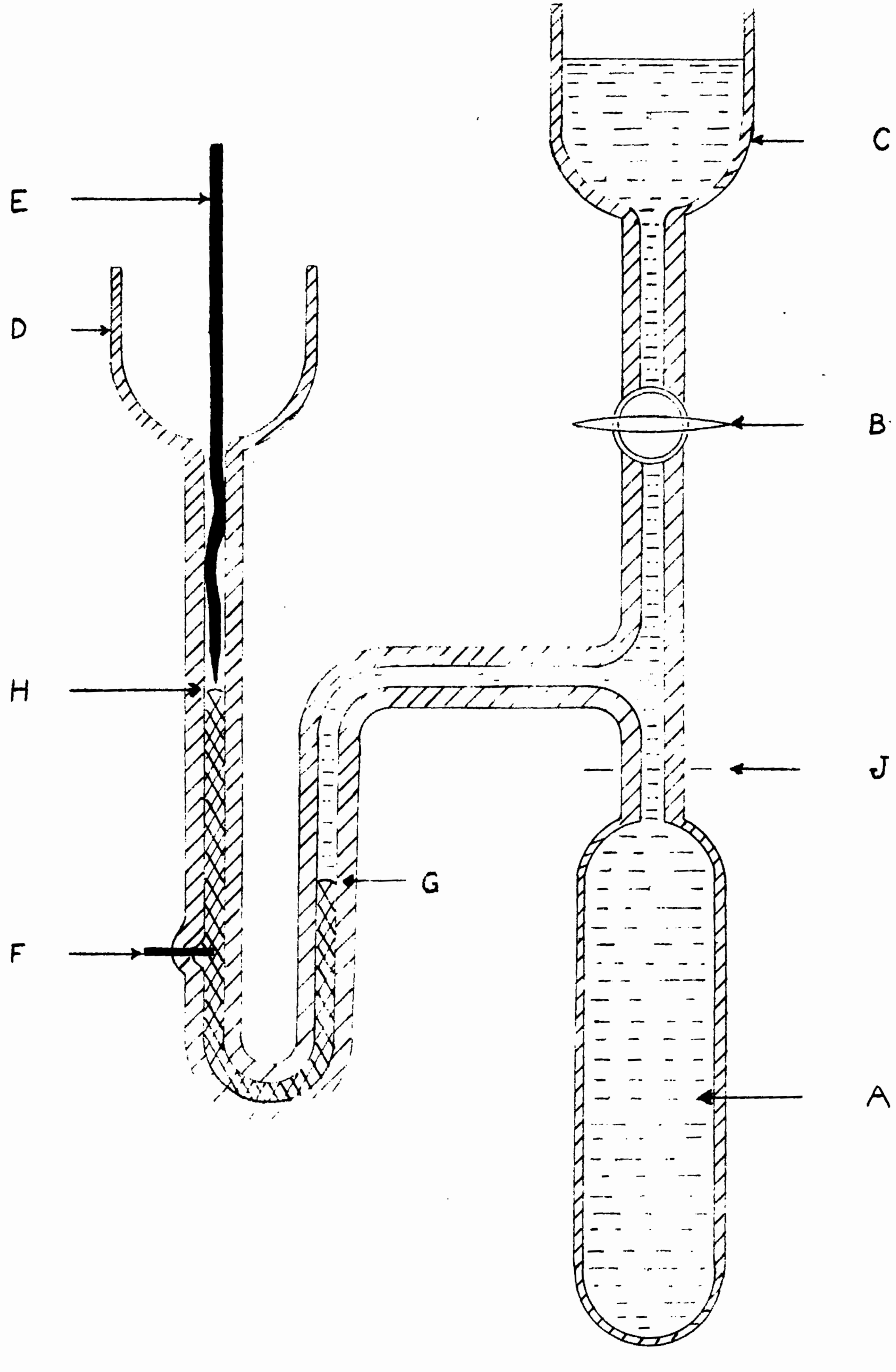

E
D
H
F
G
C
B
J
A

FIGURE 17

FIGURE 17

Dewar Finger for cooling baths to -65° C.

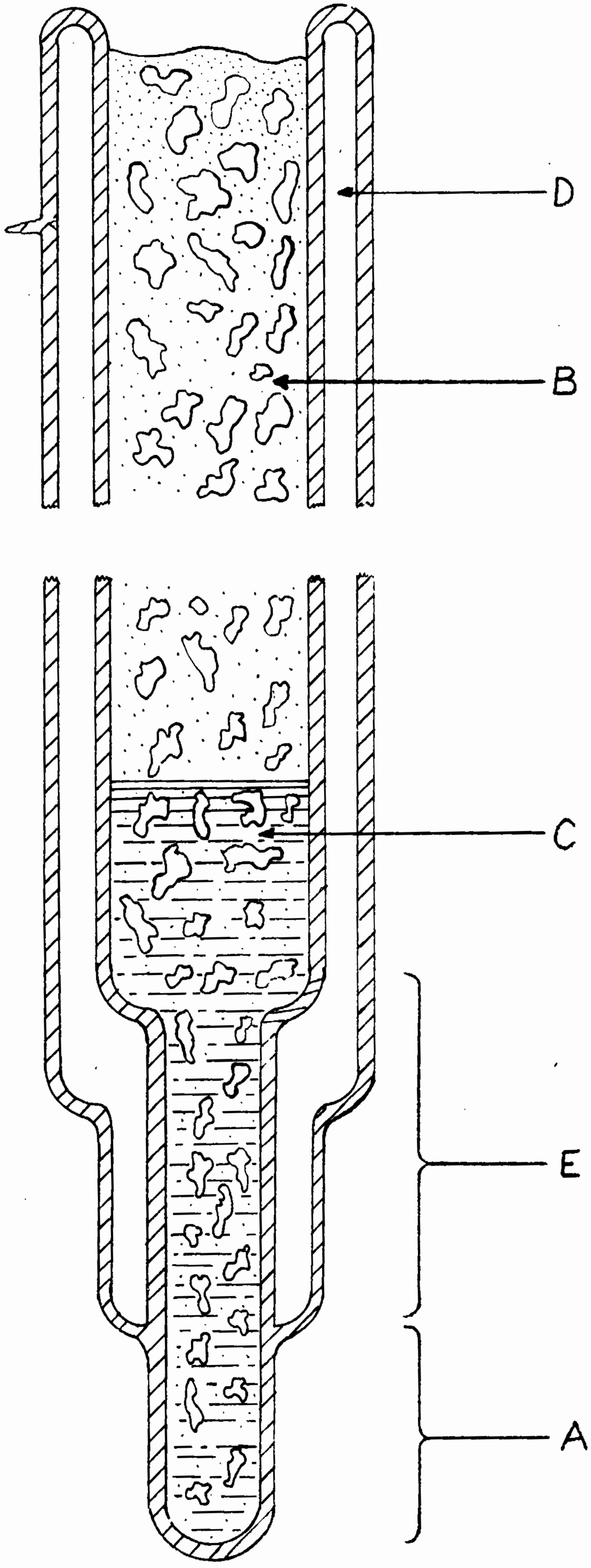

D
B
C
E
A

FIGURE 18

FIGURE 18

Vapour Conditioning System

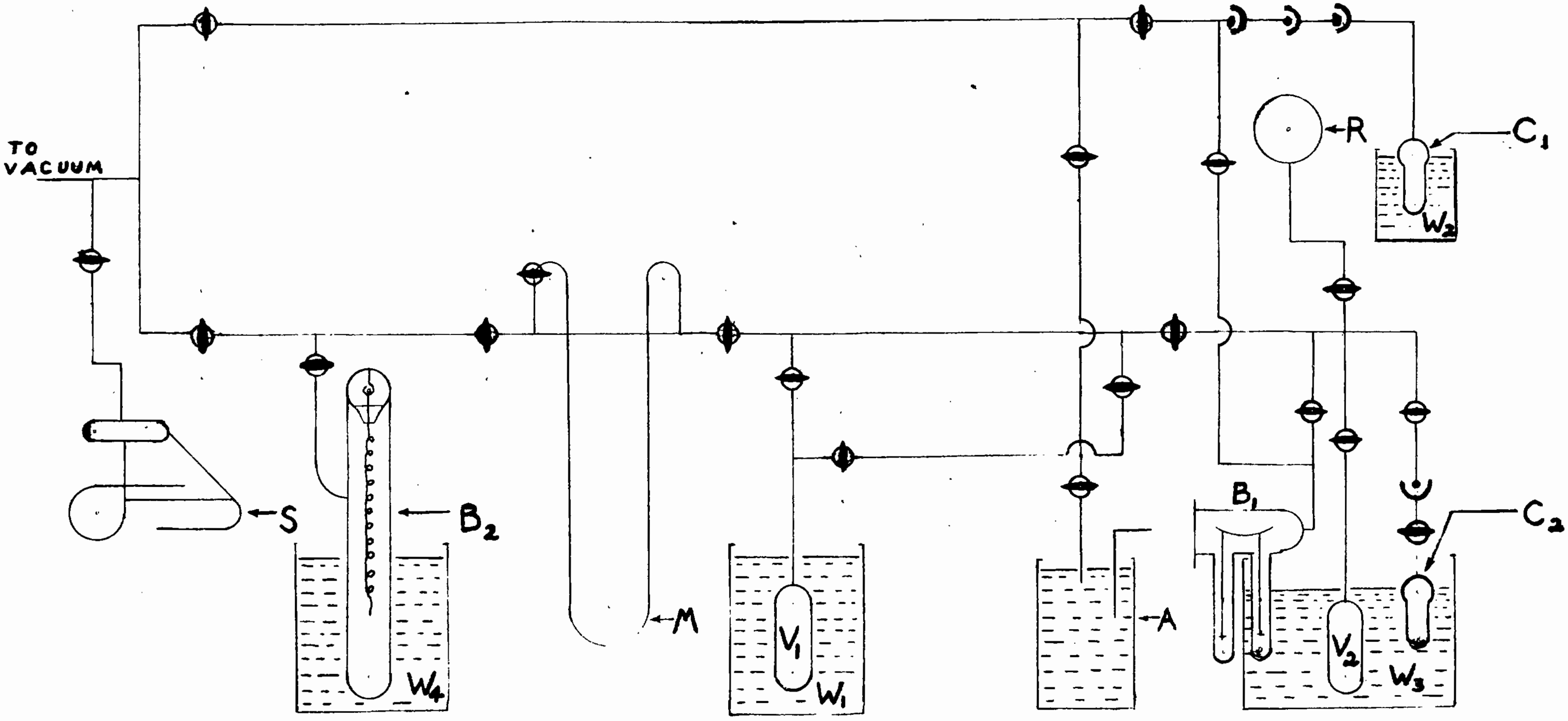

TO VACUUM
R
C₁
W₂
S
B₂
W₄
M
V₁
W₁
A
B₁
V₂
W₃
C₂

FIGURE 19

FIGURE 19

Torsion Balance Assembly

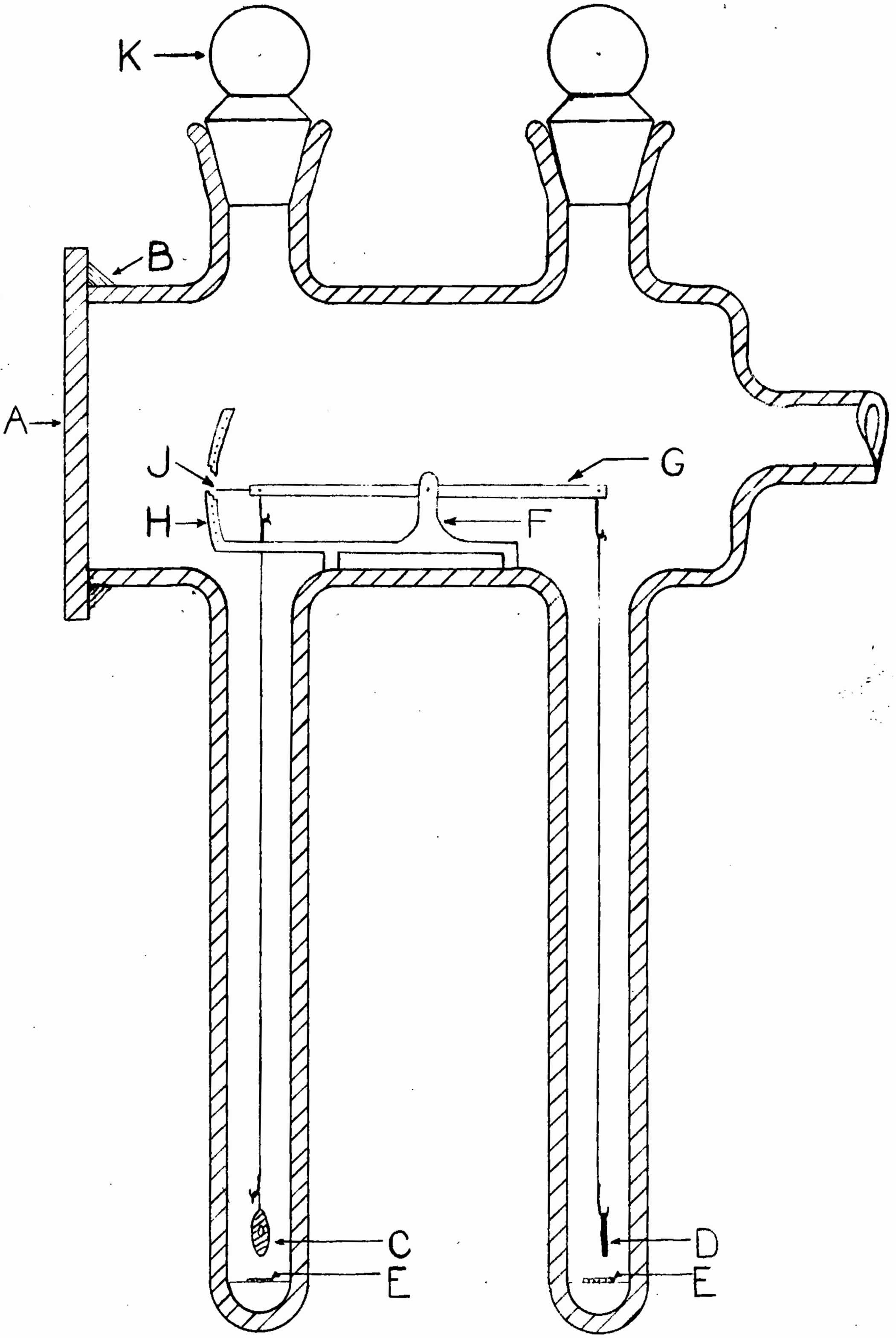

K
B
A
J
G
H
F
C
E
D
E

FIGURE 20

FIGURE 20

Torsion Balance

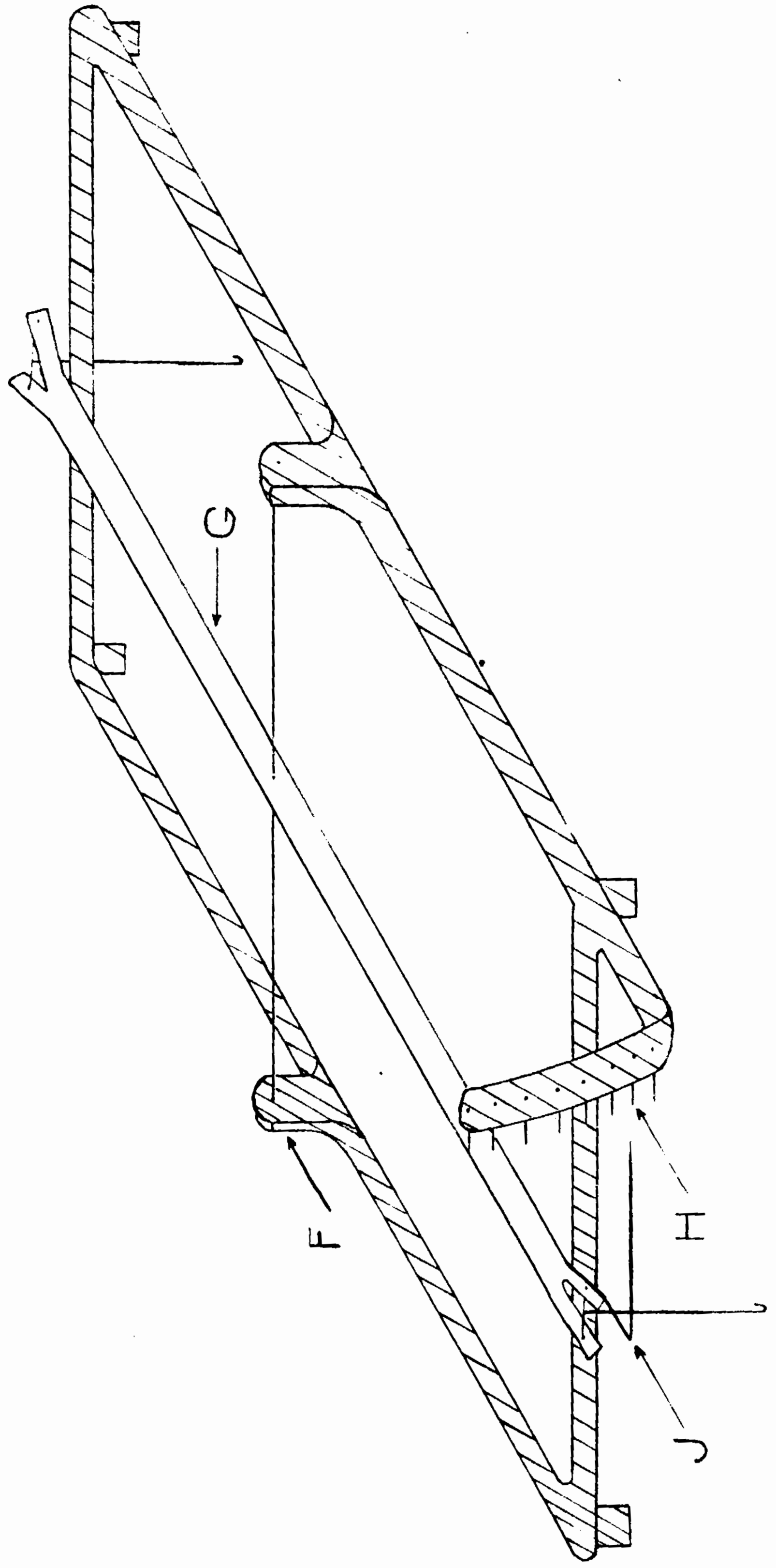
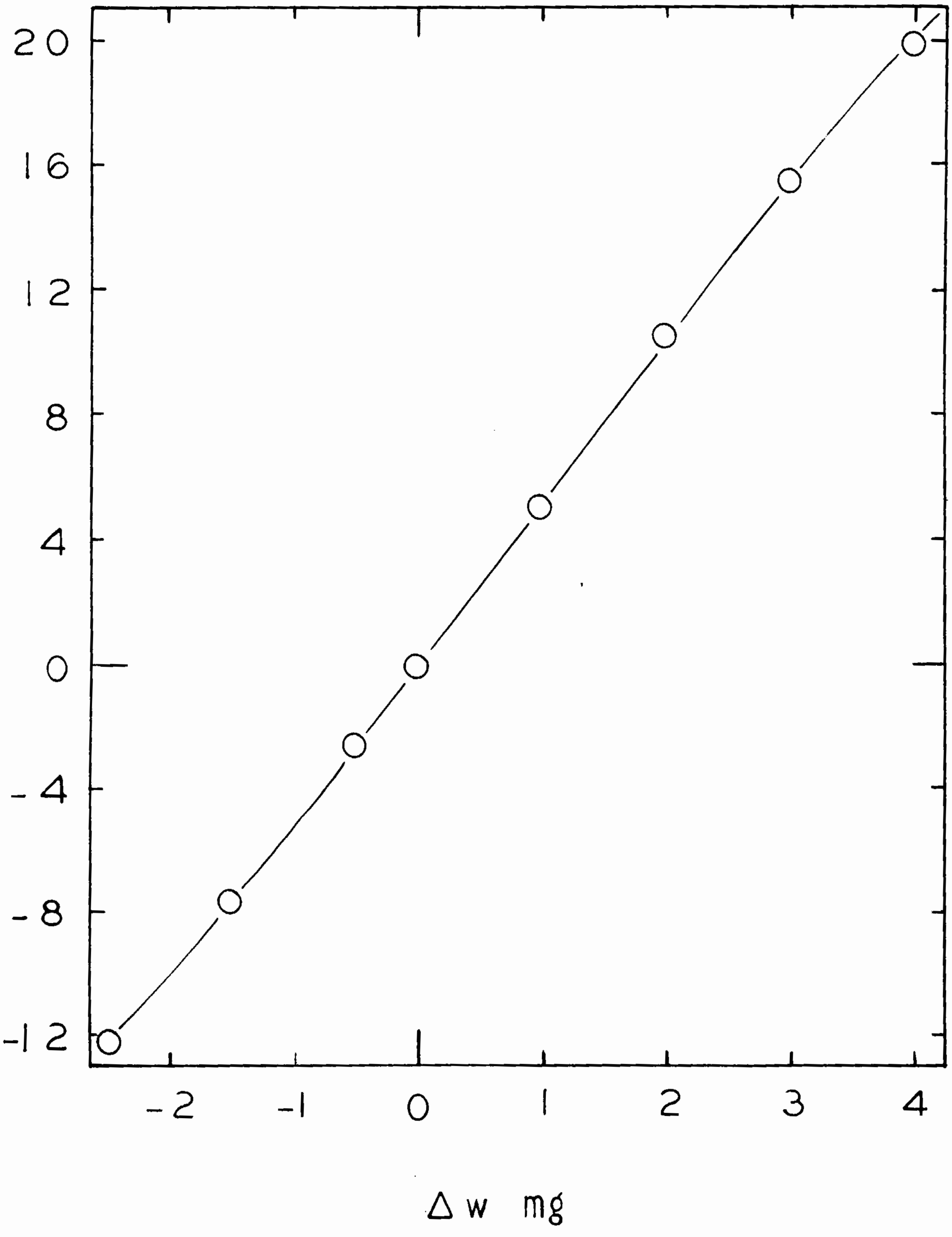

G
F
H
J

FIGURE 21

<u>FIGURE 21</u>

Calibration curve for torsion balance



20
16
12
8
4
0
-4
-8
-12
Δe mm
-2
-1
0
1
2
3
4
Δw mg

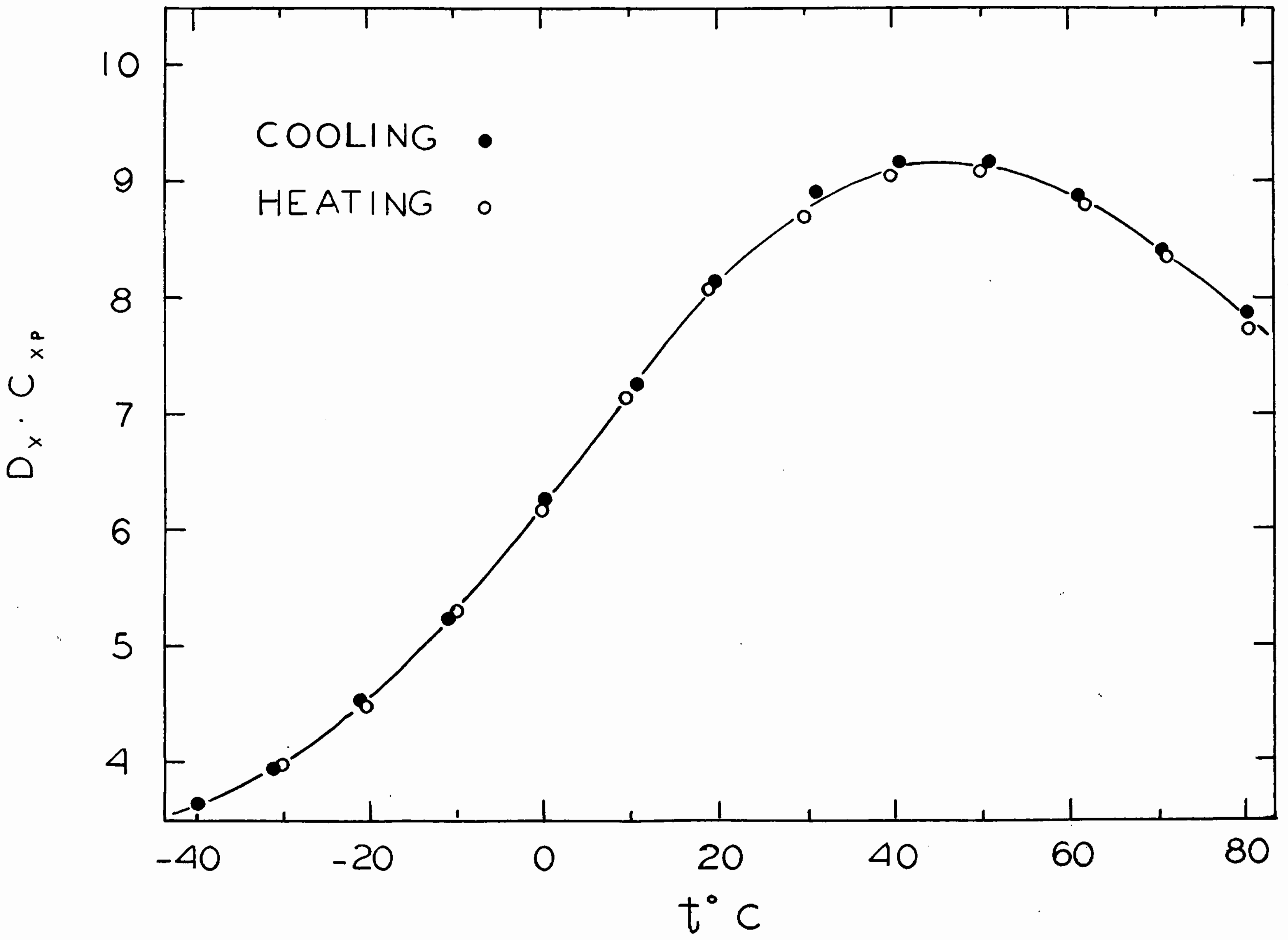
FIGURE 22

FIGURE 22

$D_x \cdot C_{xp}$ vs t°C for preliminary sample of celluloid
(40% camphor) at 100 Kc

● Cooling

○ Heating



COOLING ●
HEATING ○
$D_x \cdot C_{xp}$
10
9
8
7
6
5
4
-40
-20
0
20
40
60
80
t° C

FIGURE 23

FIGURE 23

C_{XP} vs t°C for preliminary sample of celluloid (40% camphor) at 100 Kc

● Cooling

o Heating

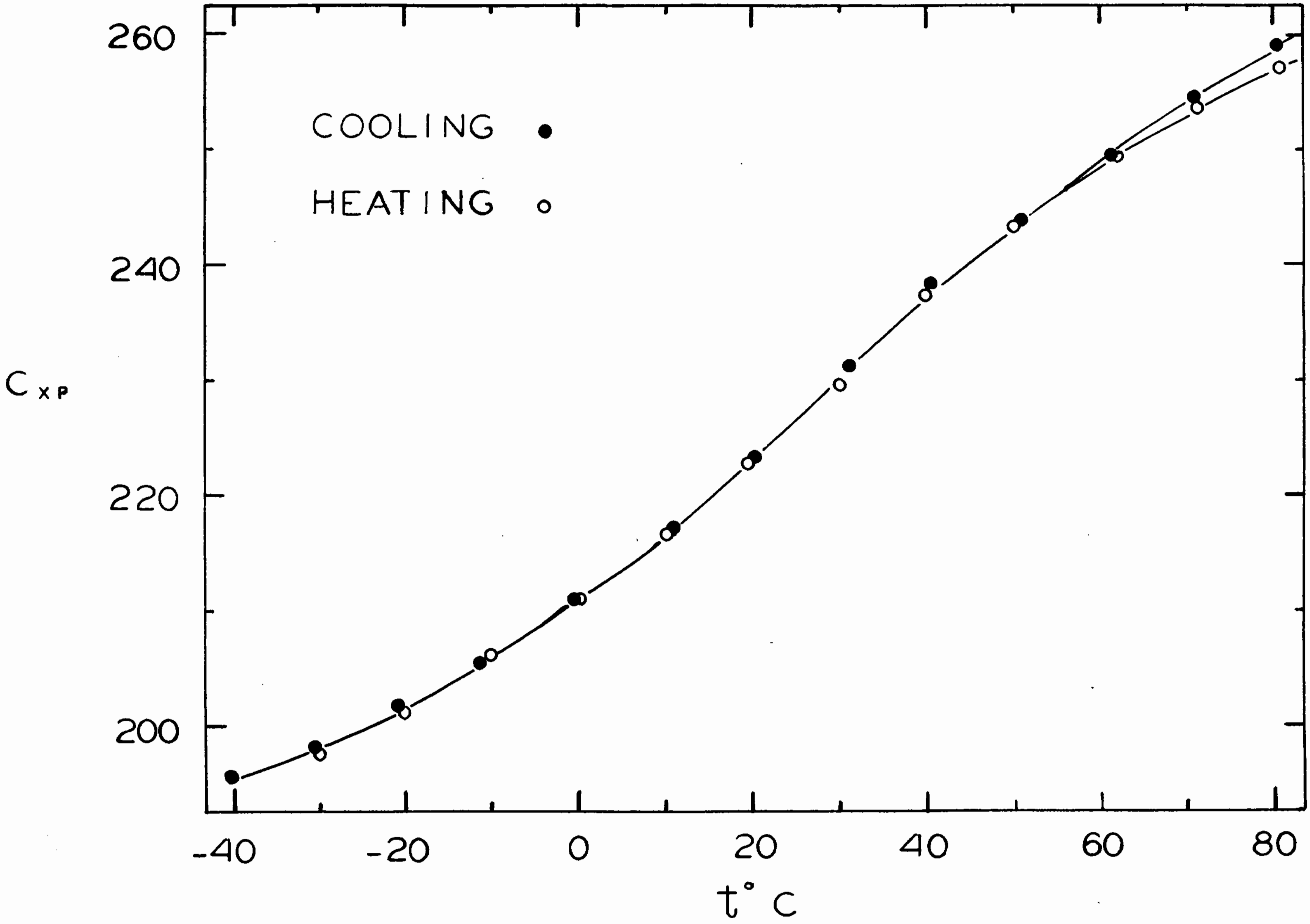

COOLING ●
HEATING ○
C_{xP}
260
240
220
200
-40
-20
0
20
40
60
80
t° C

FIGURE 24

FIGURE 24

Isotherms at 25°C of nitrocellulose and sorbed acetone

○ nitrocellulose of D.S. 2.33 - present results.

△ nitrocellulose of D.S. 2.27 - Dreschel and coworkers (67)

■ nitrocellulose of D.S. 1.97 - Dreschel and coworkers (67)

● nitrocellulose of unknown D.S. - Schulz (68)

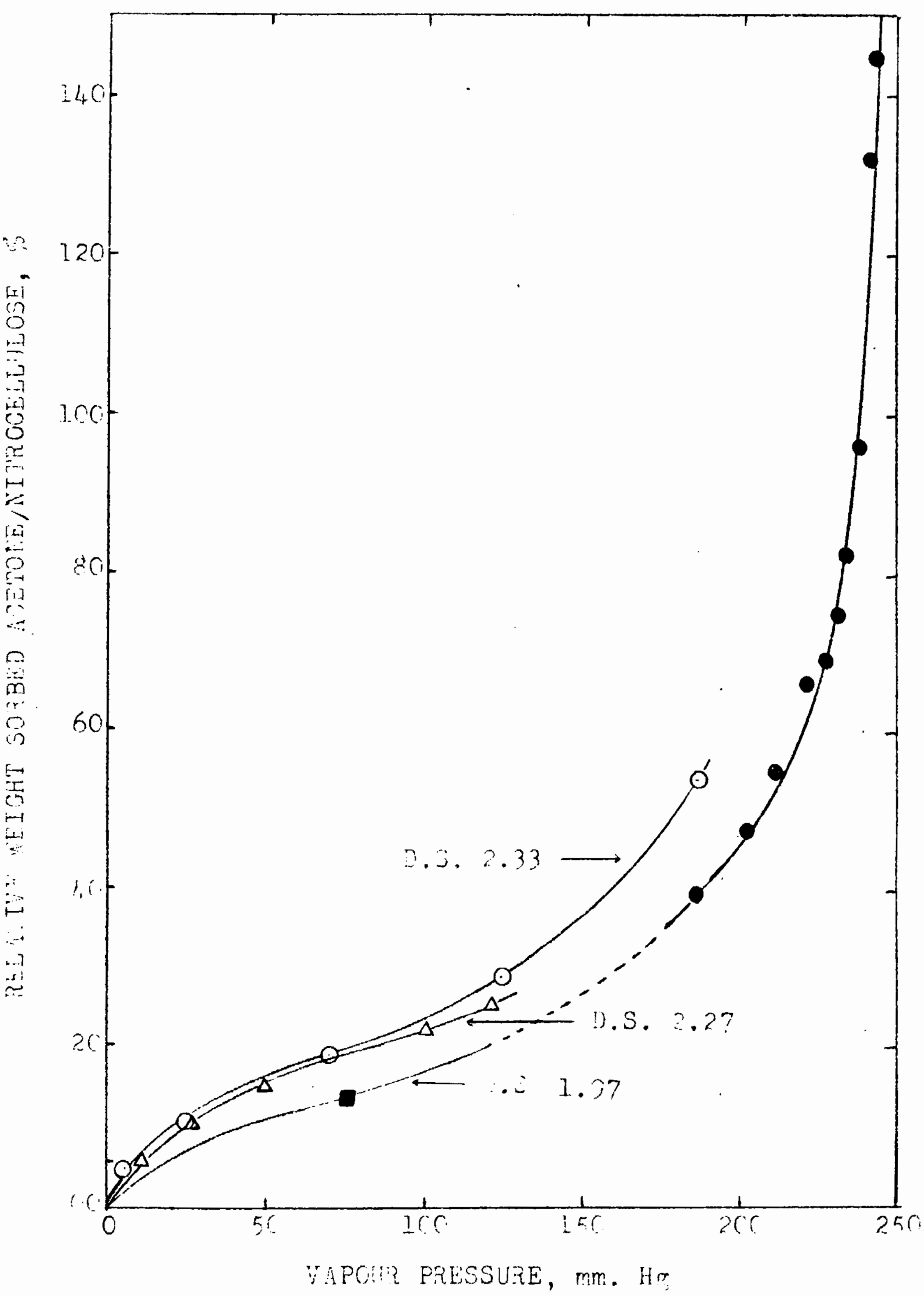

RELATIVE WEIGHT SORBED ACETONE/NITROCELLULOSE, %
140
120
100
80
60
40
20
0.0
0
50
100
150
200
250
VAPOUR PRESSURE, mm. Hg
D.S. 2.33
D.S. 2.27
D.S. 1.97

FIGURE 25

FIGURE 25

Sorption isostere of 16.0% acetone - nitrocellulose
(D.S. 2.33)

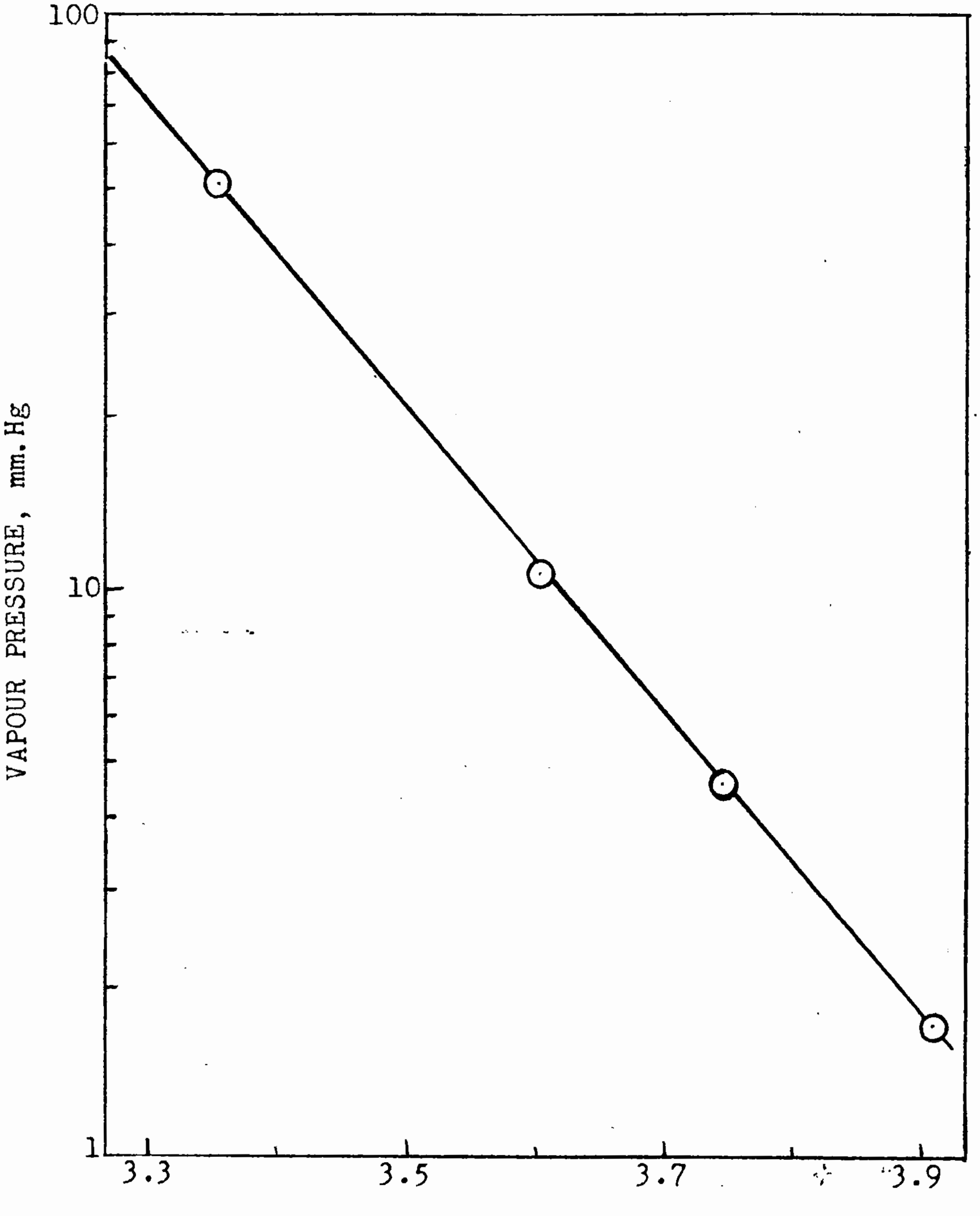

100
10
1
VAPOUR PRESSURE, mm. Hg
3.3
3.5
3.7
3.9
1000 T-1

FIGURE 26a, 26b, 26c, 26d

FIGURE 26a

ϵ'_m vs f (Kc) for solution No. 1 at 24.4 ° C.

FIGURE 26b

ϵ''_m vs f^{-1} $(Mc)^{-1}$ for solution No. 1 at 24.4 ° C.

FIGURE 26c

ϵ'_m vs f (Kc) for solution No. 2 at 26.0 ° C.

FIGURE 26d

ϵ''_m vs f^{-1} $(Mc)^{-1}$ for solution No. 2 at 26.0 ° C.

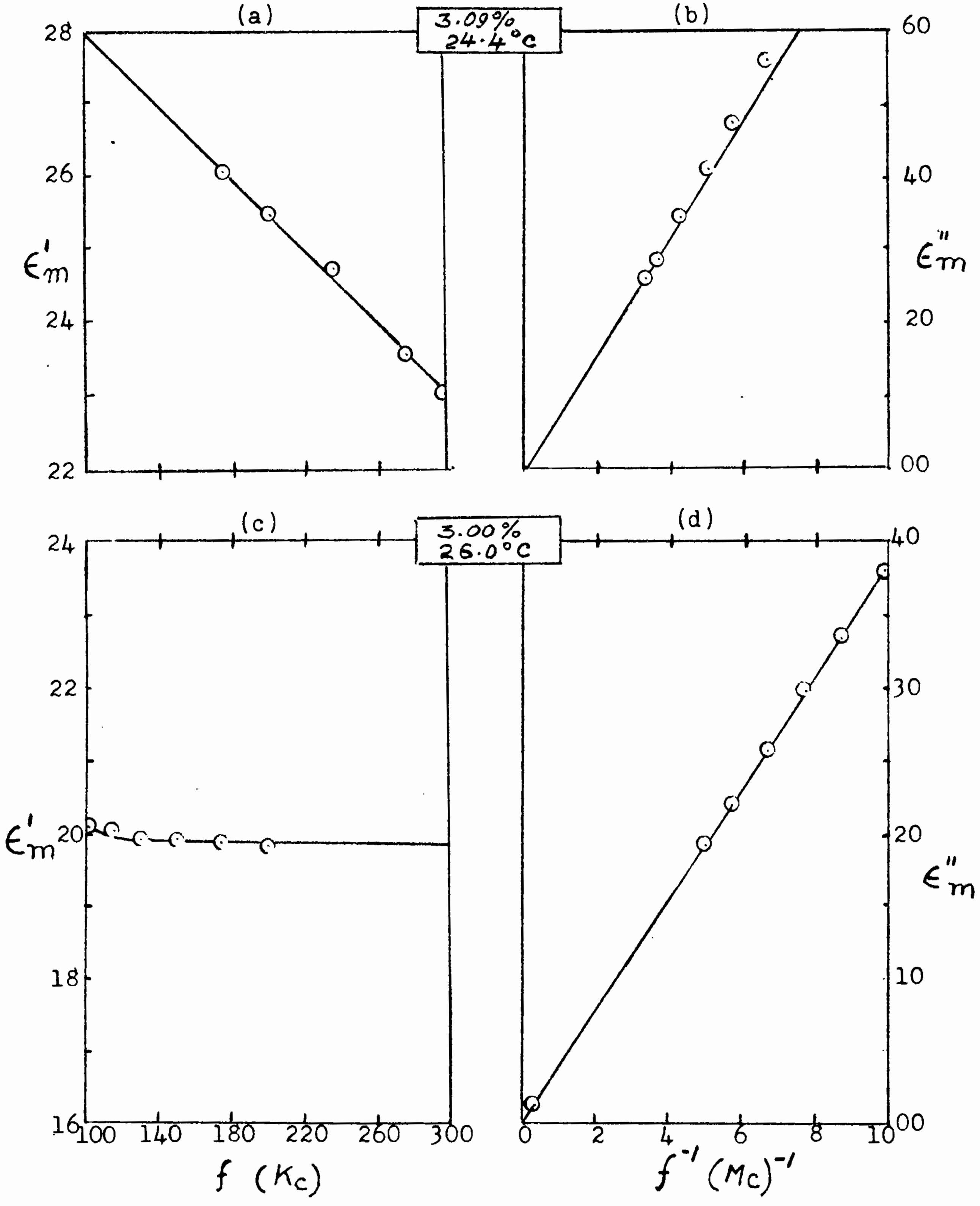

(a)
(b)
3.09%
24.4°C
(c)
(d)
3.00%
26.0°C
28
26
24
22
60
40
20
00
24
22
20
18
16
40
30
20
10
00
ϵ'_m
ϵ''_m
100
140
180
220
260
300
0
2
4
6
8
10
f (Kc)
f^{-1} (Mc)$^{-1}$

FIGURE 27a,27b

FIGURE 27a

ϵ'_m vs t°C for solution No. 2 at 100 Kc

FIGURE 27b

ϵ''_m vs t°C for solution No. 2 at 100 Kc

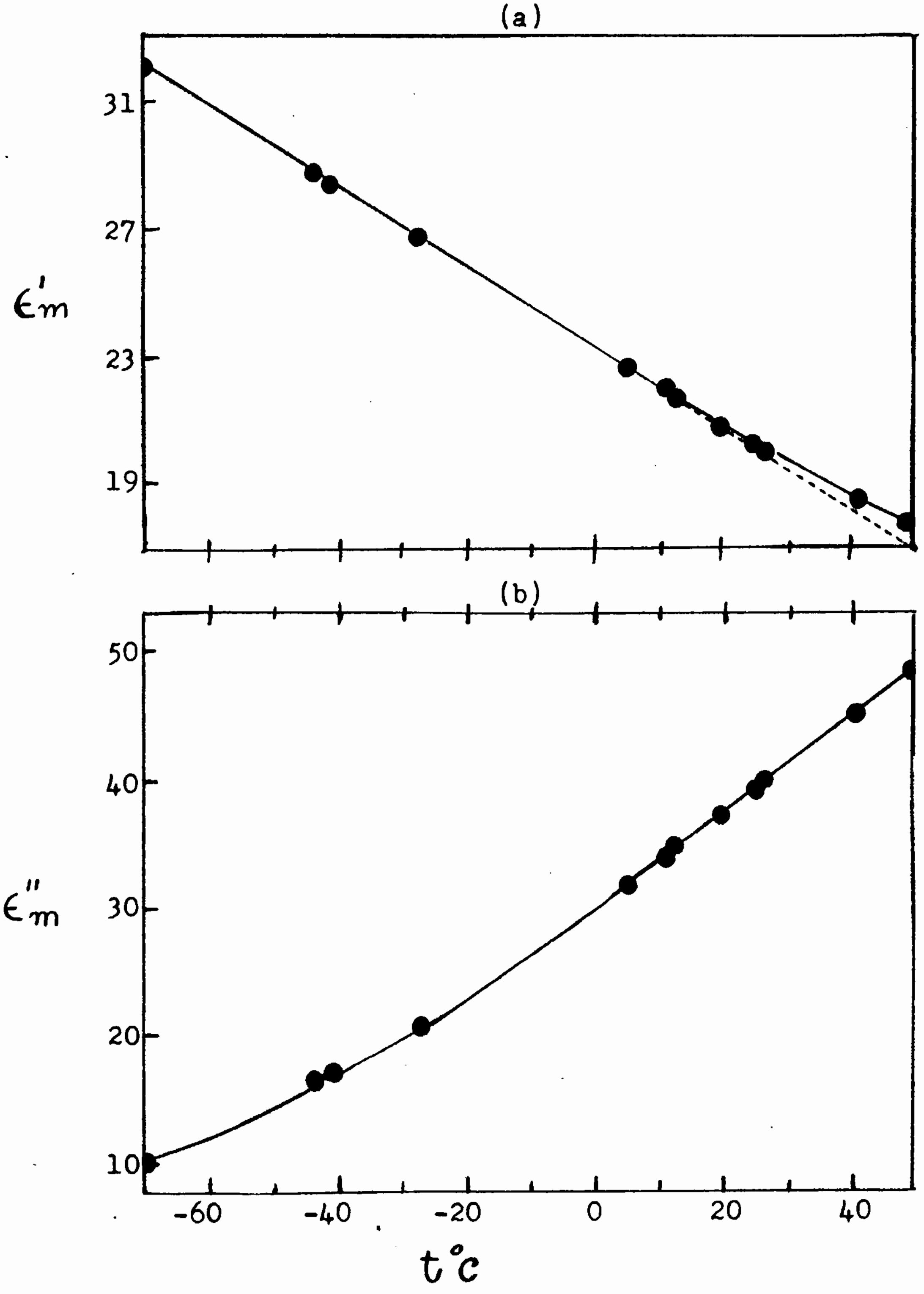

(a)
31
27
23
19
ε'm
(b)
50
40
30
20
10
ε''m
-60
-40
-20
0
20
40
t°c

FIGURE 28a, 28b, 28c, 28d.

FIGURE 28a

ϵ'_m vs f (Kc) for solution No. 3 at 21.9 ° C

FIGURE 28b

ϵ''_m vs f^{-1} $(Mc)^{-1}$ for solution No. 3 at 21.9 ° C

FIGURE 28c

ϵ'_m vs f (Mc) for solution No. 3 at 23.4 ° C

FIGURE 28d

ϵ''_m vs f^{-1} $(Mc)^{-1}$ for solution No. 3 at 23.4 ° C

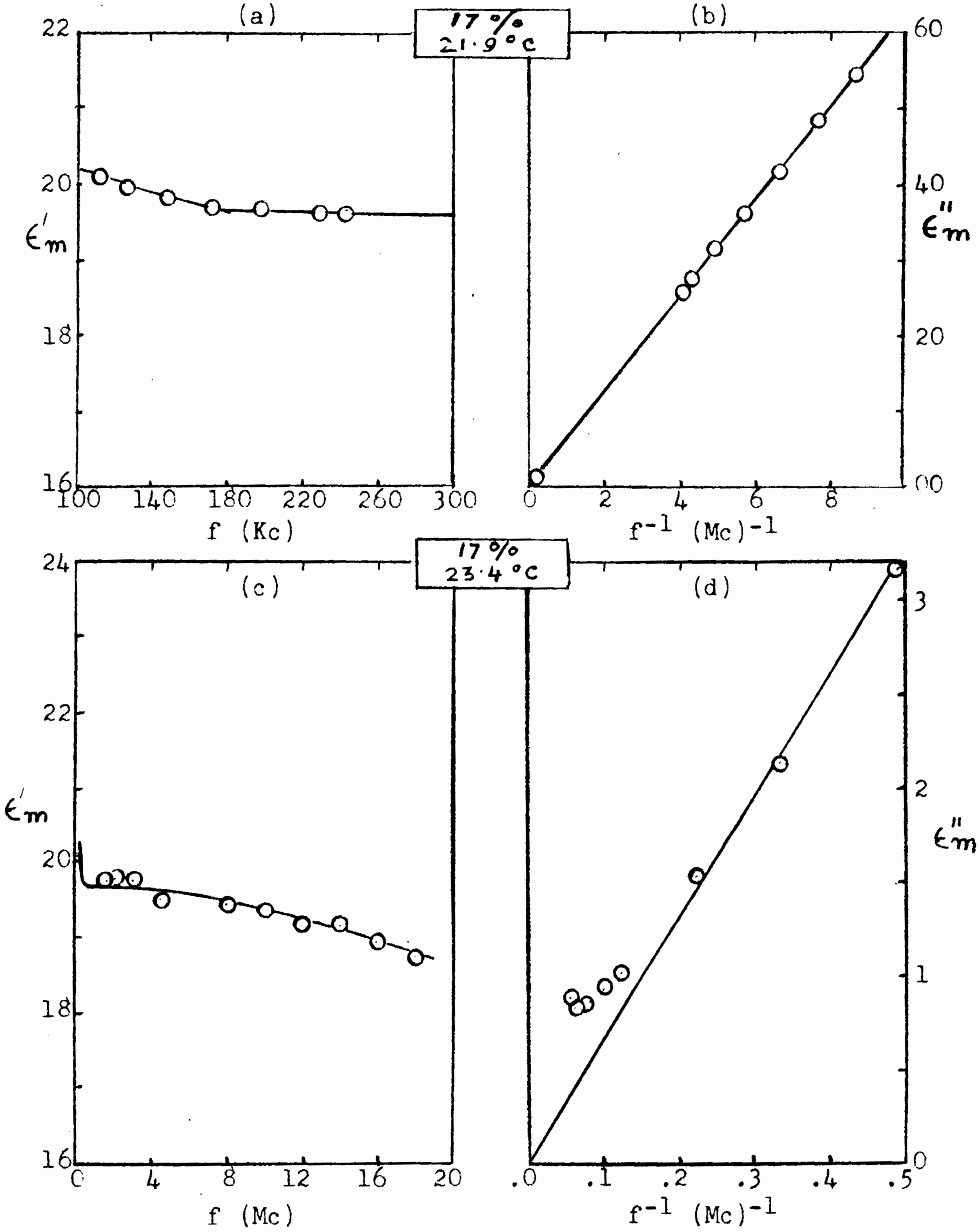

(a)
17 %
21·9 °C
(b)
22
20
18
16
ε'm
100
140
180
220
260
300
f (Kc)
60
40
20
00
ε''m
0
2
4
6
8
f-1 (Mc)-1
24
22
20
18
16
ε'm
(c)
17 %
23·4 °C
(d)
0
4
8
12
16
20
f (Mc)
3
2
1
0
ε''m
.0
.1
.2
.3
.4
.5
f-1 (Mc)-1

FIGURE 29a, 29b, 29c, 29d

FIGURE 29a

ϵ_m' vs f (Mc) solution No. 3 at 45.4 ° C

FIGURE 29b

ϵ_m'' vs f^{-1} $(Mc)^{-1}$ solution No. 3 at 45.4 ° C

FIGURE 29c

ϵ_m' vs f (Mc) solution No. 3 at -75 ° C

FIGURE 29d

ϵ_m'' vs f^{-1} $(Mc)^{-1}$ solution No. 3 at -75 ° C

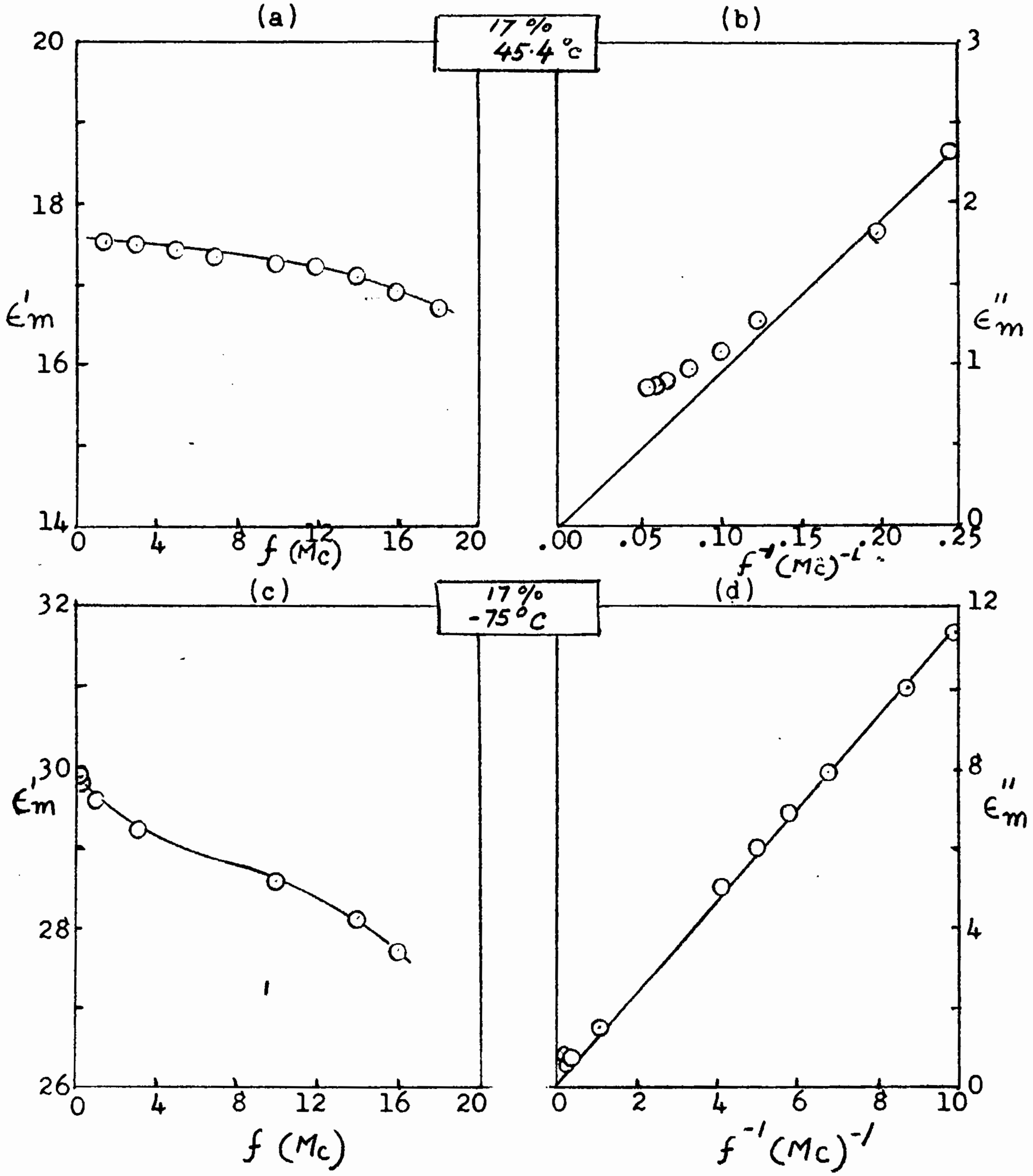

(a)
17 %
45·4 °c
(b)
20
18
16
14
ϵ'_m
0
4
8
12
16
20
f (Mc)
3
2
1
0
ϵ''_m
.00
.05
.10
.15
.20
.25
f^{-1} (Mc)$^{-1}$
(c)
17 %
-75 °C
(d)
32
30
28
26
ϵ'_m
0
4
8
12
16
20
f (Mc)
12
8
4
0
ϵ''_m
0
2
4
6
8
10
f^{-1} (Mc)$^{-1}$

FIGURE 30a, 30b

FIGURE 30a

ϵ'_m vs t°C solution No. 3 at 130 Kc

FIGURE 30b

ϵ''_m vs t°C solution No. 3 at 130 Kc

17%
130Kc

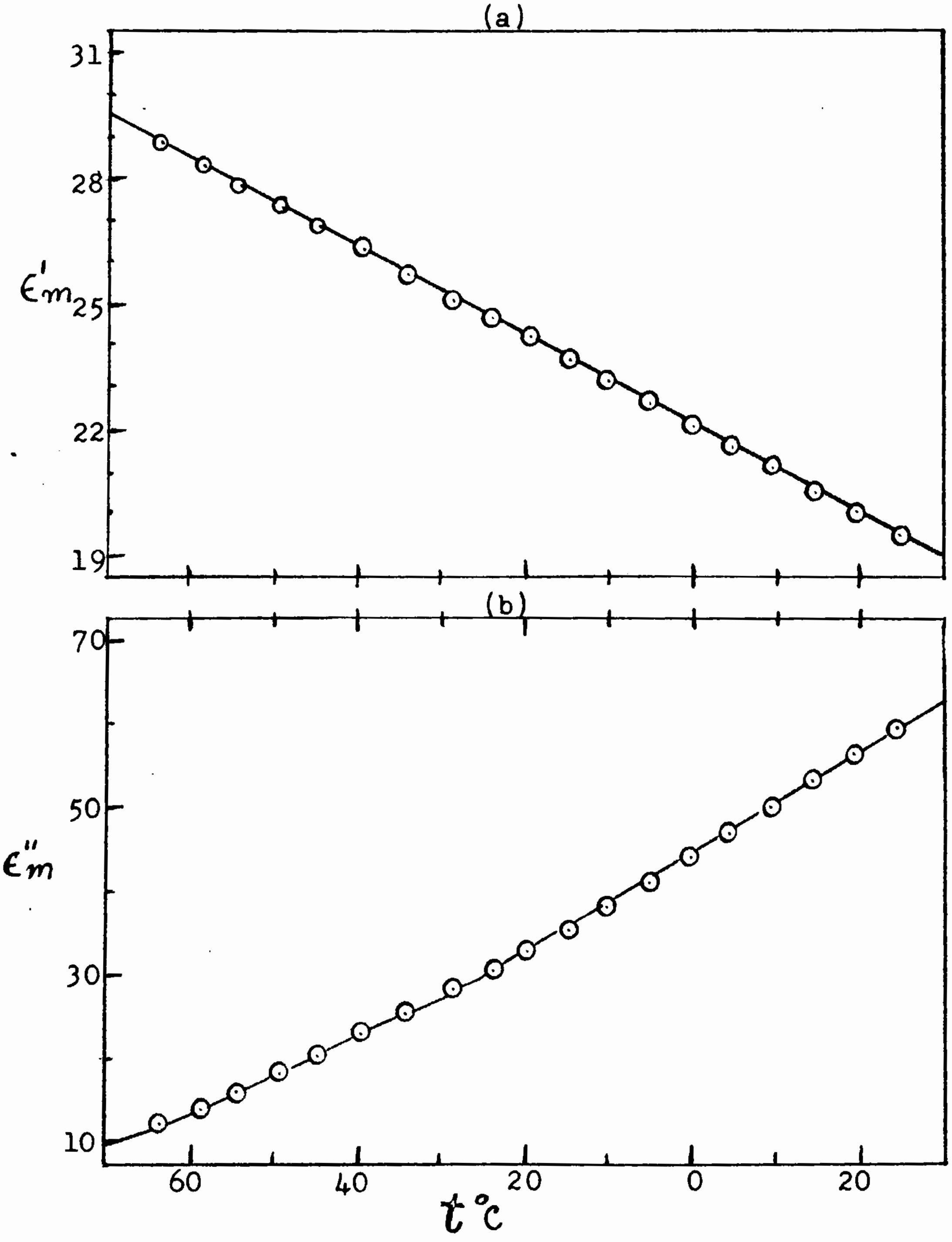
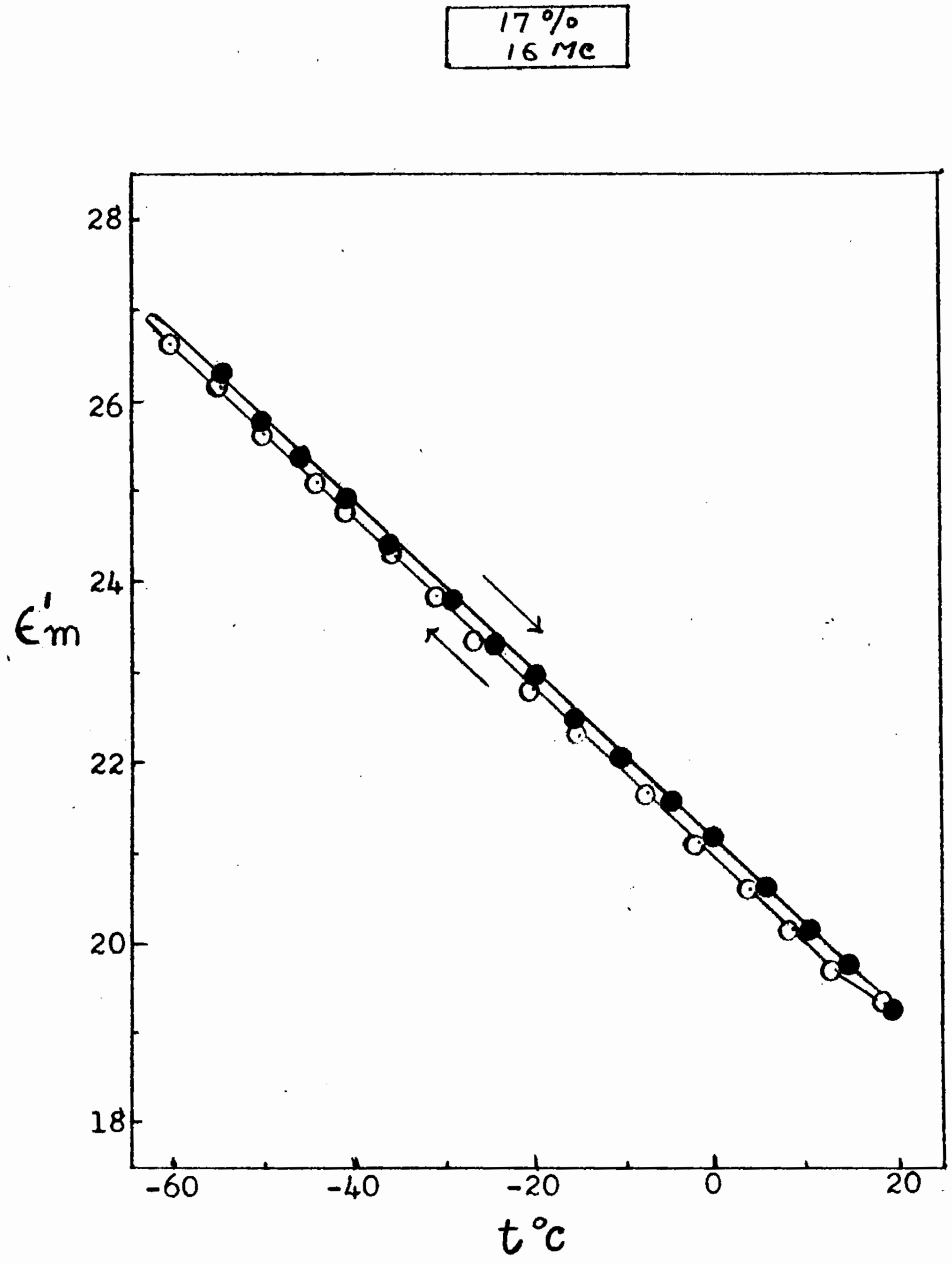


FIGURE 31

FIGURE 31

ϵ'_m vs t°C for solution No. 3 at 16 Mc



17 %
16 Mc
28
26
24
22
20
18
ϵ'_m
-60
-40
-20
0
20
t °c

FIGURE 32

FIGURE 32

ϵ''_m vs f (Kc) for solution No. 3 at - 75°C

ϵ''_m corrected for contribution from D.C. conductivity)

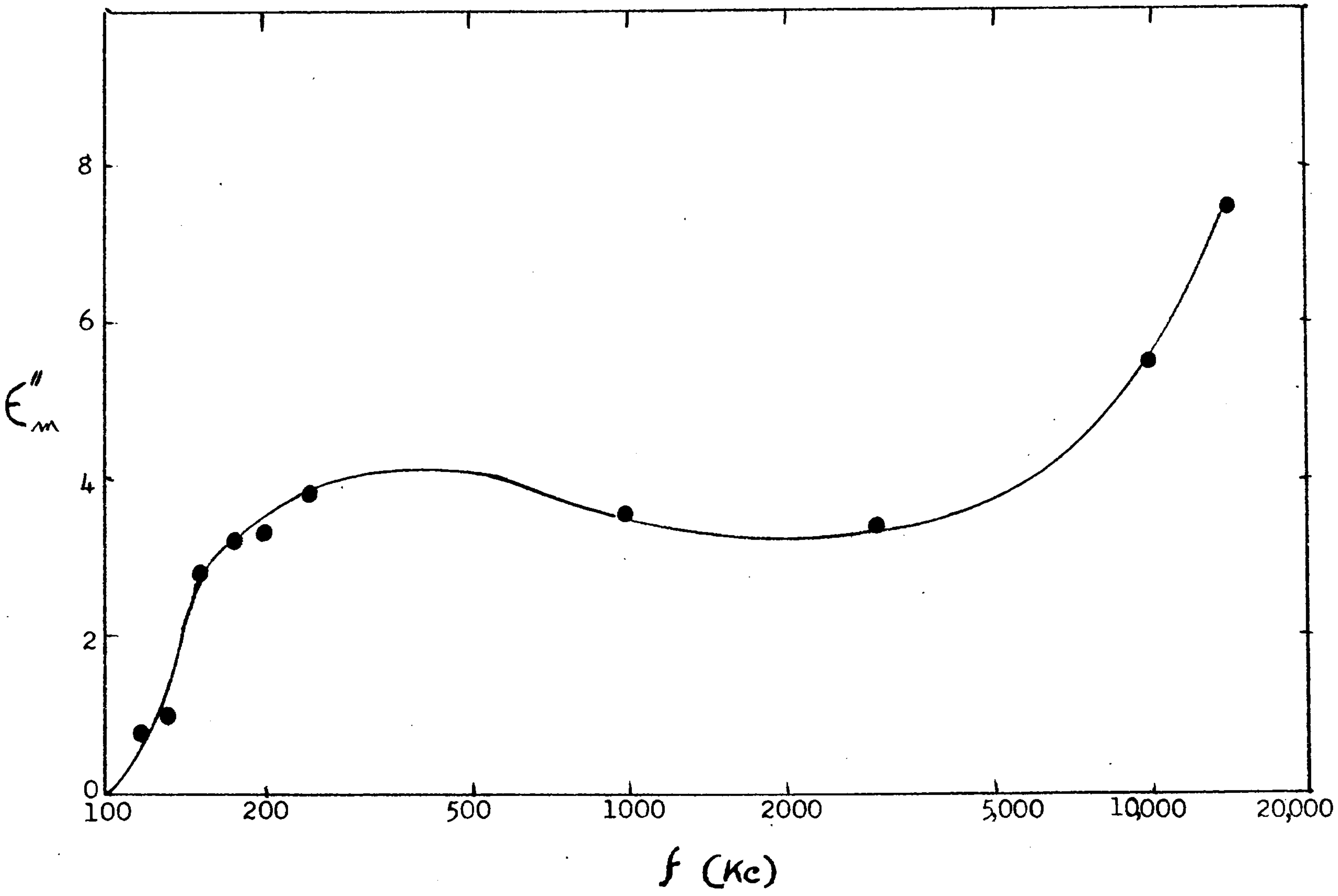

ϵ''_m
0
2
4
6
8
100
200
500
1000
2000
5,000
10,000
20,000
f (Kc)

FIGURE 33

FIGURE 33

$\epsilon'_m, \epsilon''_m$ vs t° C for a preliminary sample of celluloid (40% camphor)

○ 1000 Kc

△ 100 Kc

● 10 Kc

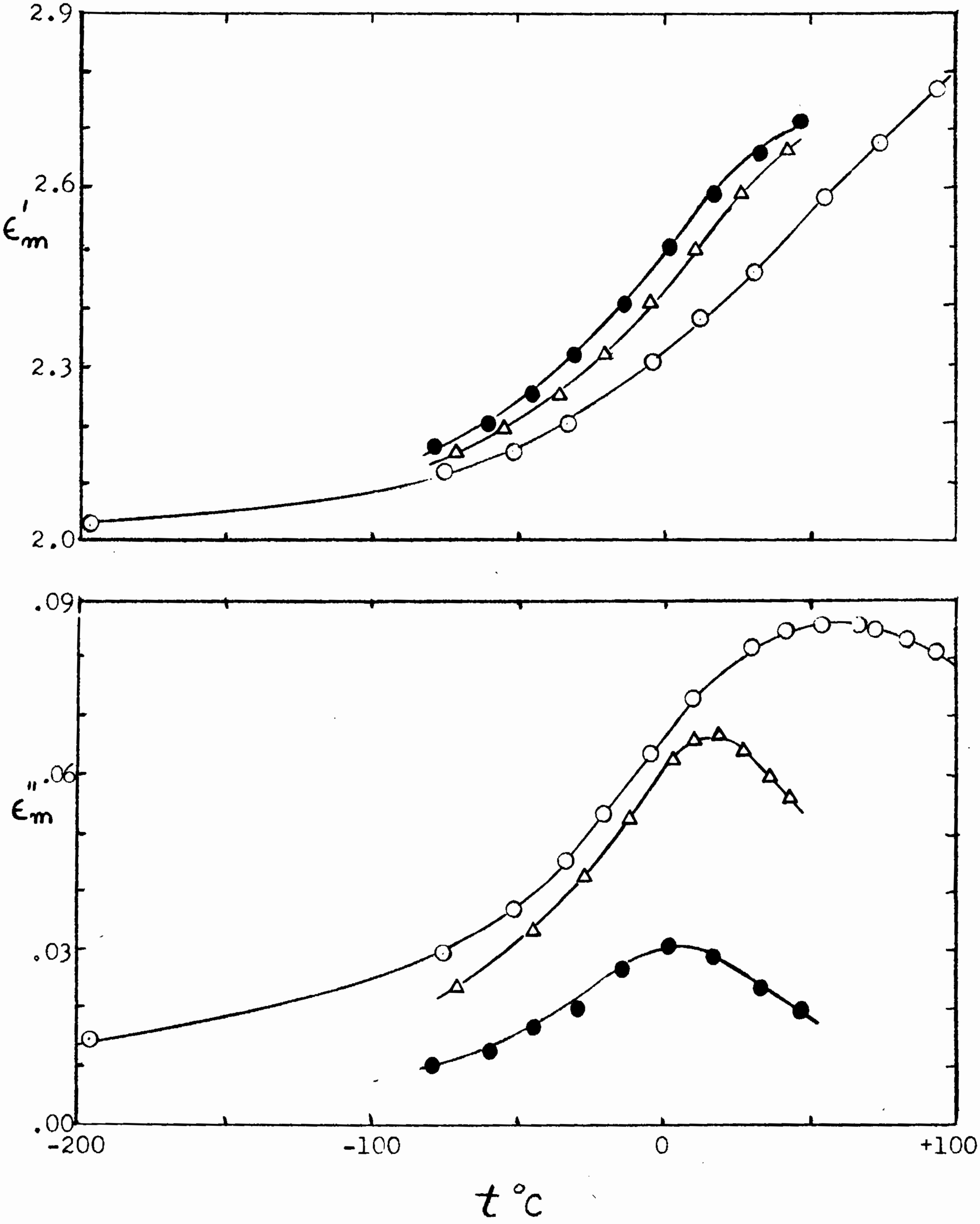

2.9
2.6
2.3
2.0
ε′m
.09
.06
.03
.00
ε″m
-200
-100
0
+100
t °C

FIGURE 34

FIGURE 34

ϵ'' vs $t^{\circ}C$ for dry celluloid (40% camphor)

■	300	Kc
●	100	Kc
△	10	Kc
□	1	Kc
○	0.2	Kc

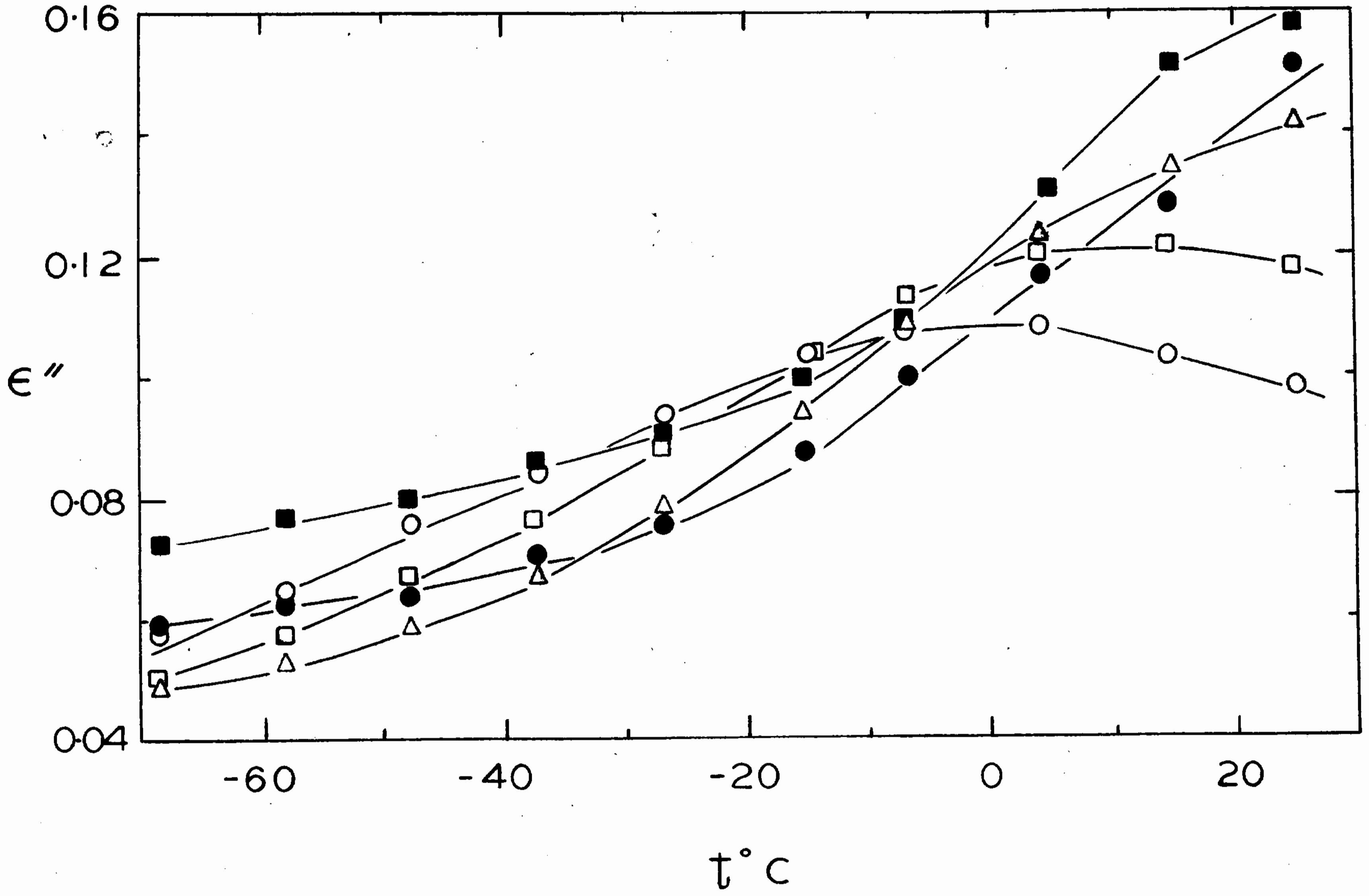

0·16
0·12
0·08
0·04
ε″
-60
-40
-20
0
20
t°C

FIGURE 35

FIGURE 35

ϵ' vs t°C for dry celluloid (40% camphor)

■	300	Kc
●	100	Kc
△	10	Kc
□	1	Kc
○	0.2	Kc

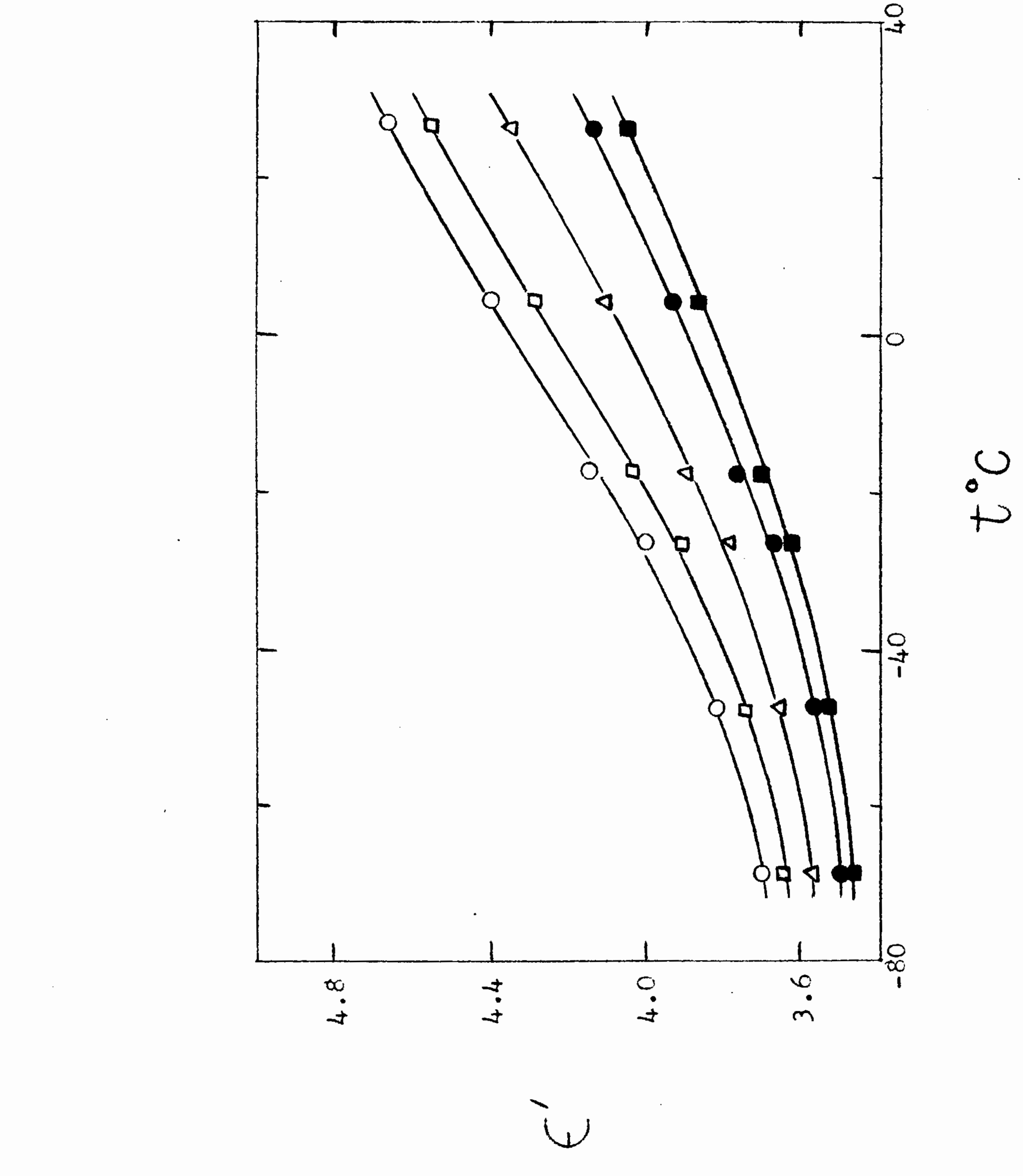
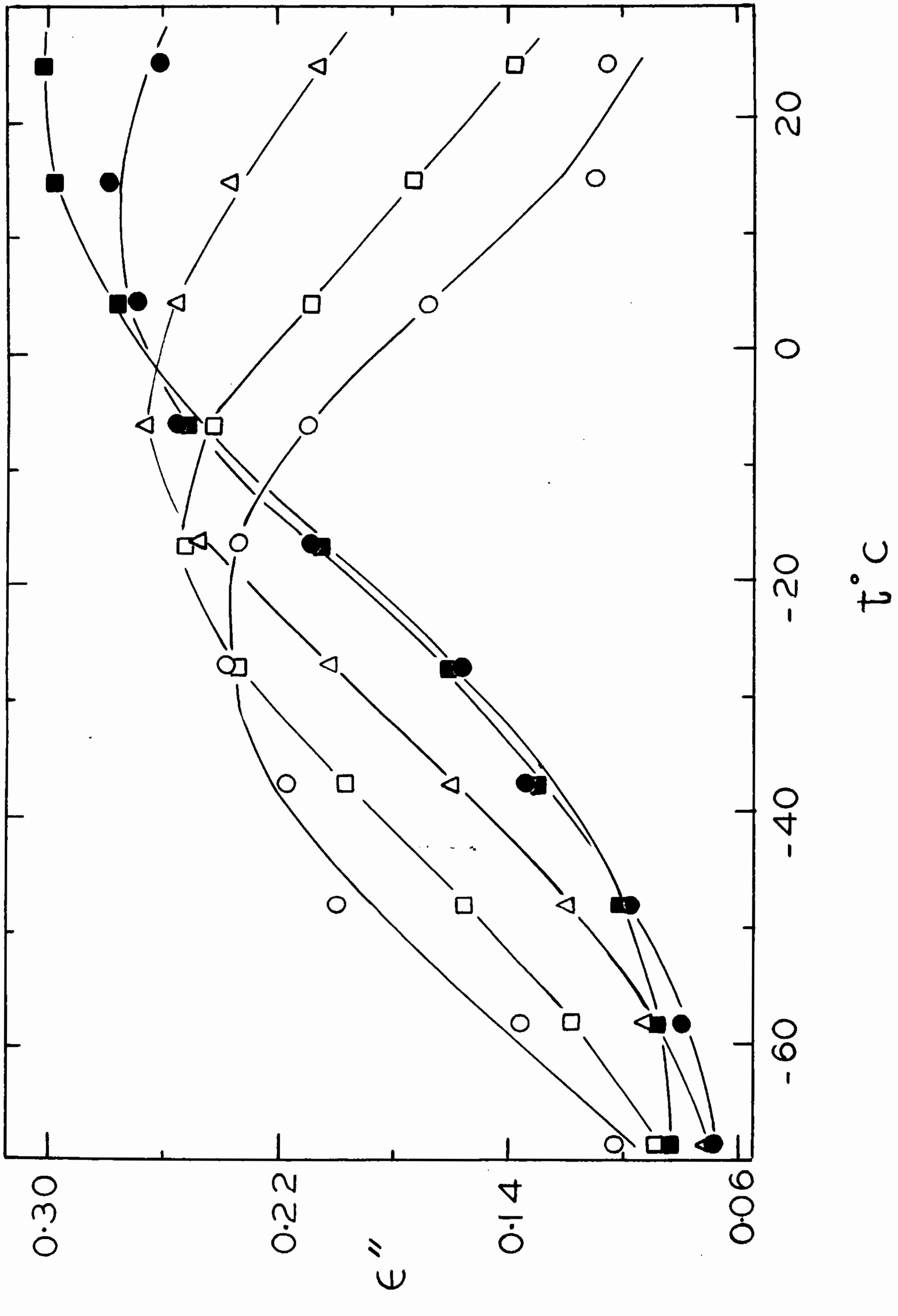

4.8
4.4
4.0
3.6
ε'
-80
-40
0
40
t°C

FIGURE 36

FIGURE 36

ϵ'' vs t°C for celluloid (40% camphor)

■ 300 Kc
● 100 Kc
△ 10 Kc
□ 1 Kc
○ 0.2 Kc



ε″
0·30
0·22
0·14
0·06
-60
-40
-20
0
20
t°C

FIGURE 37

FIGURE 37

ϵ' vs t°C for celluloid (40% camphor)
with 4% sorbed acetohe

■	300	Kc
●	100	Kc
△	10	Kc
□	1	Kc
○	0.2	Kc

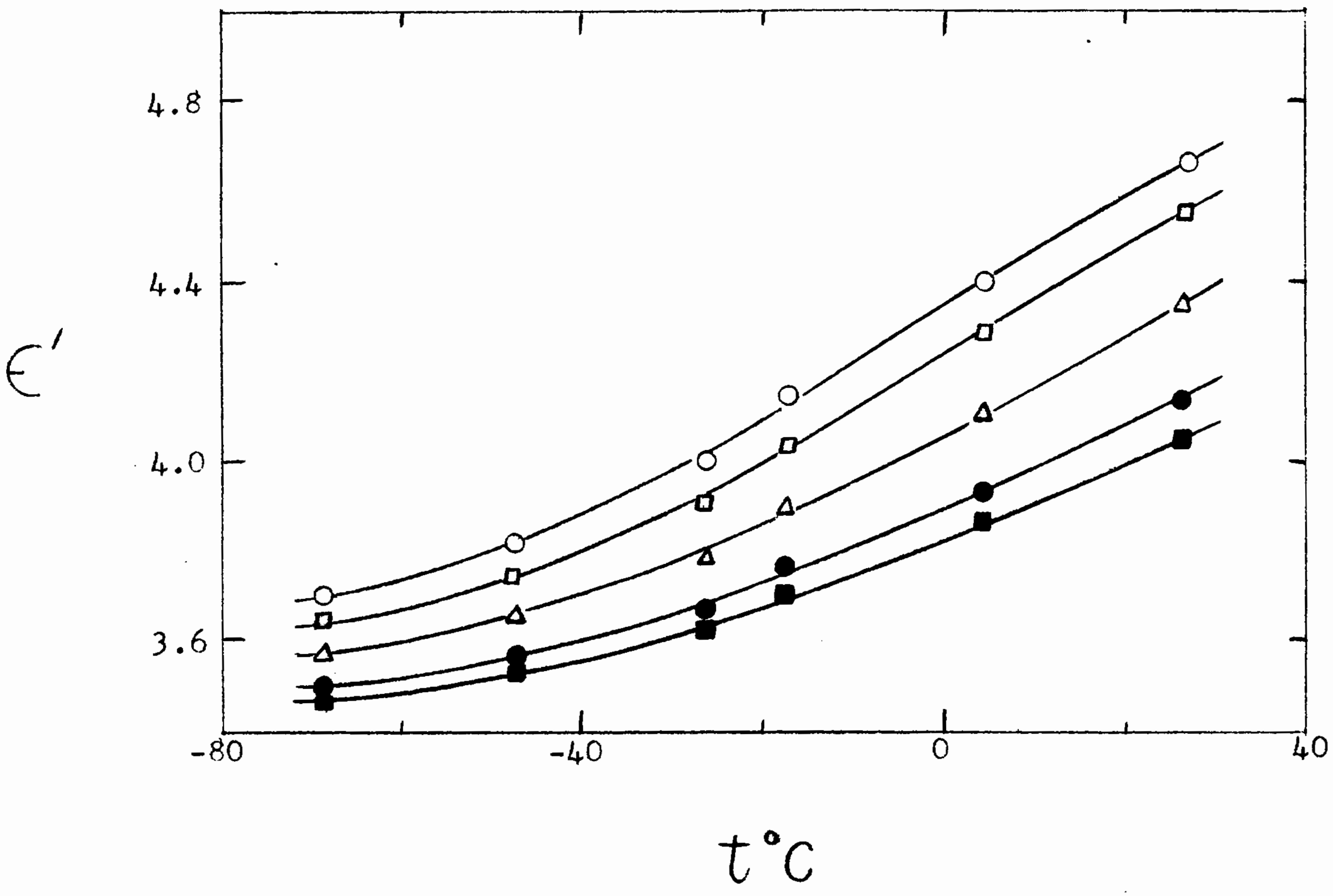

4.8
4.4
4.0
3.6
ϵ′
-80
-40
0
40
t°C

FIGURE 38

FIGURE 38

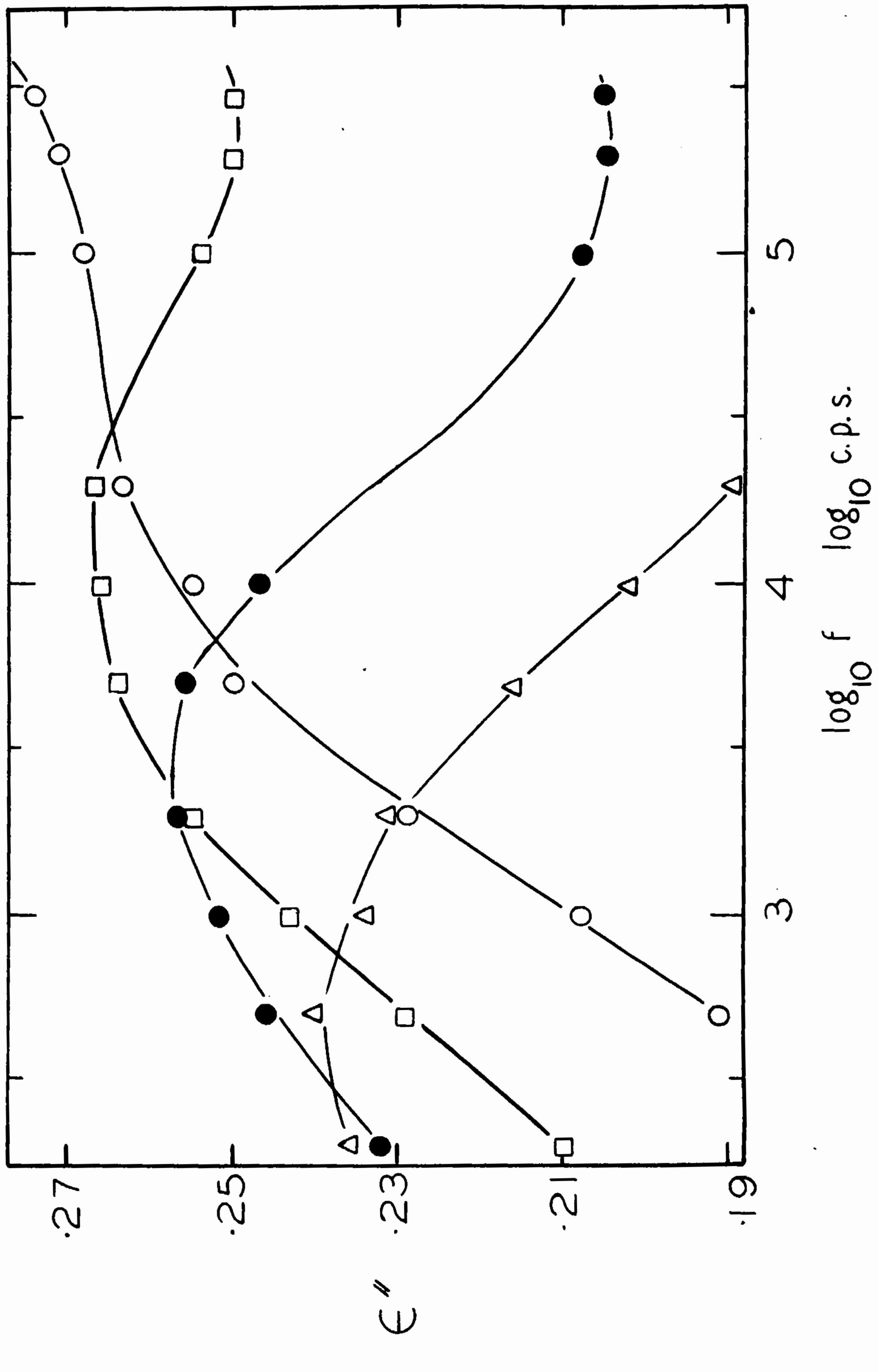
ϵ'' vs log f, in c.p.s. for celluloid (40% camphor) with 4% sorbed acetone

○ 4.2° C

□ - 6.2° C

● -16.5° C

△ -26.9° C



ε''
·27
·25
·23
·21
·19
3
4
5
log₁₀ f   log₁₀ c.p.s.

FIGURE 39

FIGURE 39

ϵ' vs log f, f in c.p.s. for celluloid (40% camphor) with 4% sorbed acetone.

○ 4.2° C

□ - 6.2° C

● -16.5° C

△ -26.9° C

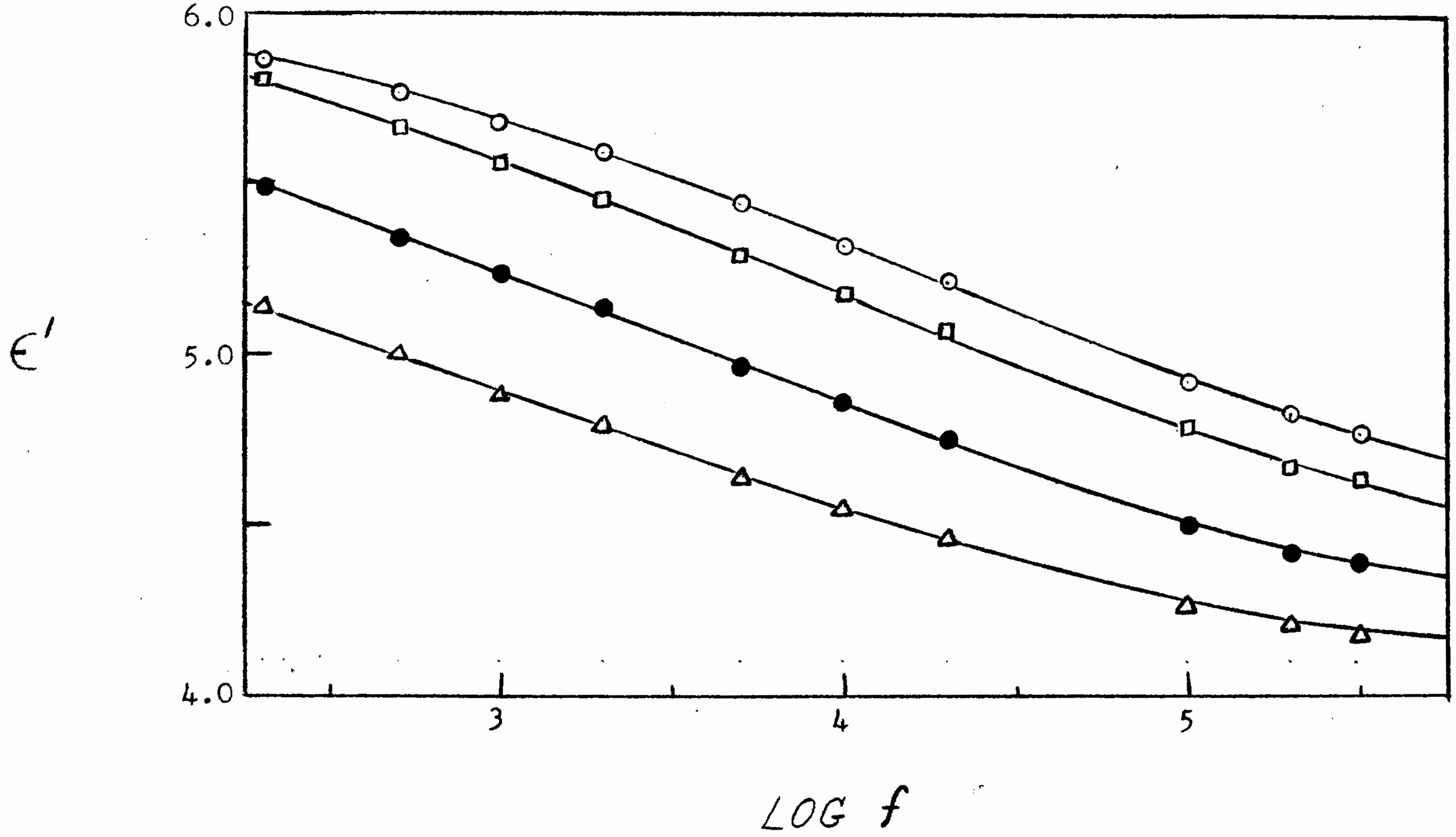

6.0
5.0
4.0
ϵ'
3
4
5
LOG f

FIGURE 40

FIGURE 40

ϵ'' vs $t^{\circ}C$ for celluloids of 40, 35.3, 29.8, 27.2% camphor

△ 5 Kc

● 1 Kc

○ 0.2 Kc

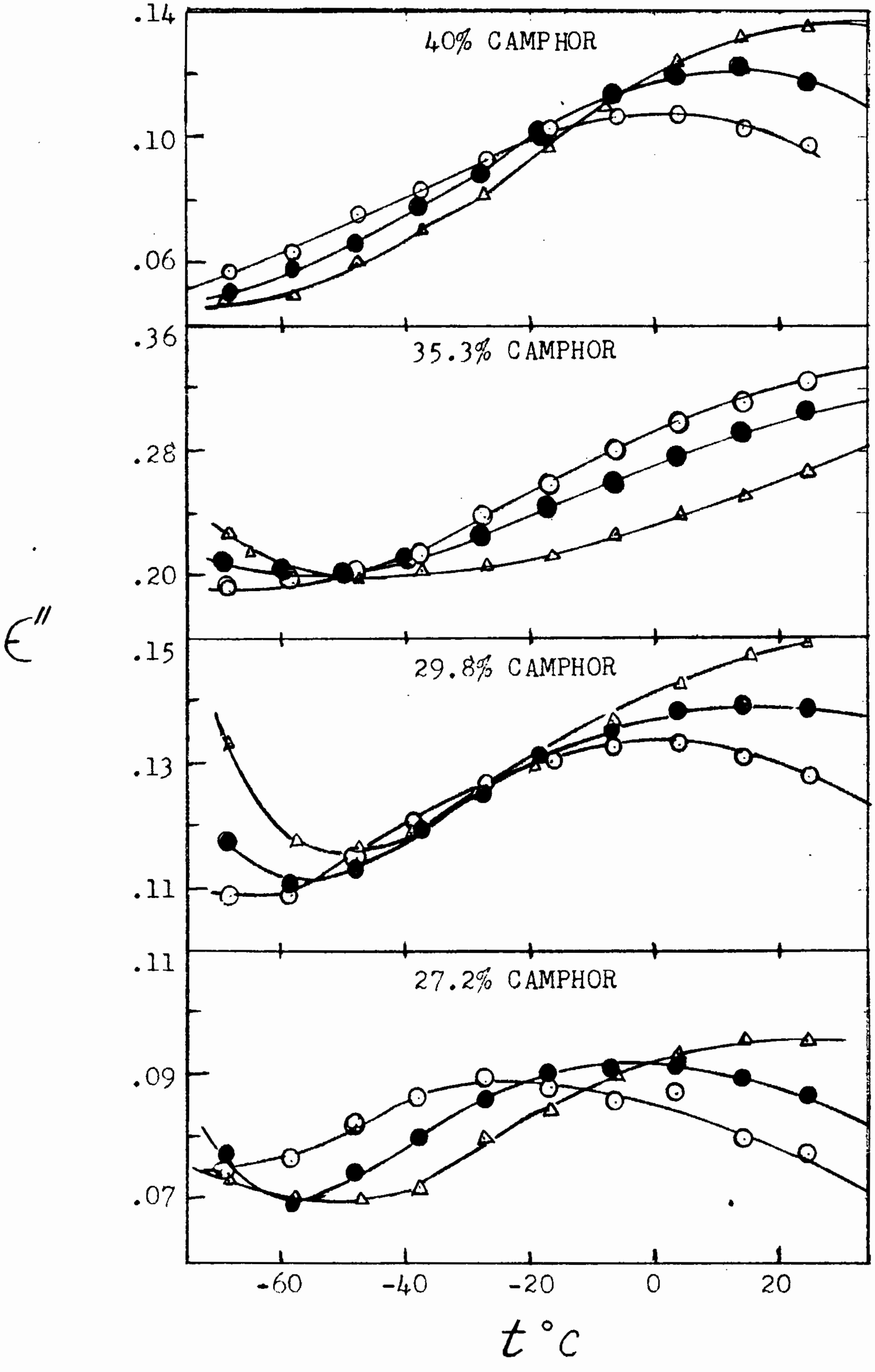

40% CAMPHOR
35.3% CAMPHOR
29.8% CAMPHOR
27.2% CAMPHOR
.14
.10
.06
.36
.28
.20
.15
.13
.11
.11
.09
.07
ε''
-60
-40
-20
0
20
t °c

FIGURE 41

FIGURE 41

Frequency- temperature dependence of dielectric relaxation for celluloid

○ 40% camphor and 4% sorbed acetone.

● 40% camphor

× 29.8% camphor

△ 27.2% camphor

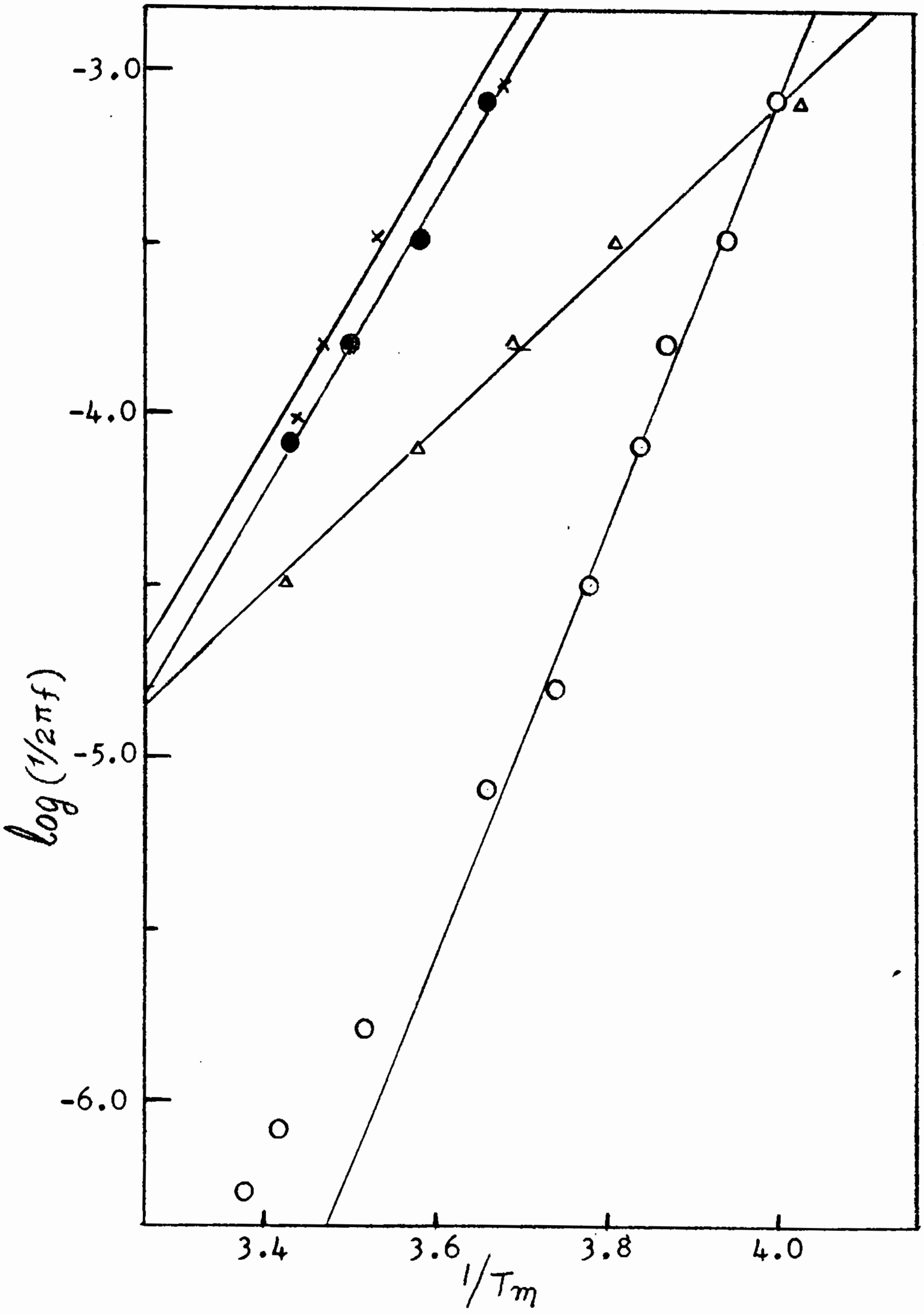

-3.0
-4.0
-5.0
-6.0
log (1/2πf)
3.4
3.6
3.8
4.0
1/Tm

FIGURE 42

<u>FIGURE 42</u>

ϵ'' vs t°C showing dispersion D in celluloids at 200 Kc

○ 27.2% camphor

● 29.8% camphor

□ 35.3% camphor

■ 40.0% camphor

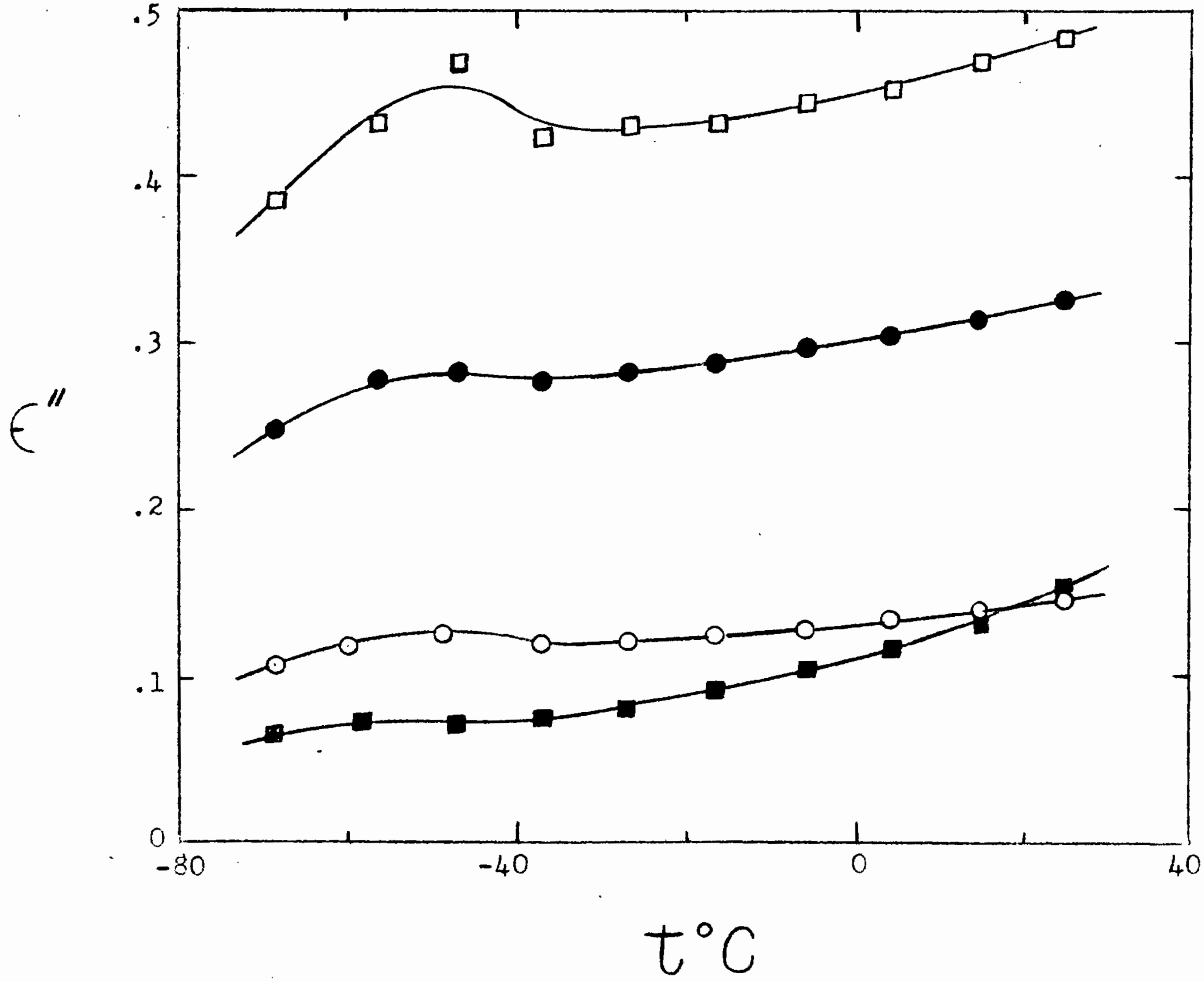

.5
.4
.3
.2
.1
0
ϵ''
-80
-40
0
40
t°C

FIGURE 43

FIGURE 43

ϵ'' vs t°C for nitrocellulose film No. 1

■	300	Kc
●	100	Kc
△	10	Kc
□	1	Kc
○	0.2	Kc

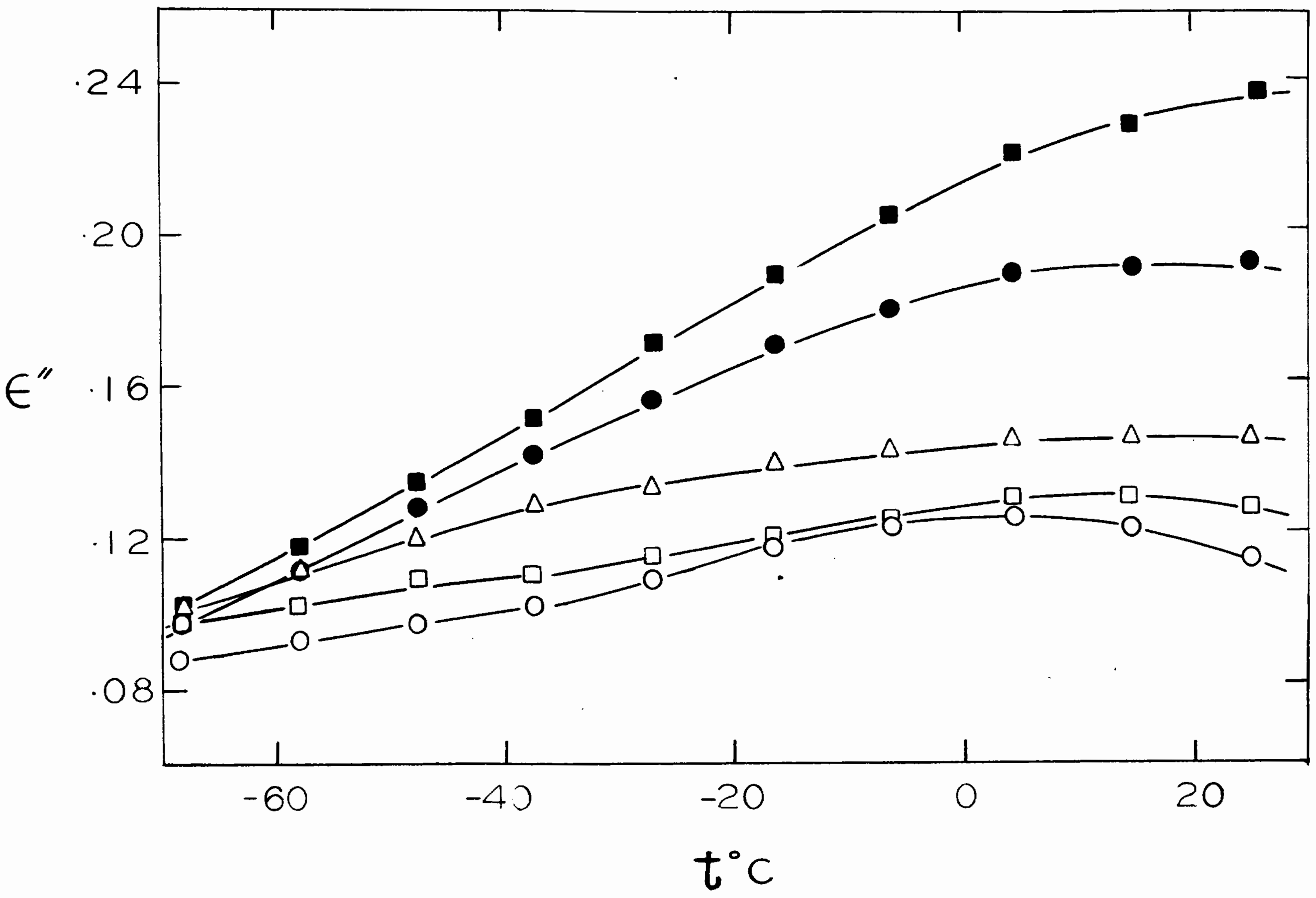

·24
·20
·16
·12
·08
ε''
-60
-40
-20
0
20
t°C

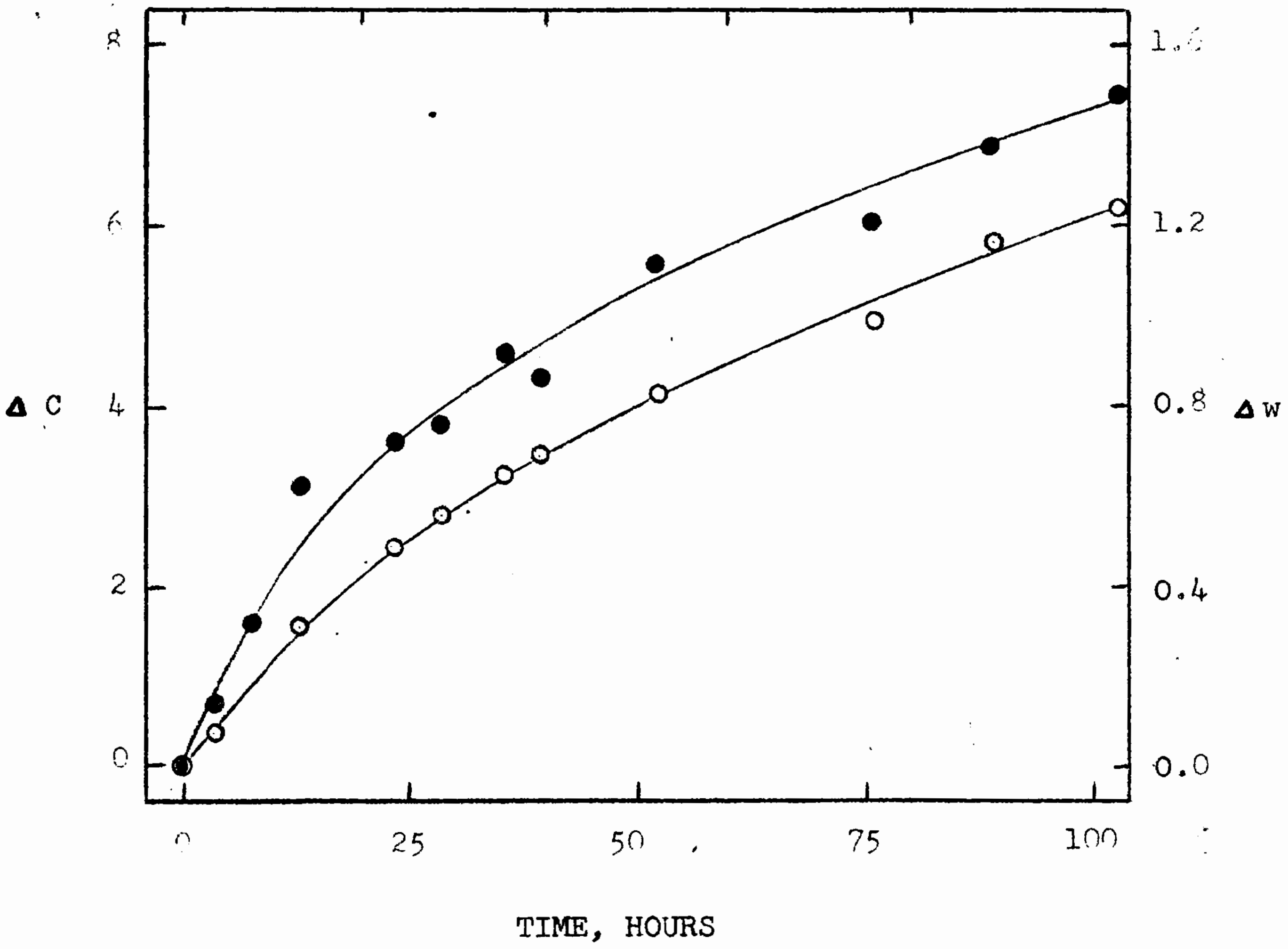
FIGURE 44

FIGURE 44

Loss in weight Δw and capacitance ΔC vs time
of coated and uncoated nitrocellulose
films

○ ΔW vs time

● ΔC vs time



Δ C
8
6
4
2
0
Δ W
1.6
1.2
0.8
0.4
0.0
0
25
50
75
100
TIME, HOURS

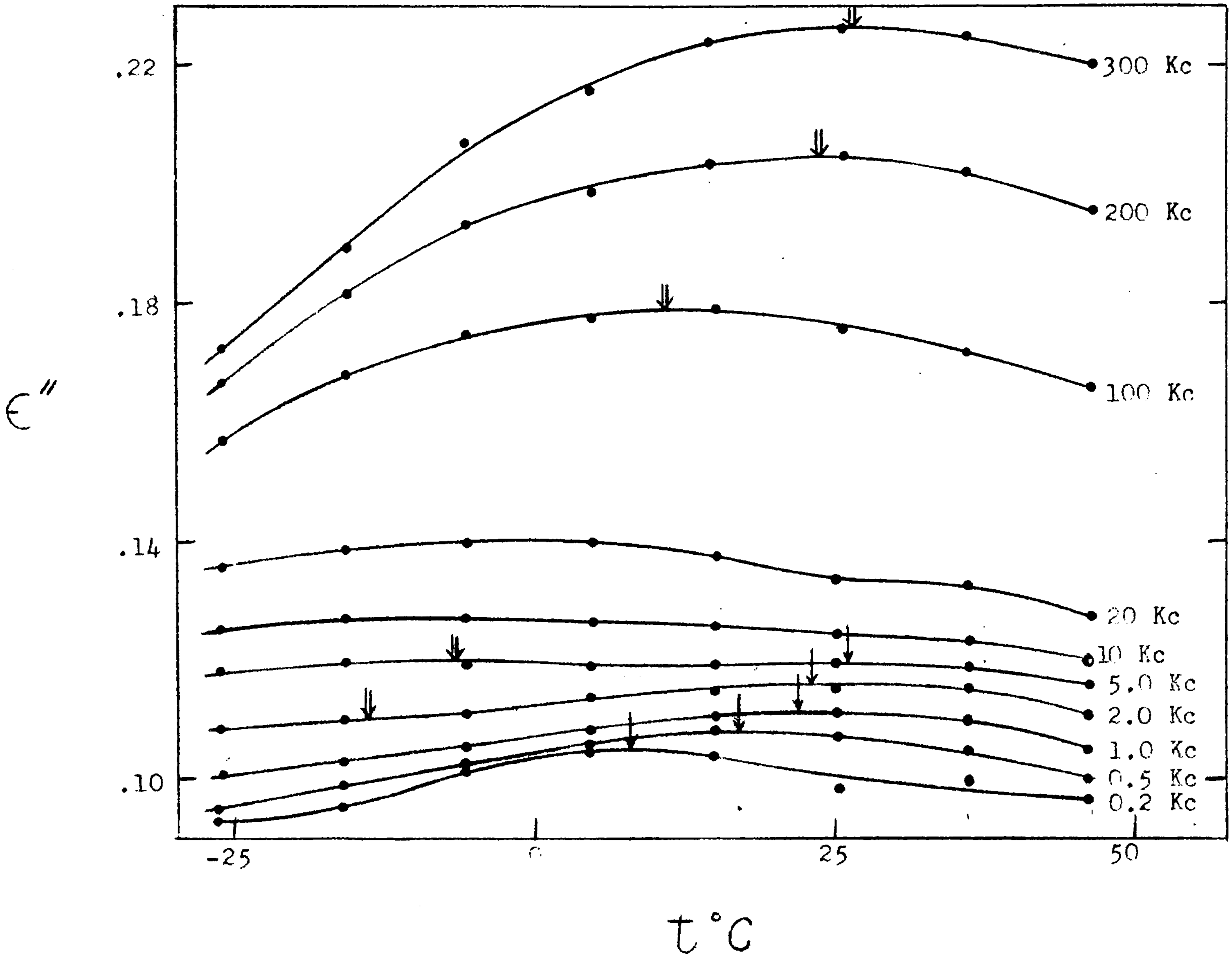
FIGURE 45

FIGURE 45

ϵ'' vs t°C for nitrocellulose film No. 2

$\Downarrow$ dispersion A

$\downarrow$ dispersion B



.22
.18
.14
.10
ϵ''
300 Kc
200 Kc
100 Kc
20 Kc
10 Kc
5.0 Kc
2.0 Kc
1.0 Kc
0.5 Kc
0.2 Kc
-25
0
25
50
t°C

FIGURE 46a, 46b

FIGURE 46a

Frequency-temperature dependence of dielectric relaxation for nitrocellulose films.

□ curve 1 - film No. 1, dispersions A and B

● curve 2 - film No. 2, dispersion A.

○ curve 3 - film No. 2, dispersion B.

□ curve 4 - film No. 3, dispersion A and B

△ curve 5 - film No. 4, dispersion A.

FIGURE 46b

Frequency-temperature dependence of dielectric relaxation for introcellulose films having different concentrations of sorbed acetone.

● 0.7% film No. 2,dispersion A

○ 4.3% film No. 5,dispersion A

△ 9.9% film No. 6,dispersion A

□ 16.0% film No. 7,dispersion A

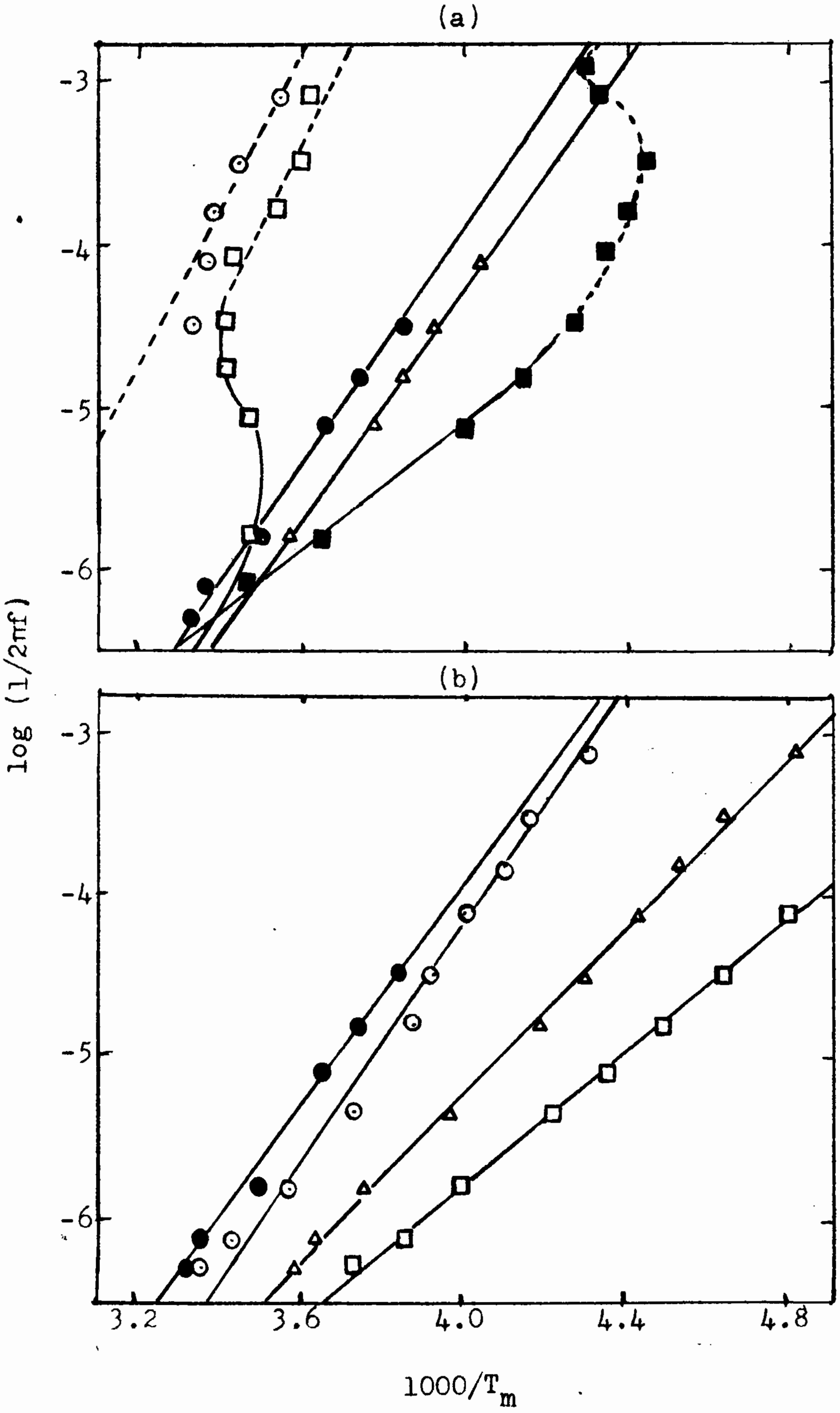

(a)
-3
-4
-5
-6
(b)
-3
-4
-5
-6
log (1/2πf)
3.2
3.6
4.0
4.4
4.8
1000/T_m

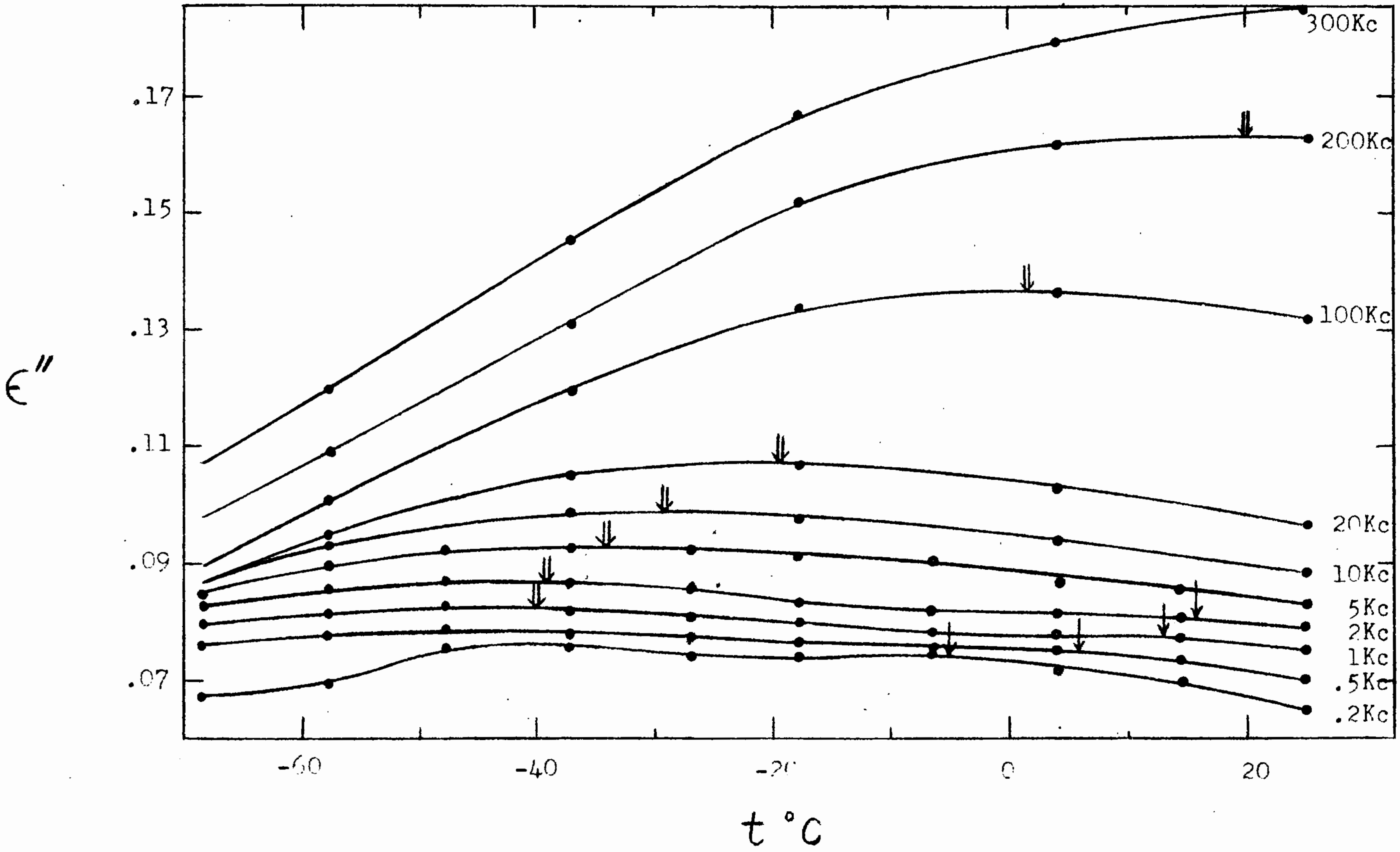
FIGURE 47

FIGURE 47

ϵ'' vs t°C for nitrocellulose film No. 3

$\Downarrow$ dispersion A

$\downarrow$ dispersion B

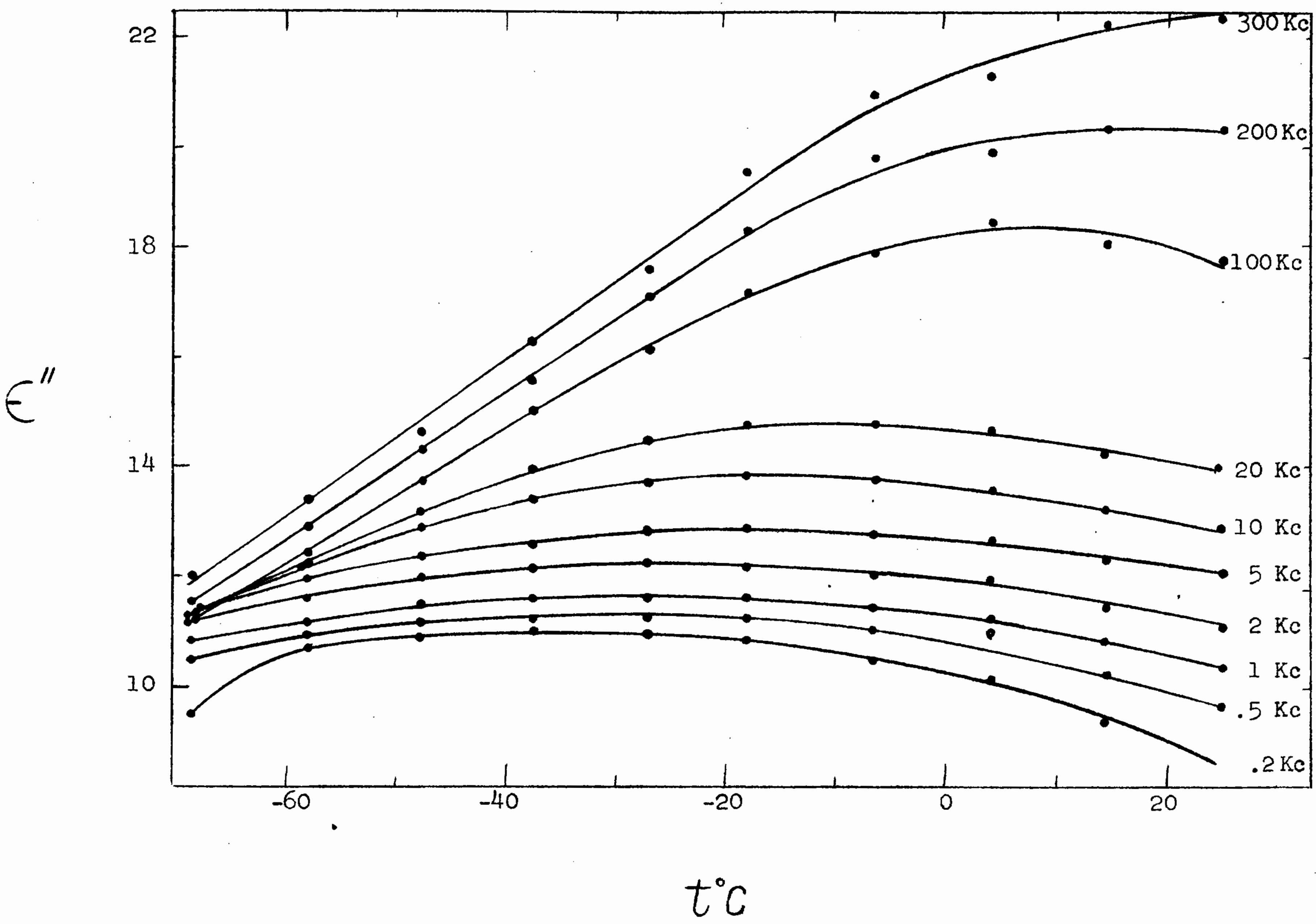


.17
.15
.13
.11
.09
.07
ϵ″
300Kc
200Kc
100Kc
20Kc
10Kc
5Kc
2Kc
1Kc
.5Kc
.2Kc
-60
-40
-20
0
20
t °C

FIGURE 48

FIGURE 48

ϵ'' vs t°C for nitrocellulose film No. 4



22
18
14
10
ϵ''
300 Kc
200 Kc
100 Kc
20 Kc
10 Kc
5 Kc
2 Kc
1 Kc
.5 Kc
.2 Kc
-60
-40
-20
0
20
t°C

FIGURE 49

FIGURE 49

Thermodynamic parameters of dielectric relaxation for different concentrations of acetone sorbed on nitrocellulose films

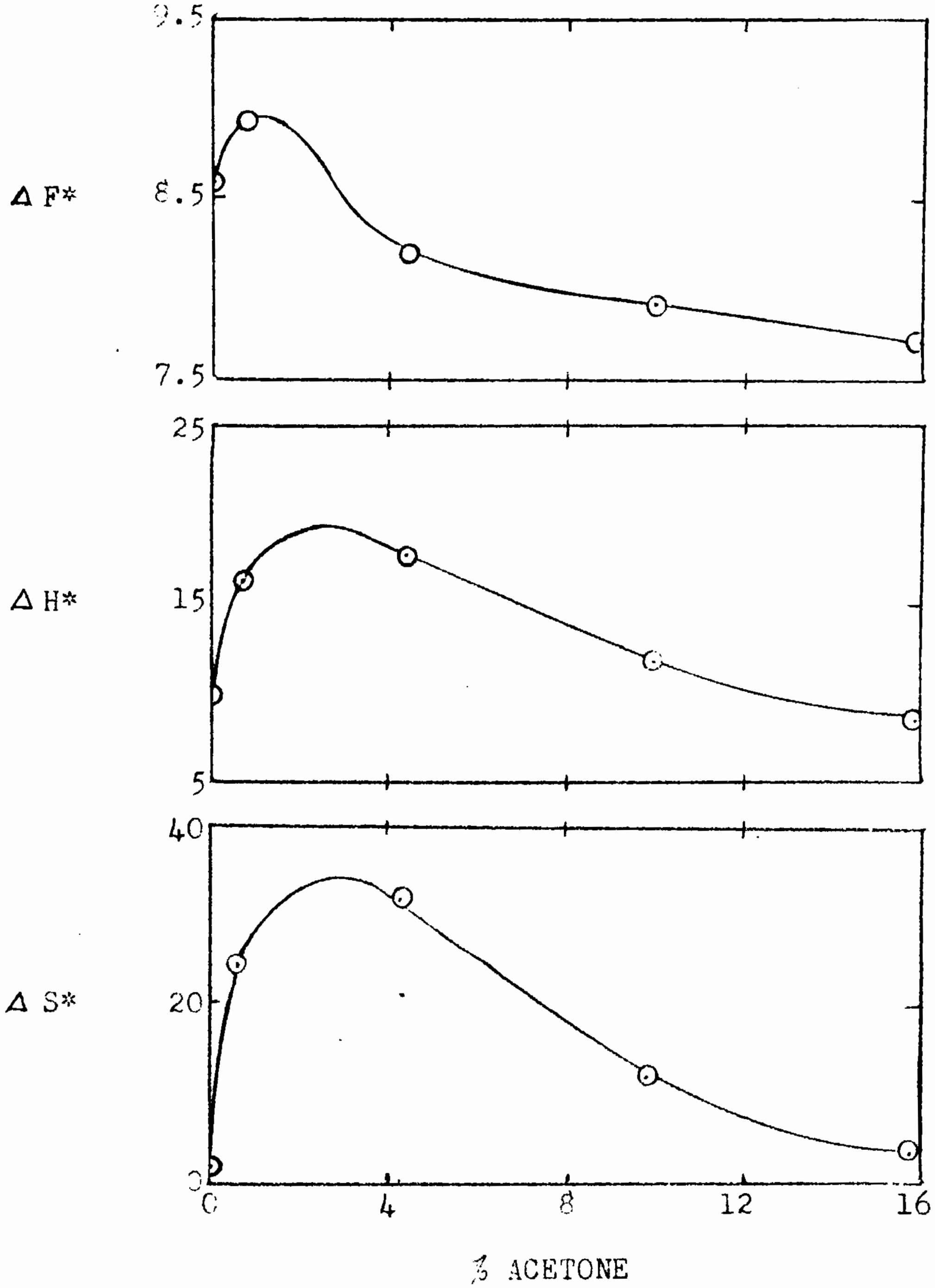

ΔF*
9.5
8.5
7.5
ΔH*
25
15
5
ΔS*
40
20
0
0
4
8
12
16
% ACETONE

FIGURE 50

FIGURE 50

" vs t°C for nitrocellulose film No. 6

300 Kc

100 Kc

10 Kc

1 Kc

.116 Kc

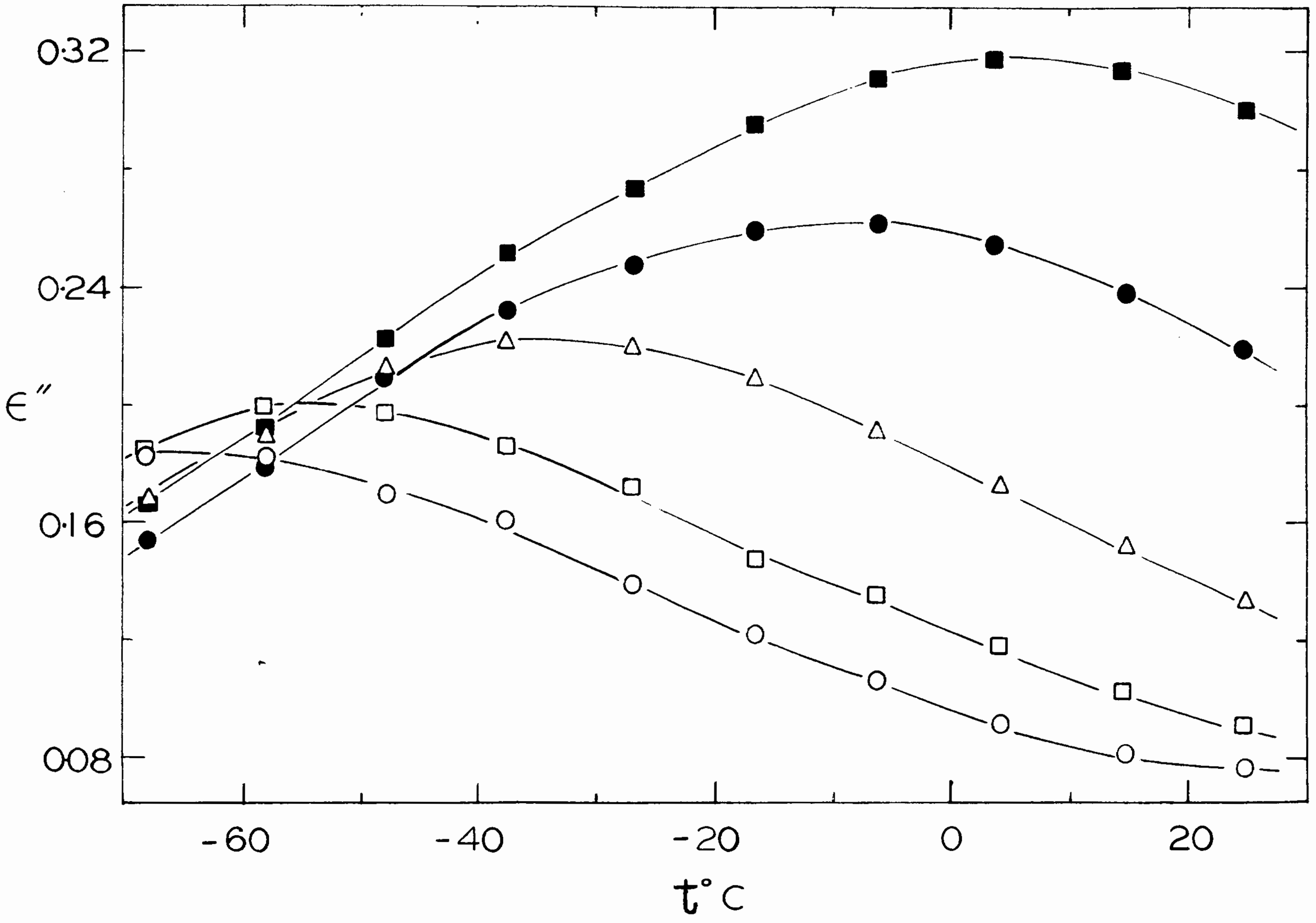
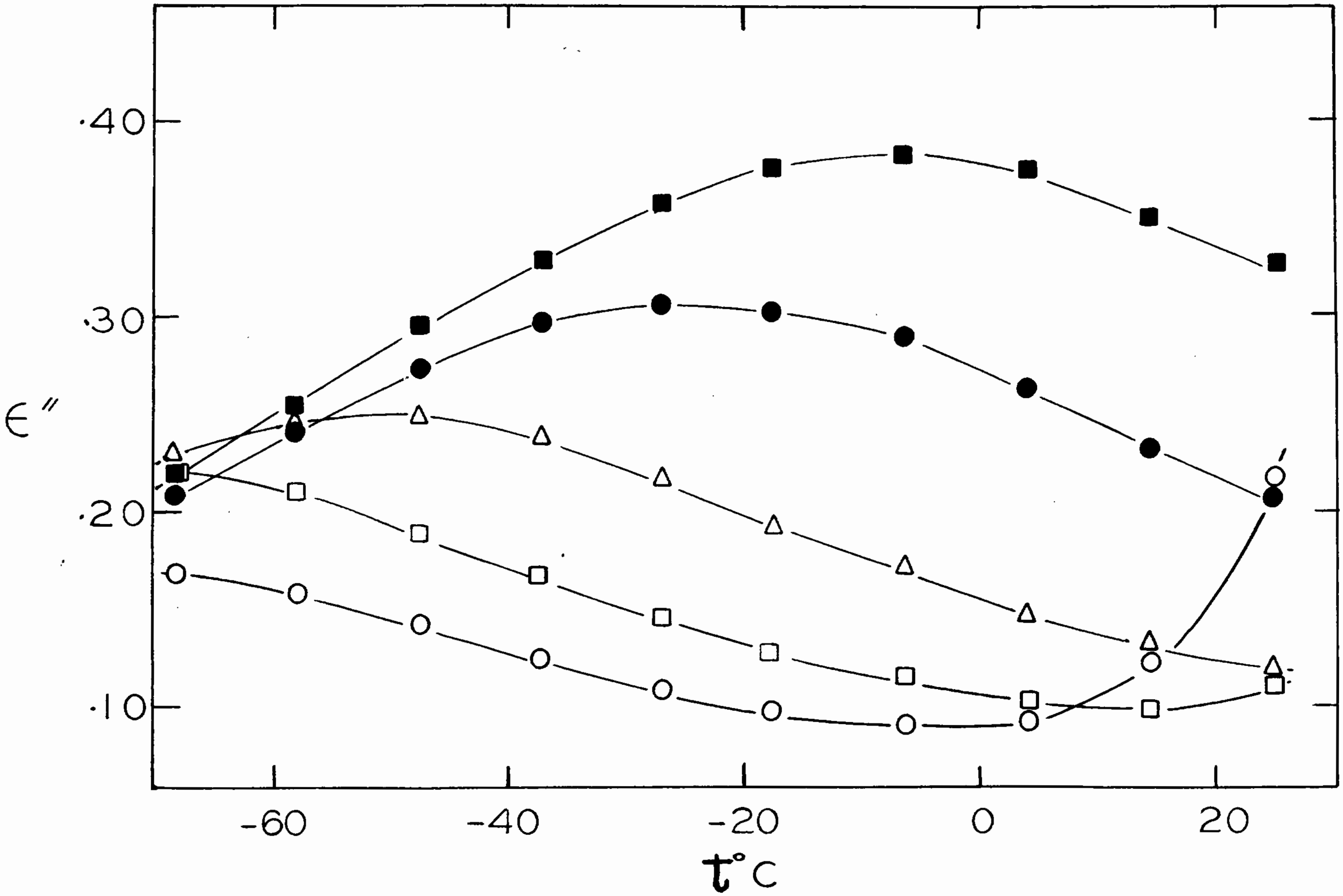

0·32
0·24
0·16
0·08
ϵ″
-60
-40
-20
0
20
t°C

FIGURE 51

FIGURE 51

ϵ'' vs t°C for nitrocellulose film No. 7

■ 300 Kc
● 100 Kc
△ 10 Kc
□ 1 Kc
○ .116 Kc



ε''
.40
.30
.20
.10
-60
-40
-20
0
20
t°C

FIGURE 52

FIGURE 52

ϵ''_m vs t°C for mitrocellulose paper of D.S. 2.16

▲	2000	Kc
●	200	Kc
■	20	Kc
△	2	Kc
○	0.2	Kc

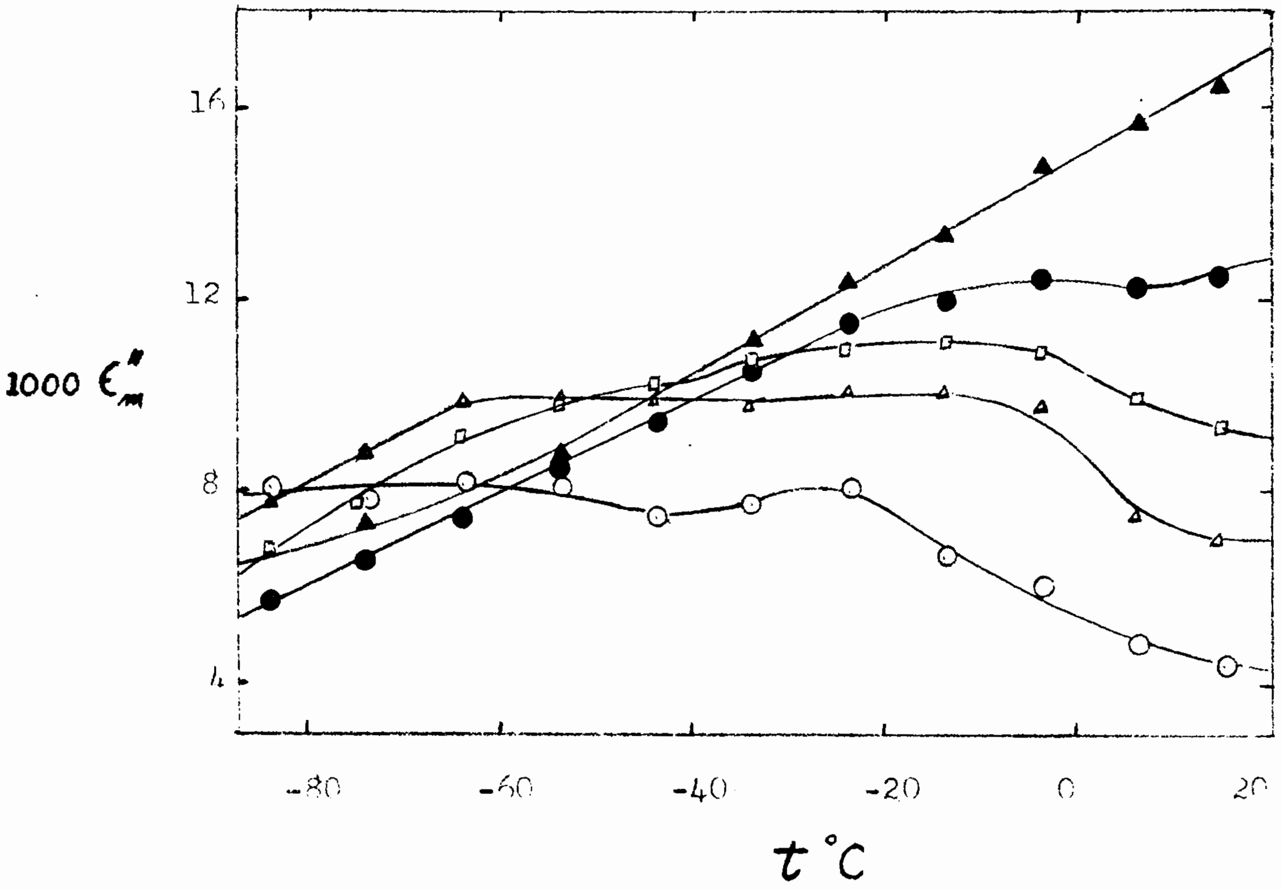

1000 ϵ''_m
16
12
8
4
-80
-60
-40
-20
0
20
t °C

FIGURE 53

FIGURE 53

ϵ''_m vs t^oC for nitrocellulose paper of D.S. 3.00

▲ 2000 Kc

● 200 Kc

■ 20 Kc

△ 2 Kc

○ 0.2 Kc

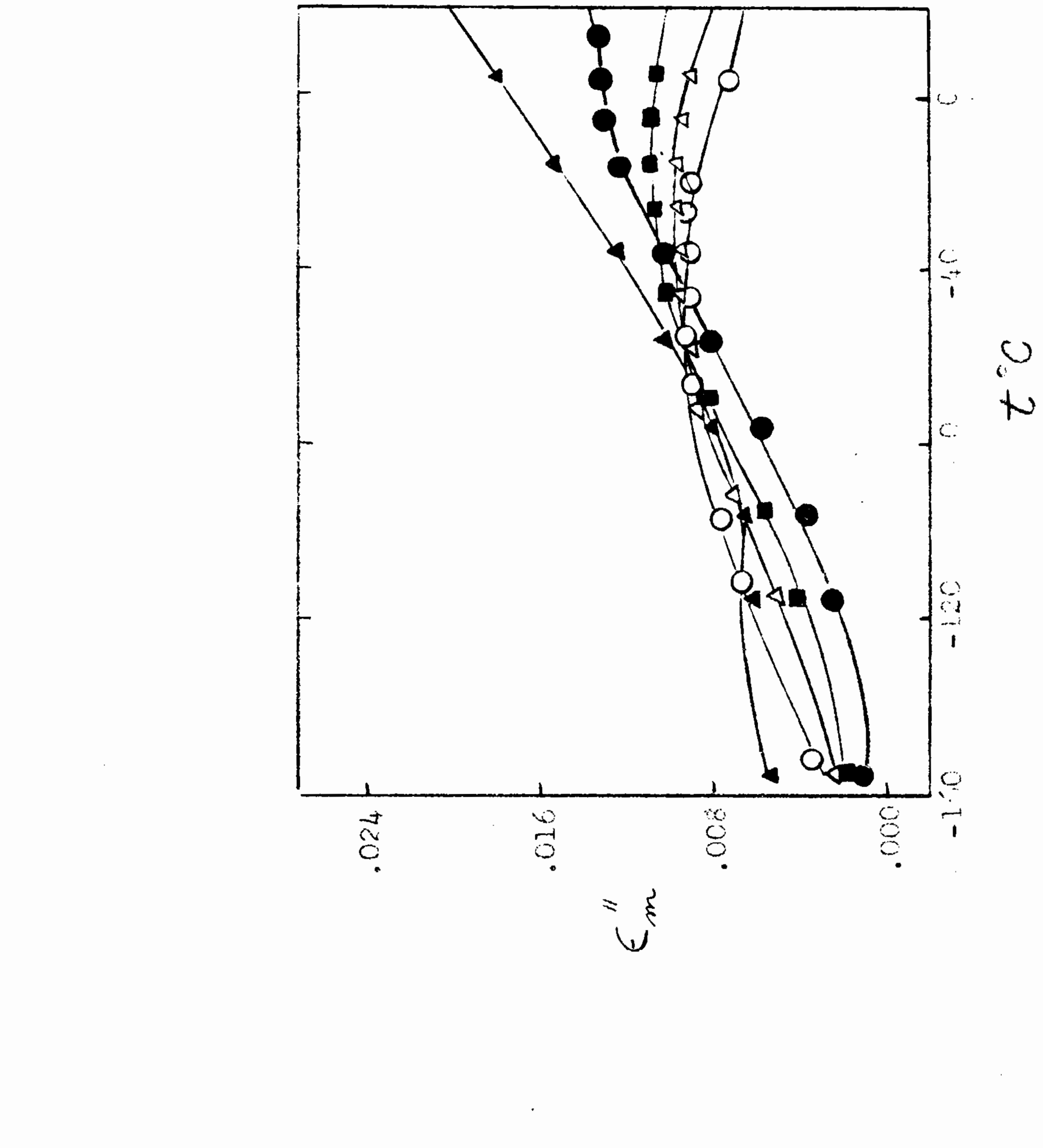

ϵ''_m
.024
.016
.008
.000
-160
-120
0
-40
0
t°C

FIGURE 54

FIGURE 54

ϵ'_m vs t°C for nitrocellulose paper of D.S. 2.16

▲ 2000 Kc

● 20 Kc

○ 0.2 Kc

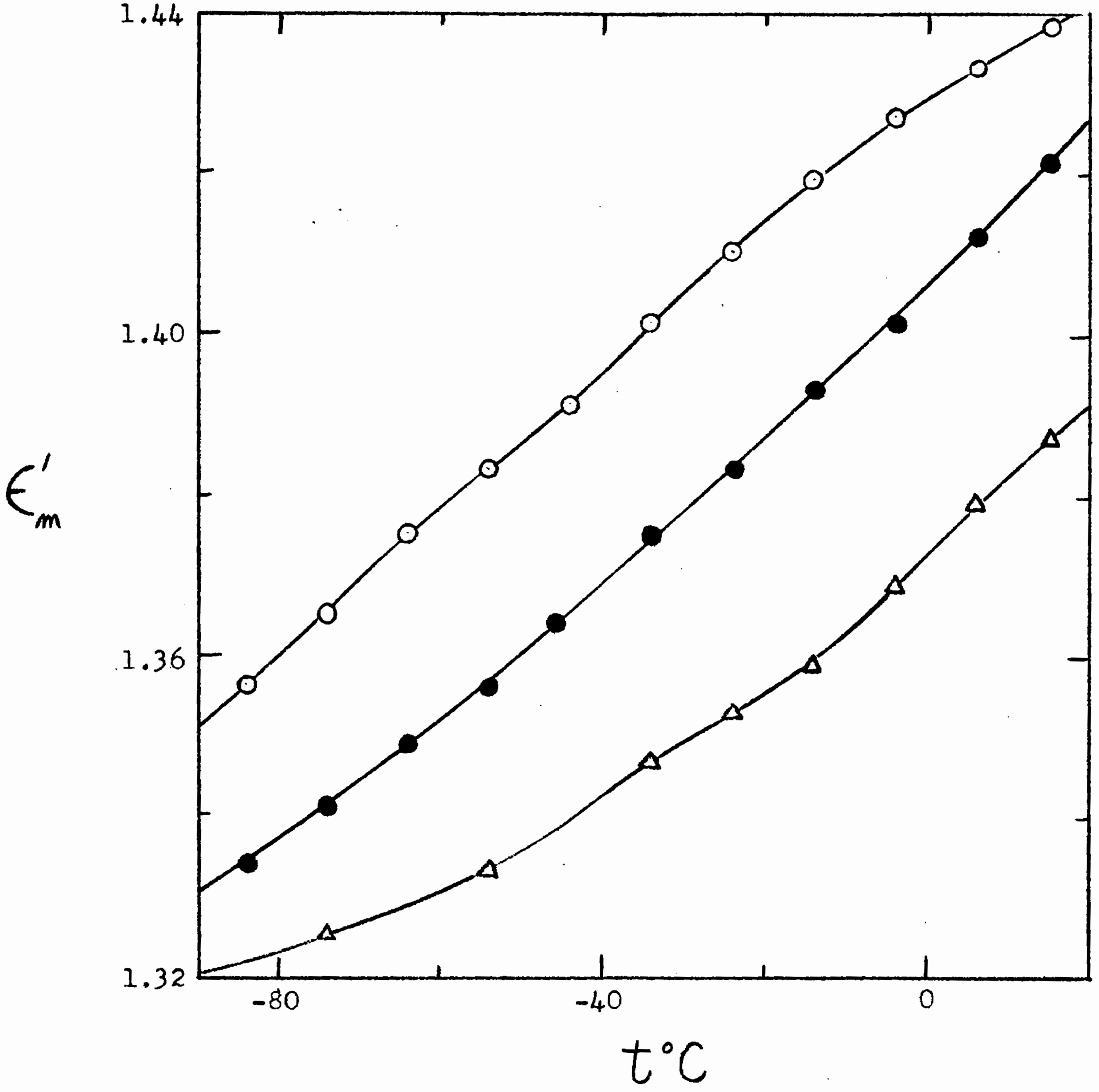

1.44
1.40
1.36
1.32
ϵ'_m
-80
-40
0
t°C

FIGURE 55

FIGURE 55

ϵ'_m vs t°C for nitrocellulose paper of D.S. 3.00

▲ 2000 Kc

● 20 Kc

○ 0.2 Kc

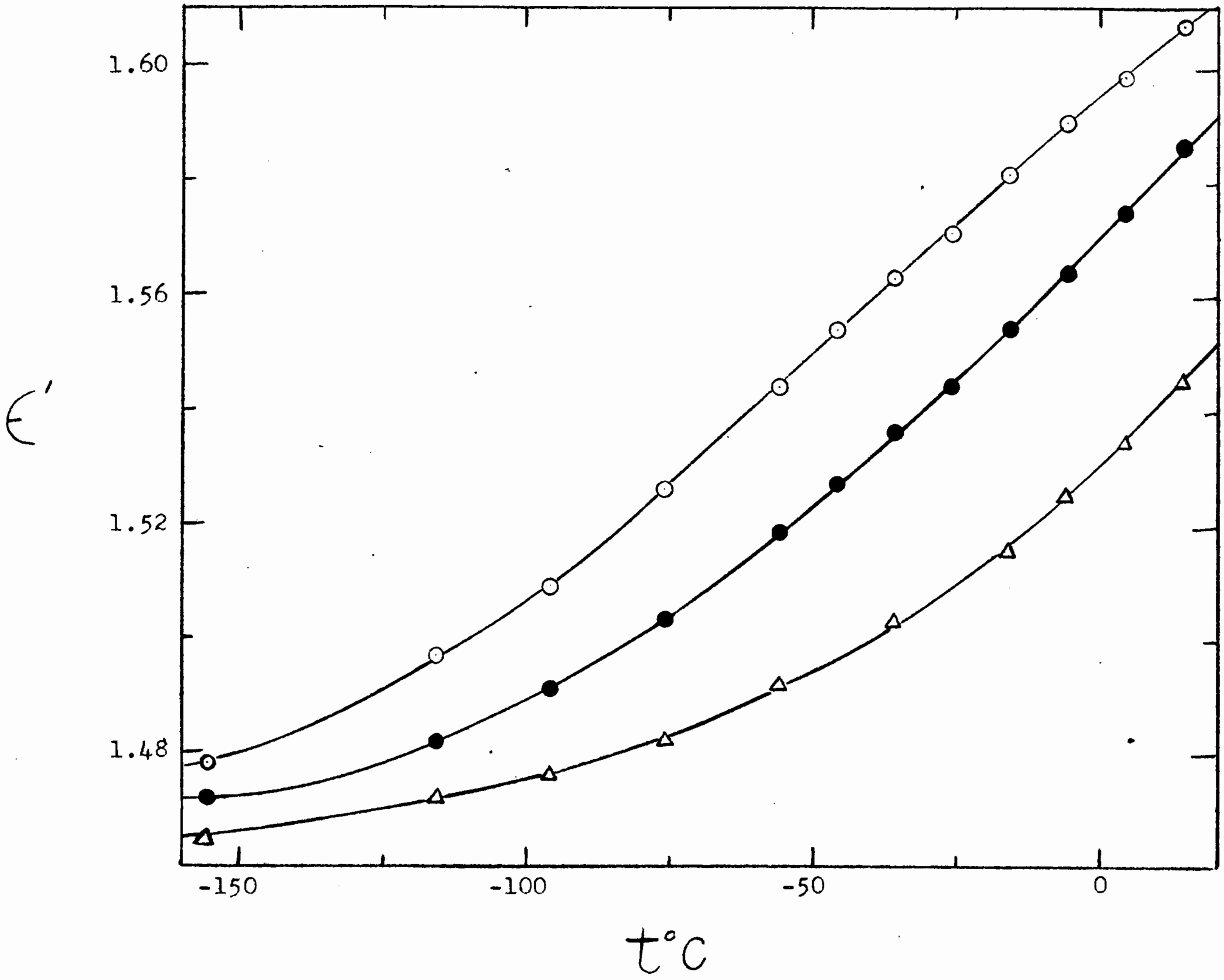

1.60
1.56
1.52
1.48
ε′
-150
-100
-50
0
t°C

FIGURE 56

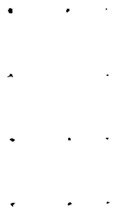


FIGURE 56

Frequency-temperature dependence of dielectric relaxation for nitrocellulose papers.

● D.S. 2.13 dispersion A

▲ D.S. 3.00 dispersion A

○ D.S. 2.13 dispersion B

△ D.S. 3.00 dispersion B

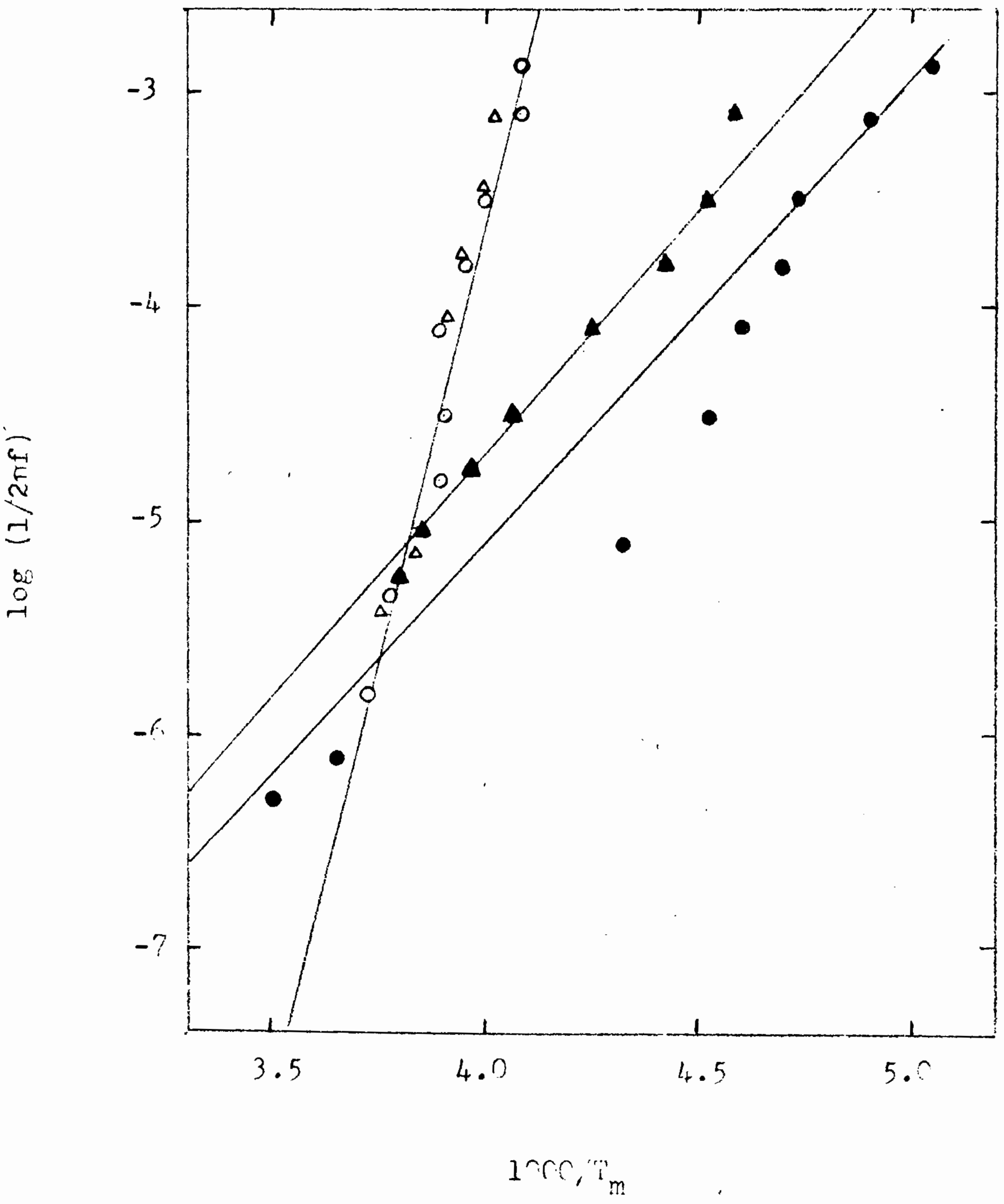

-3
-4
-5
-6
-7
log (1/2πf)
3.5
4.0
4.5
5.0
1000/T_m

FIGURE 57

FIGURE 57

ϵ''_m vs log f with and without lead corrections

○ curve 1, $C_m . \epsilon'_m$ vs log f (with corrections)

● curve 2, $C_{XP} . \epsilon'_m$ vs log f (without corrections)

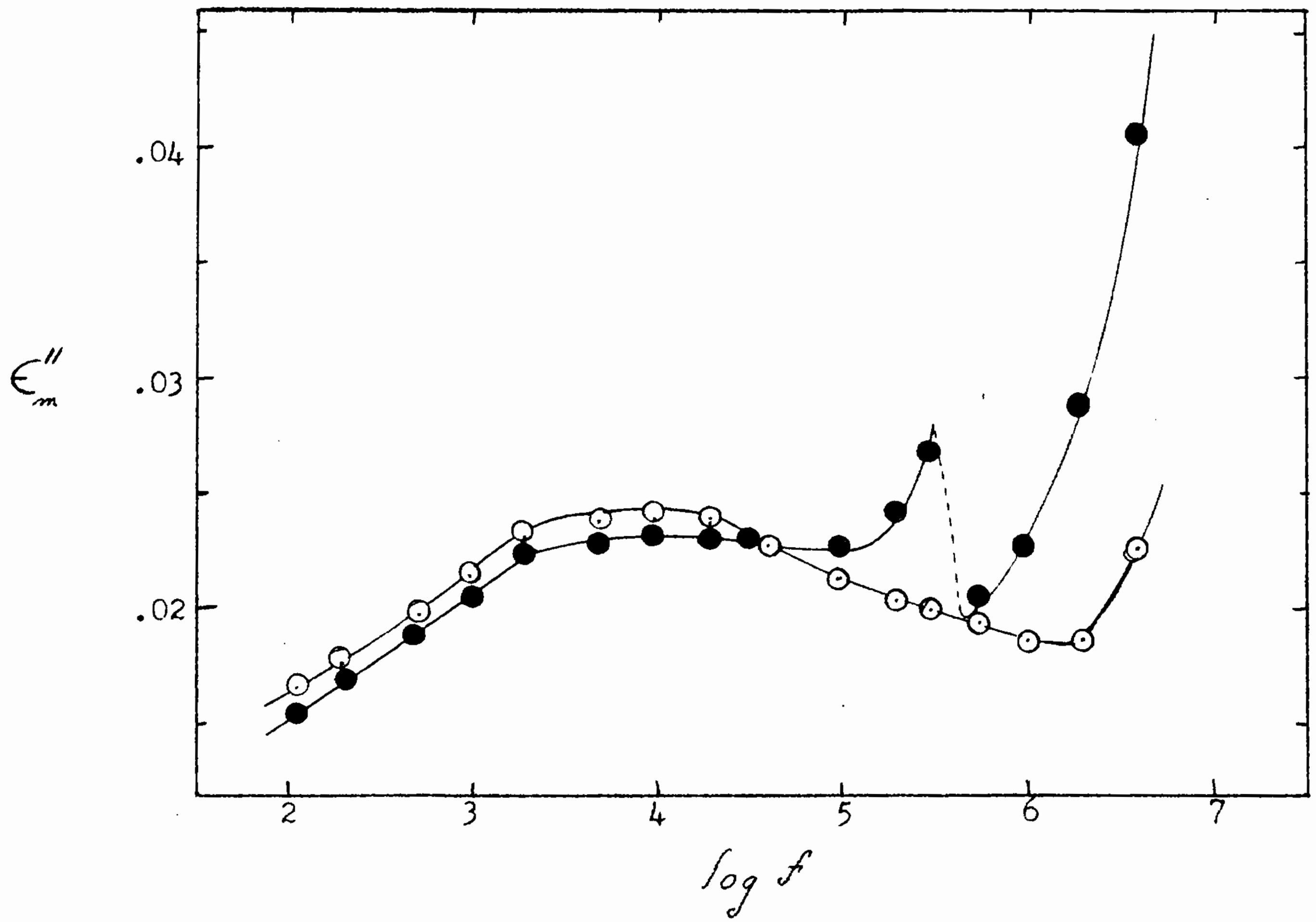
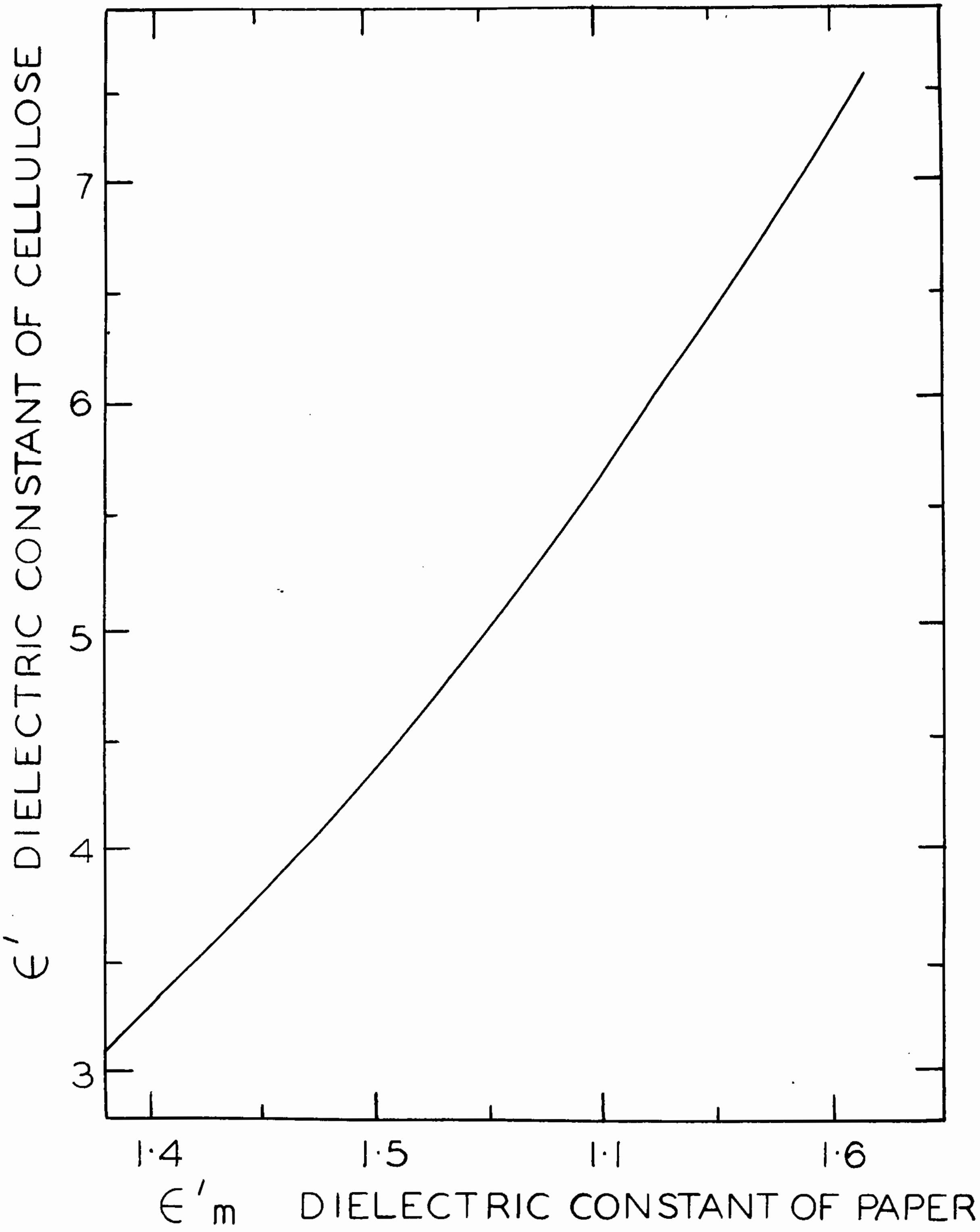

ϵ''_m
.04
.03
.02
2
3
4
5
6
7
log f

FIGURE 58

FIGURE 58

ϵ' vs ϵ'_m relating dielectric constants of cellulose and cellulose paper

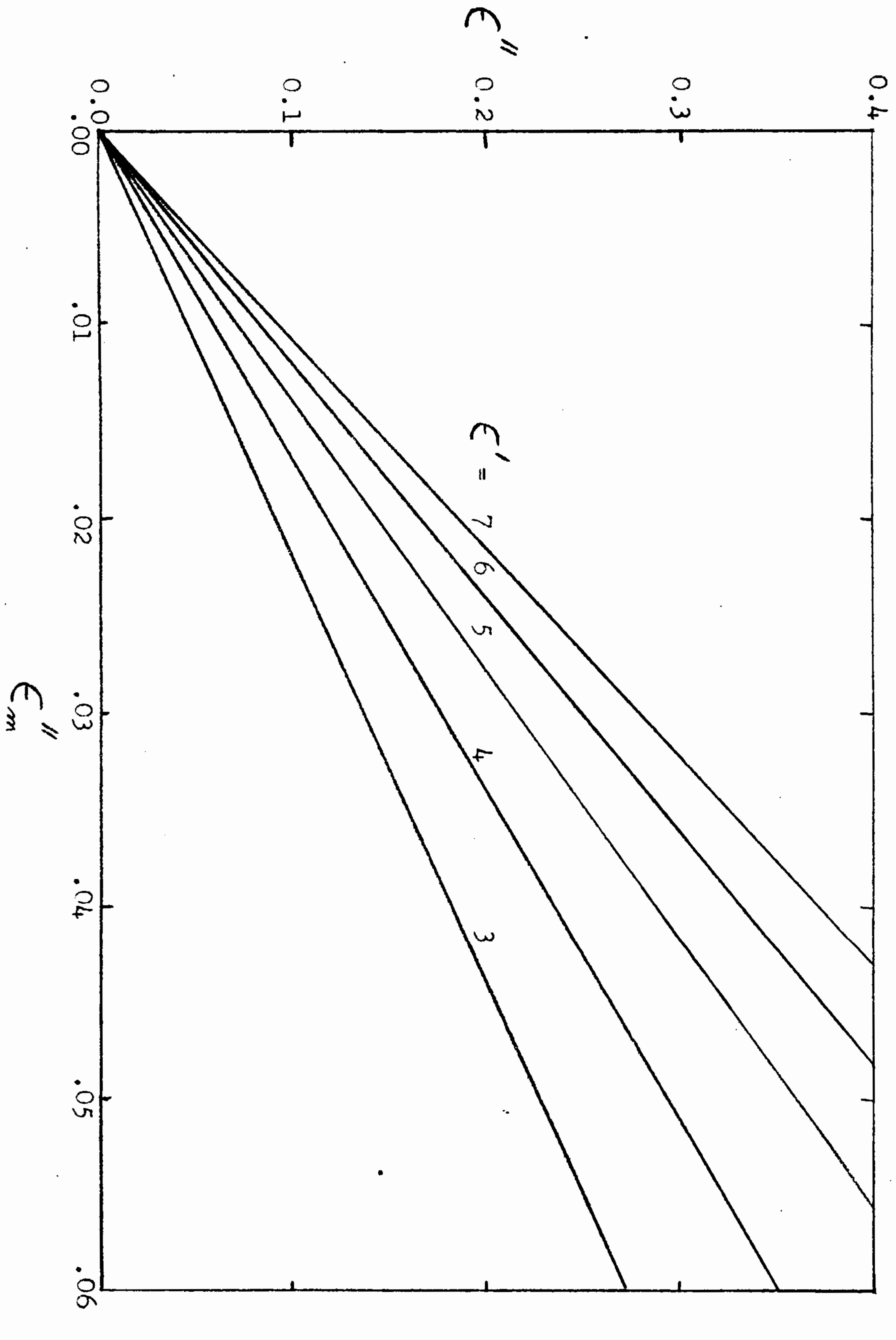


ϵ' DIELECTRIC CONSTANT OF CELLULOSE
7
6
5
4
3
1·4
1·5
1·1
1·6
ϵ'_m DIELECTRIC CONSTANT OF PAPER

FIGURE 59

FIGURE 59

ϵ' vs ϵ'_m relating dielectric losses of cellulose and cellulose paper



ϵ''
0.0
0.1
0.2
0.3
0.4
.00
.01
.02
.03
.04
.05
.06
ϵ''_m
$\epsilon' = 7$
6
5
4
3

FIGURE 60

FIGURE 60

ϵ' vs t°C for cellulose

□	0.2 Kc
■	2 Kc
△	20 Kc
●	200 Kc
○	2000 Kc

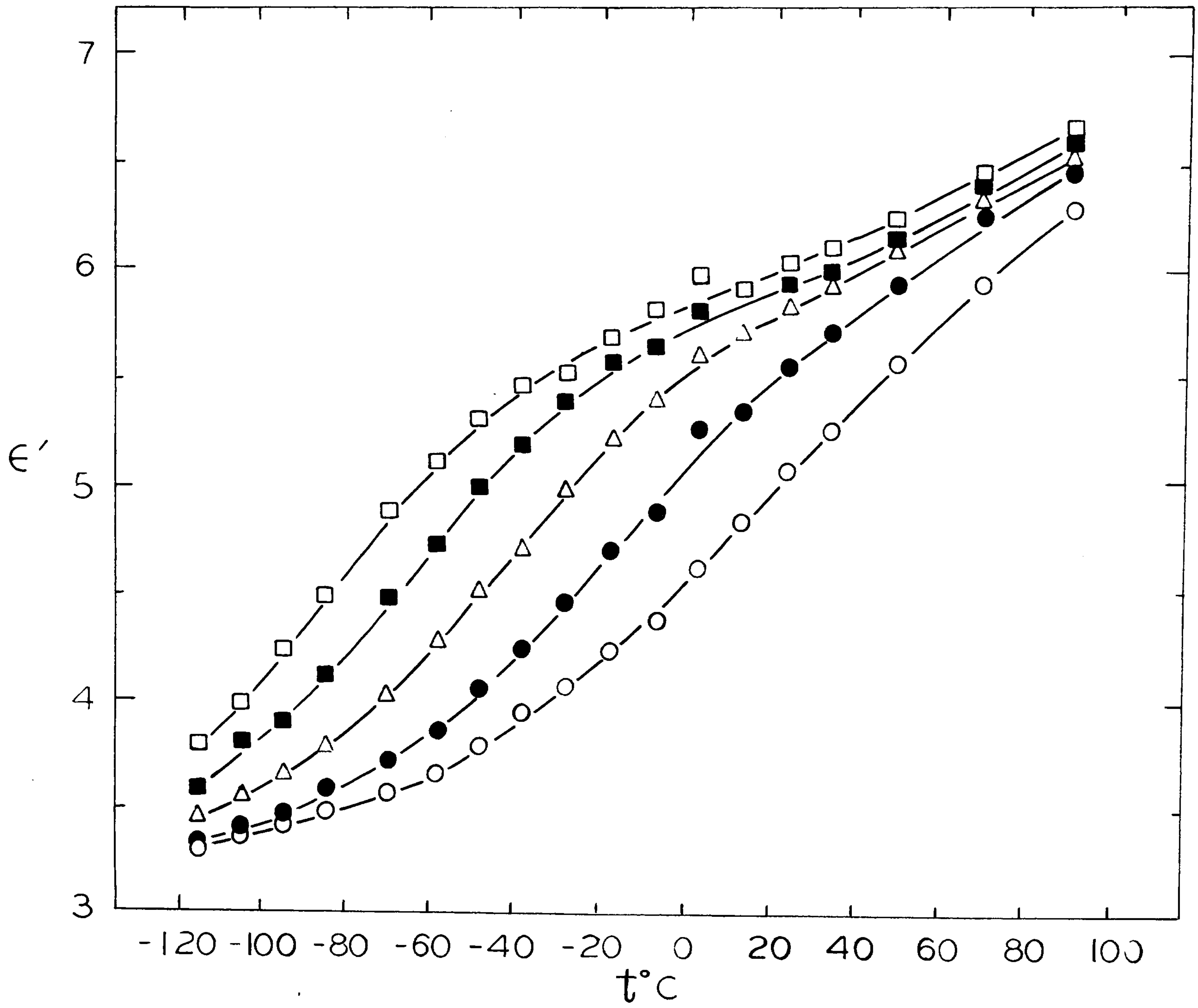

7
6
5
4
3
ε′
-120
-100
-80
-60
-40
-20
0
20
40
60
80
100
t°C

FIGURE 61

FIGURE 61

ϵ'' vs t°C for cellulose

□ 0.2 Kc

■ 2 Kc

△ 20 Kc

● 200 Kc

○ 2000 Kc

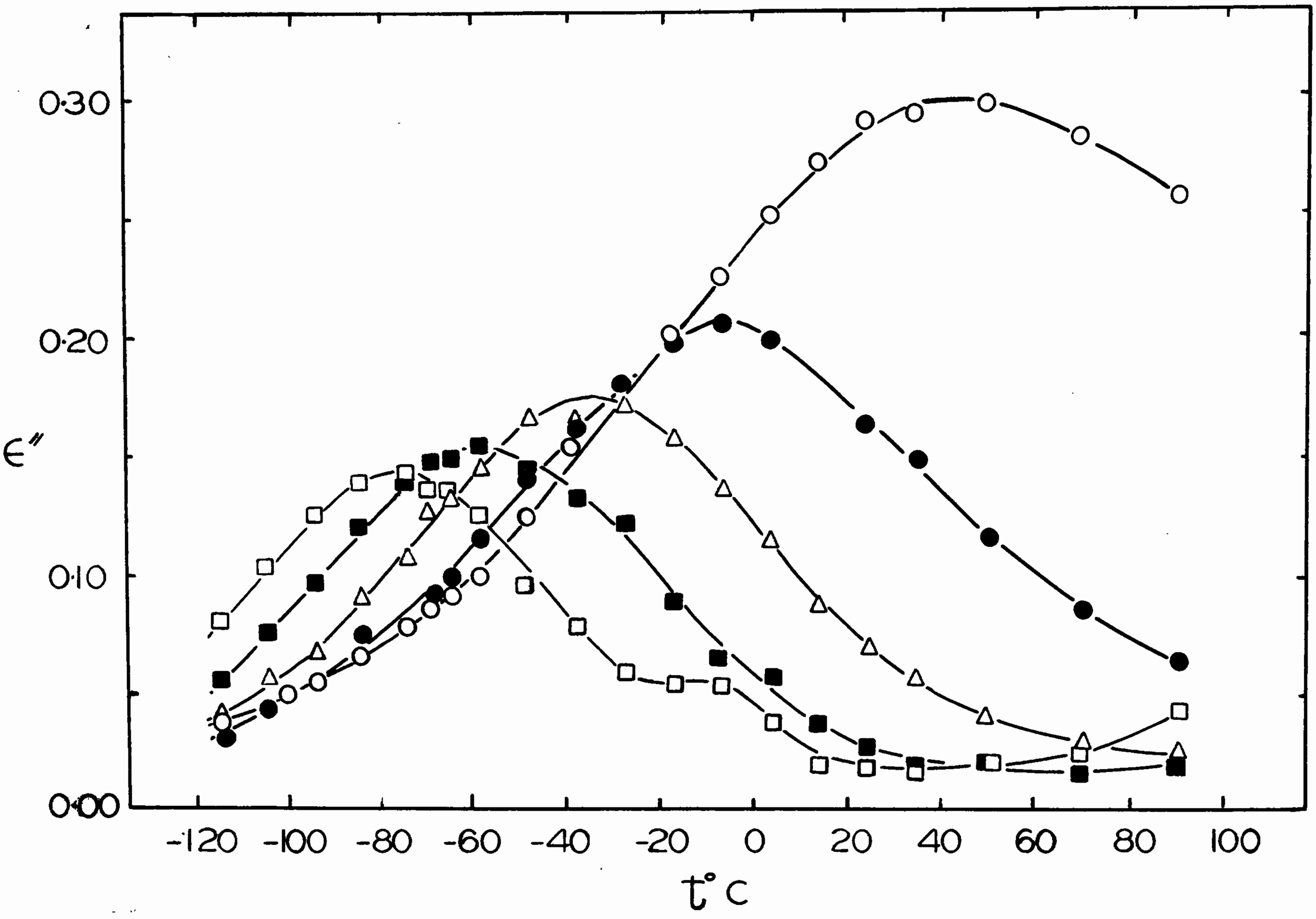

0·30
0·20
0·10
0·00
ϵ″
-120
-100
-80
-60
-40
-20
0
20
40
60
80
100
t° c

FIGURE 62a, 62b

FIGURE 62a

C_{XP} vs t°C for empty Seidman cell with ethanol bath

○	0.2 Kc
□	2 Kc
△	35 Kc
●	200 Kc

FIGURE 62b

D_X vs t°C for empty Seidman cell with ethanol bath

○	0.2 Kc
□	2 Kc
△	35 Kc
●	200 Kc

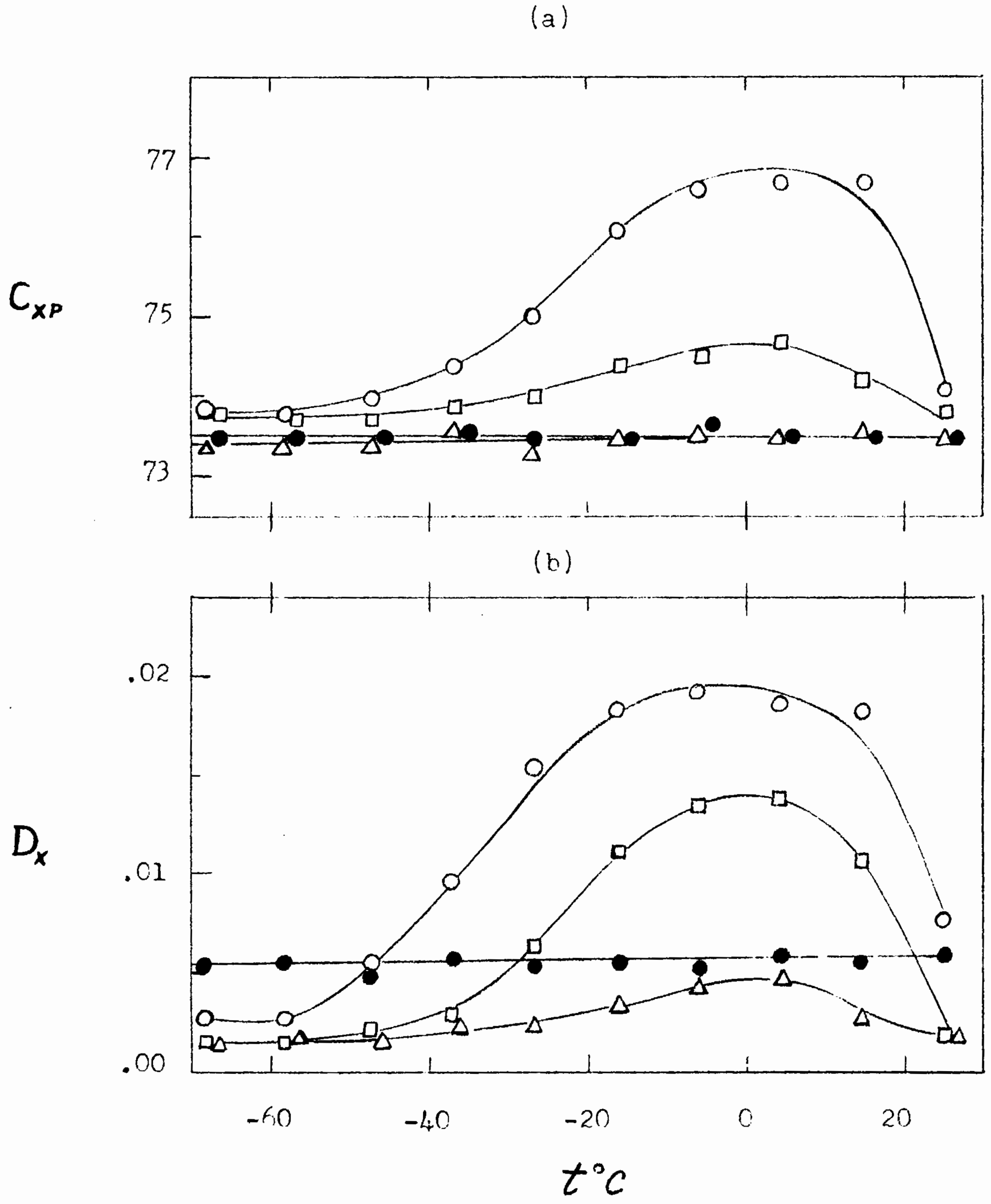
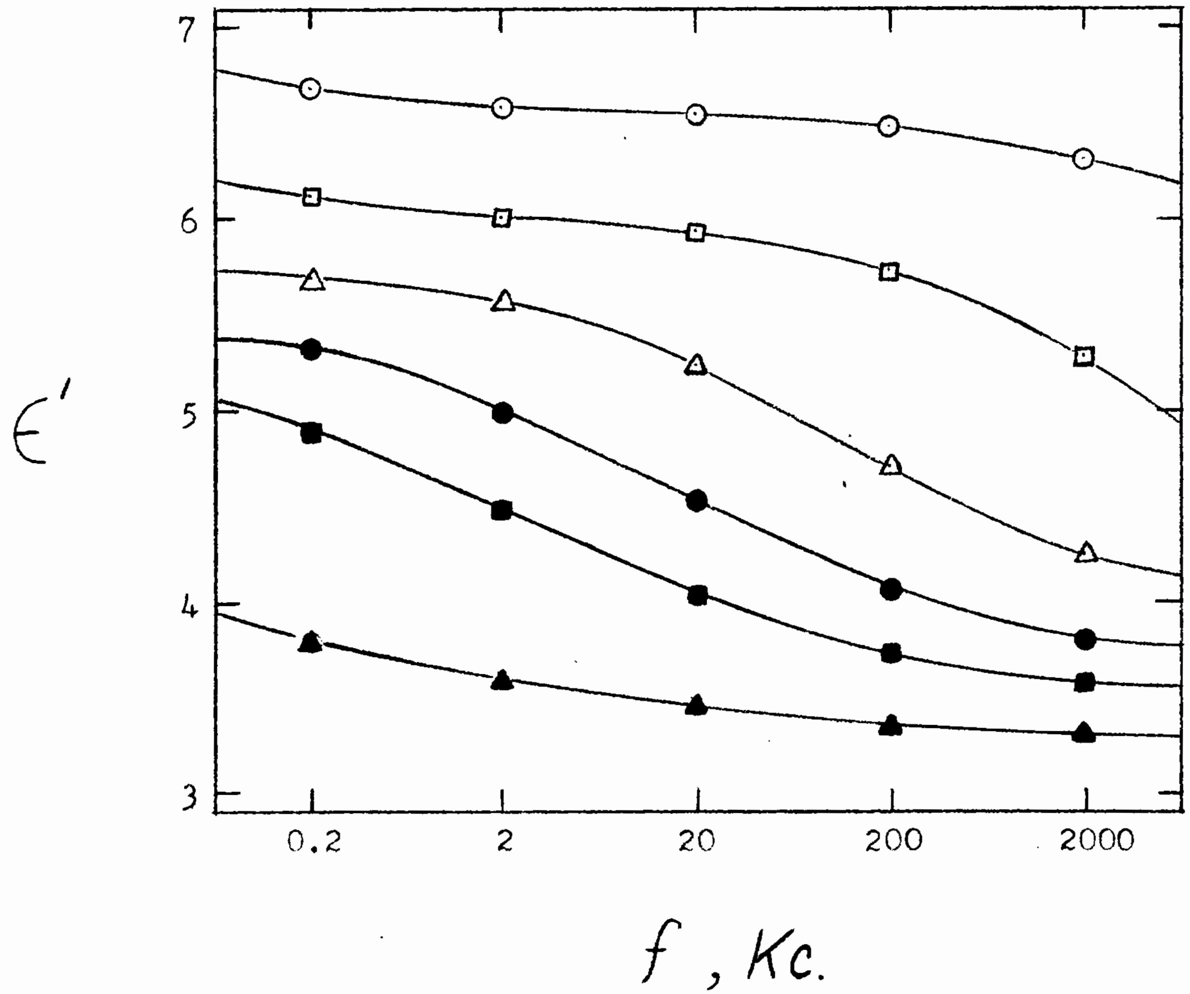

(a)
C_{XP}
77
75
73
(b)
D_x
.02
.01
.00
-60
-40
-20
0
20
t°c

FIGURE 63

FIGURE 63

ϵ' vs log f for cellulose

○ 91.1 °C
□ 35.1 °C
△ -16.3 °C
● -47.6 °C
■ -68.8 °C
▲ -114.4 °C



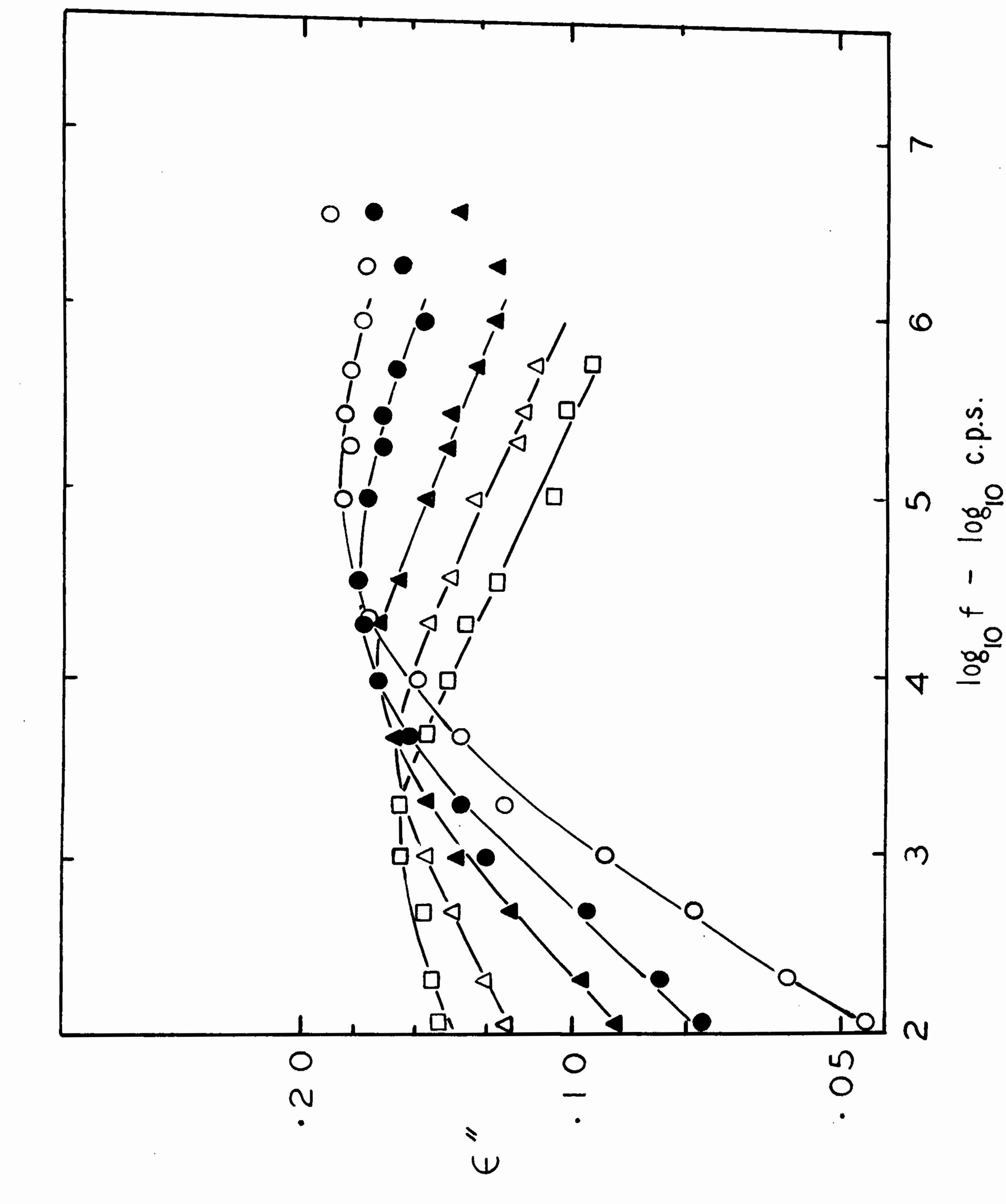
7
6
5
4
3
ϵ'
0.2
2
20
200
2000
f , Kc.

FIGURE 64

FIGURE 64

ϵ'' vs log f for cellulose

□ -69 °C
△ -58 °C
▲ -48 °C
● -37 °C
○ -27 °C



ε''
·20
·10
·05
2
3
4
5
6
7
$\log_{10} f - \log_{10}$ c.p.s.

FIGURE 65

FIGURE 65

Frequency-temperature dependence of dielectric relaxation for cellulose.

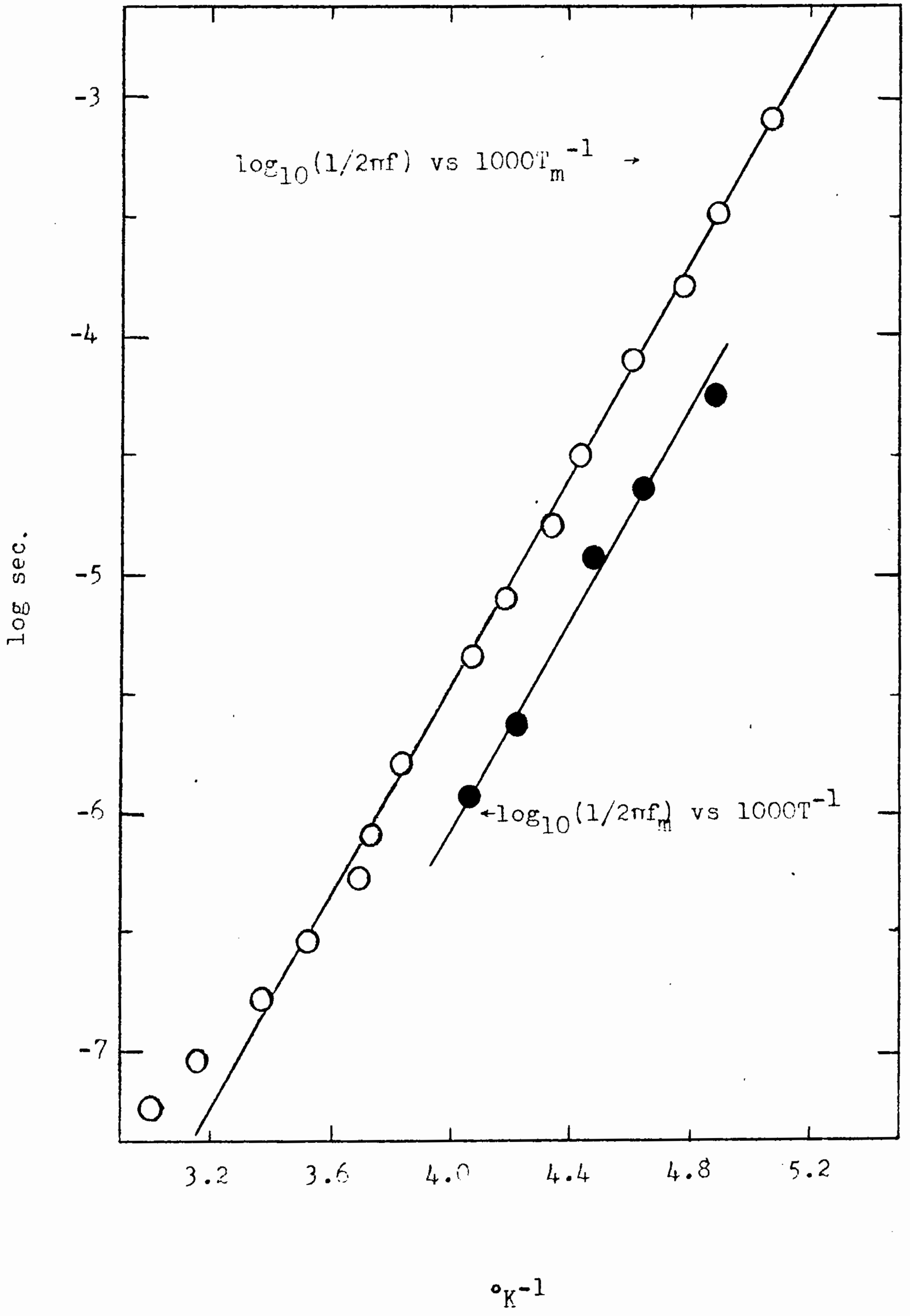

log sec.
-3
-4
-5
-6
-7
log10(1/2πf) vs 1000Tm-1 →
←log10(1/2πfm) vs 1000T-1
3.2
3.6
4.0
4.4
4.8
5.2
°K-1

FIGURE 66

ϵ'_m vs log f for high temperature dispersion of cellulose paper

△	249°C
○	224°C
▲	199°C
□	174°C
◎	129°C
◐	91°C

FIGURE 66

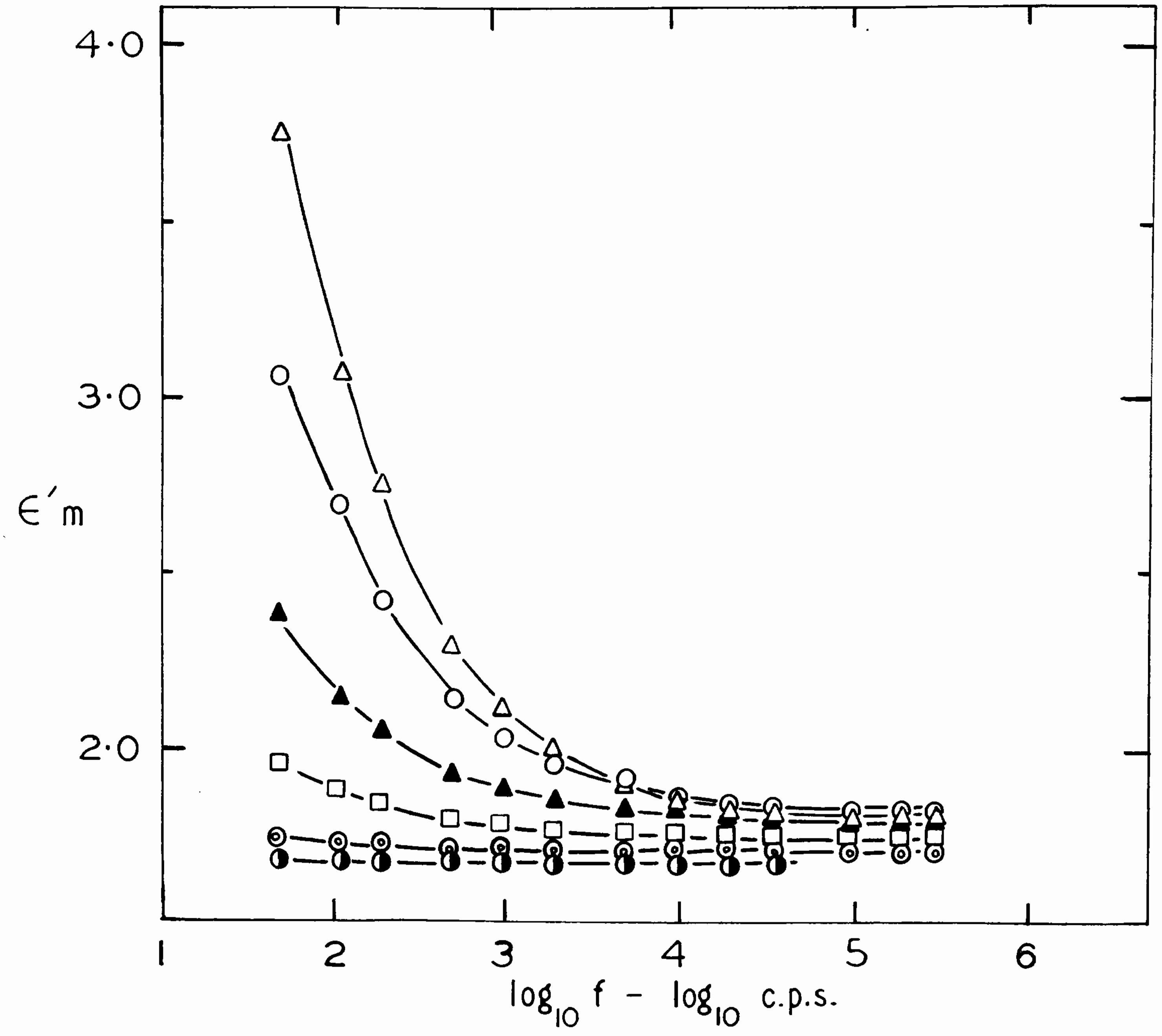
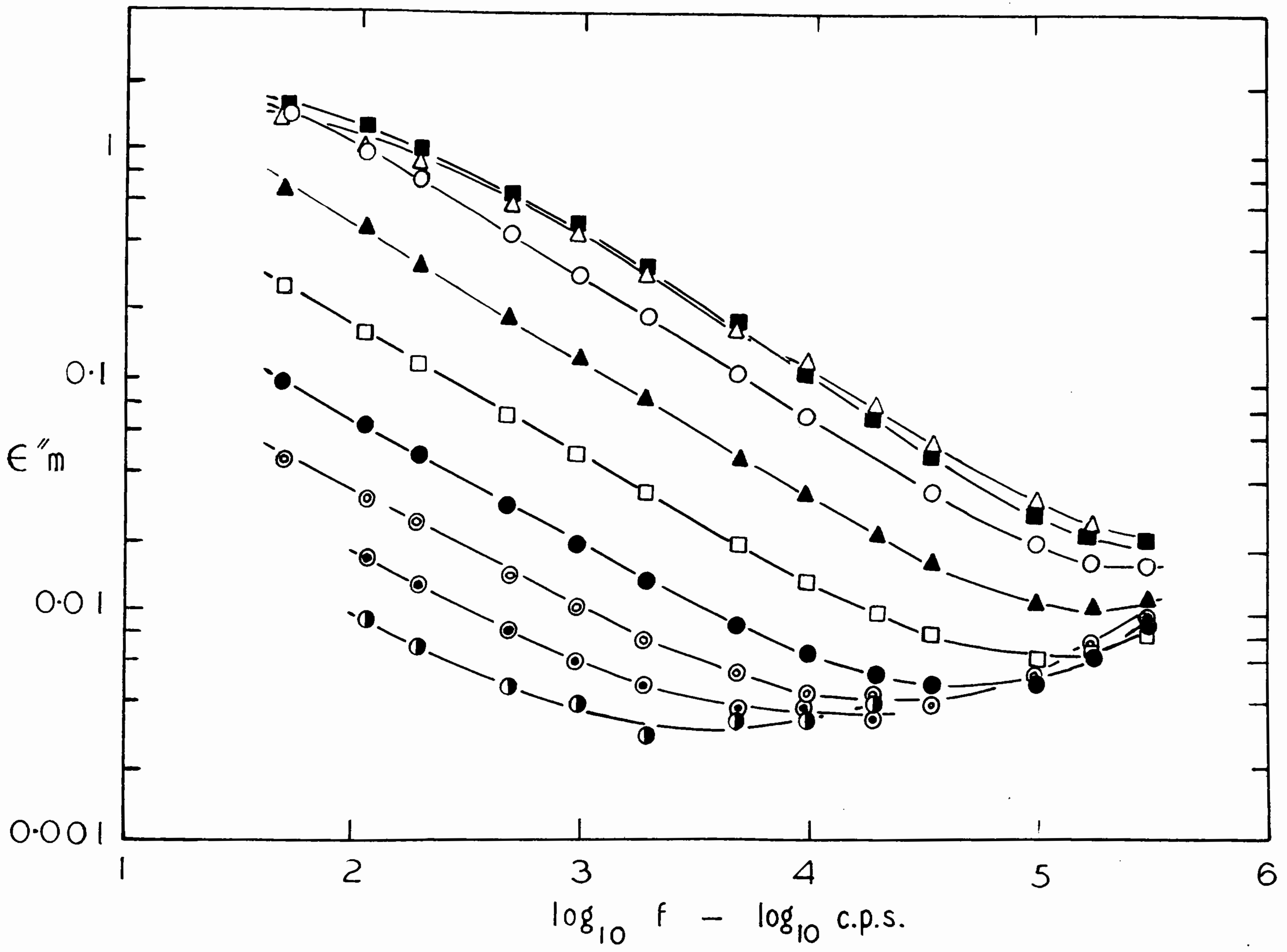

4·0
3·0
2·0
ϵ'_m
1
2
3
4
5
6
$\log_{10} f - \log_{10}$ c.p.s.

FIGURE 67

FIGURE 67

ϵ''_m vs log f for high temperature dispersion of cellulose paper

△ 264 °C
■ 249 °C
○ 224 °C
▲ 199 °C
□ 174 °C
● 149 °C
◎ 129 °C
◉ 111 °C
◑ 91 °C



1
0·1
0·01
0·001
ϵ″m
1
2
3
4
5
6
log10 f — log10 c.p.s.

FIGURE 68

FIGURE 68

Cole-Cole plot for high temperature
dispersion of cellulose paper
at 249 °C

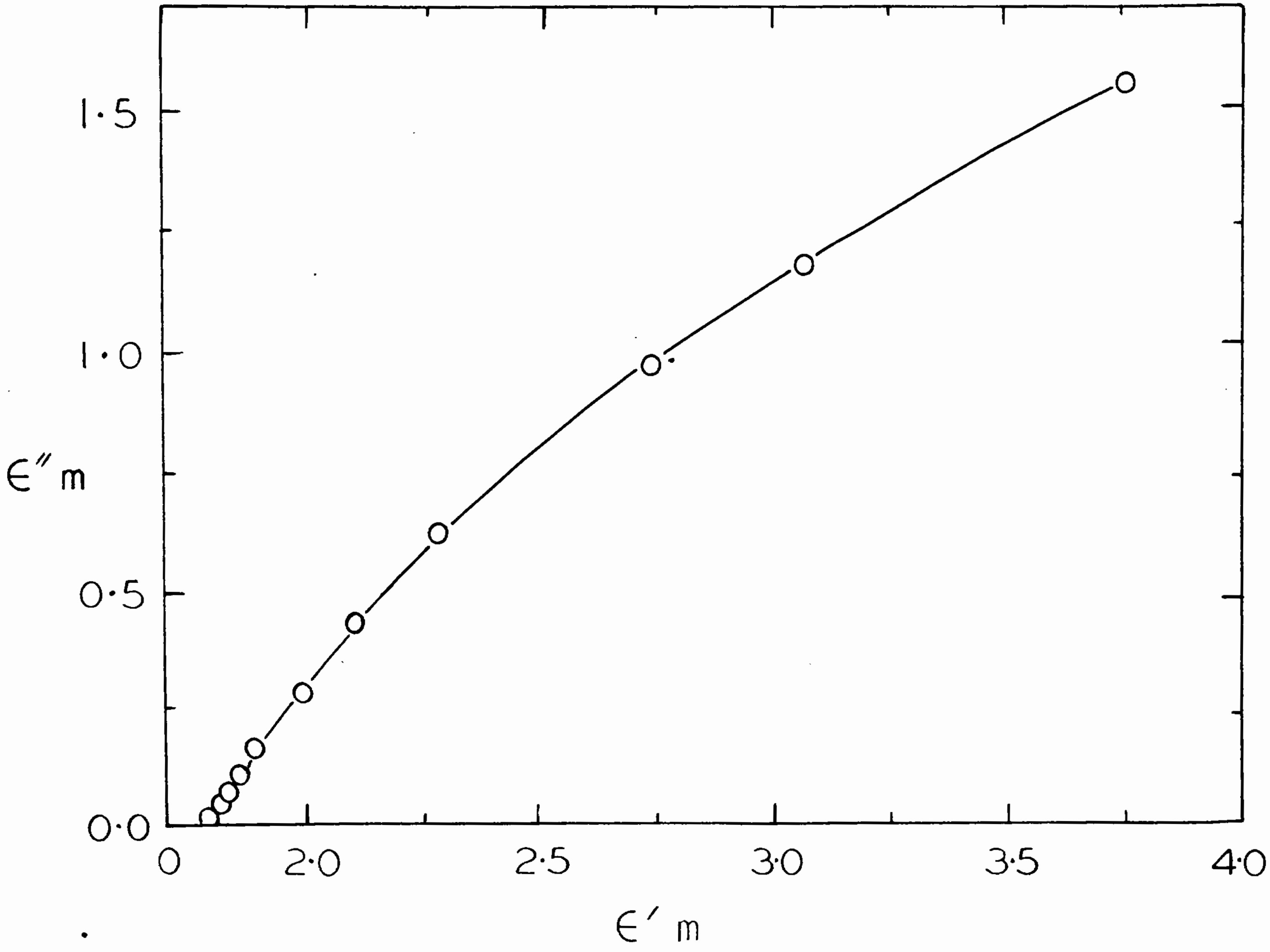

1·5
1·0
0·5
0·0
ε″m
0
2·0
2·5
3·0
3·5
4·0
ε′m

FIGURE 69

<u>FIGURE 69</u>

ϵ_{p1} vs t°C for high temperature dispersion of cellulose paper

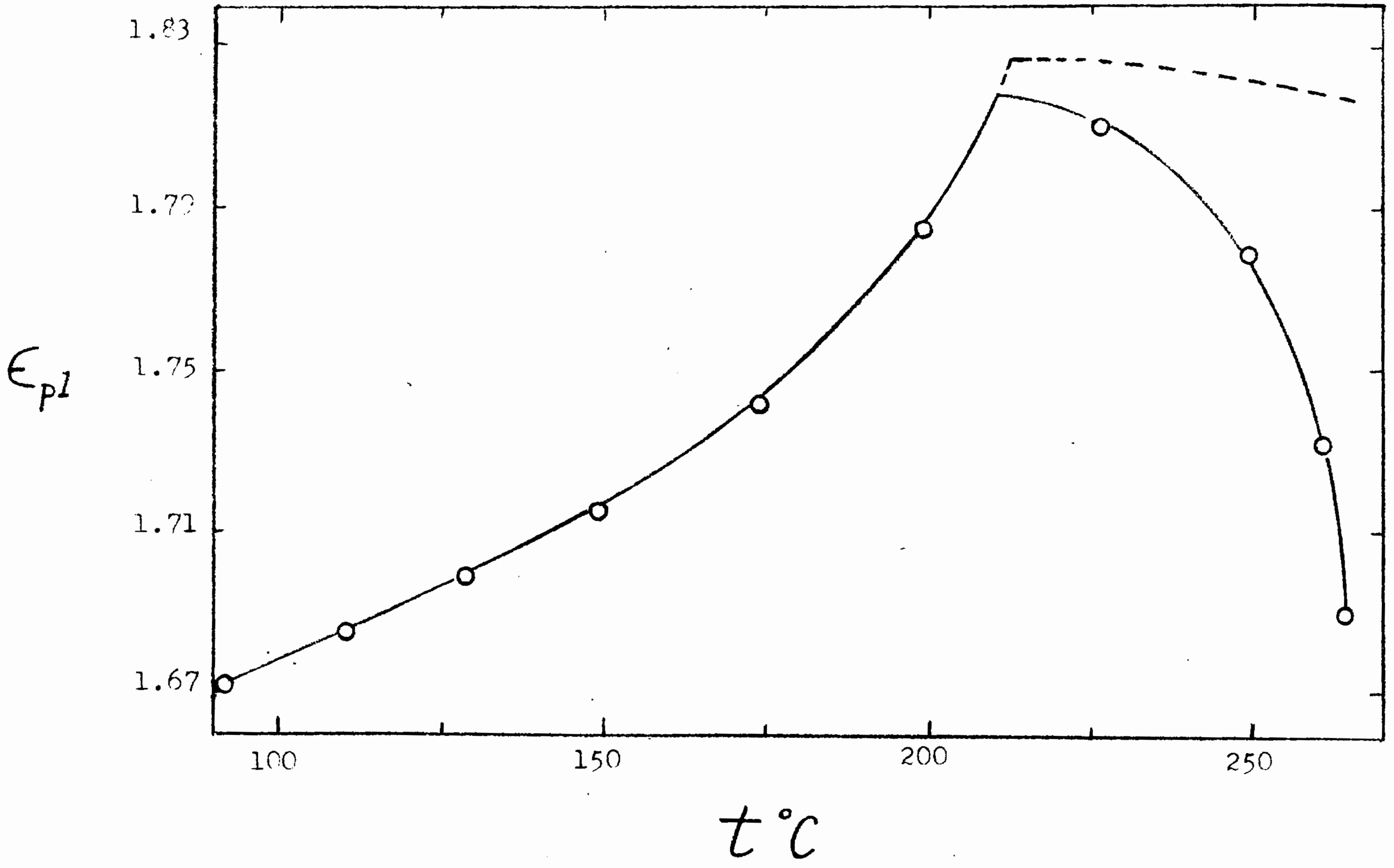

1.83
1.79
1.75
1.71
1.67
ϵ_{pl}
100
150
200
250
t °C

FIGURE 70a,70b

FIGURE 70a

Cole-Cole plots for cellulose and films
of nitrocellulose at 0.2 Kc

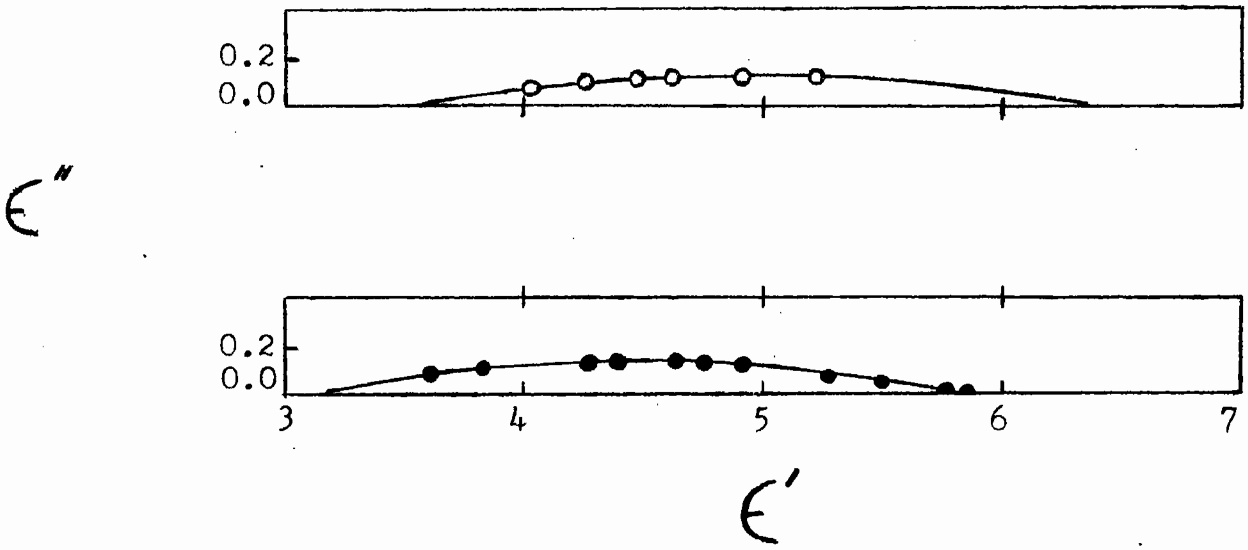
○ nitrocellulose

● cellulose

FIGURE 70b

Cole-Cole plot for nitrocellulose film
No. 7 at 0.2 Kc

(a)



(b)

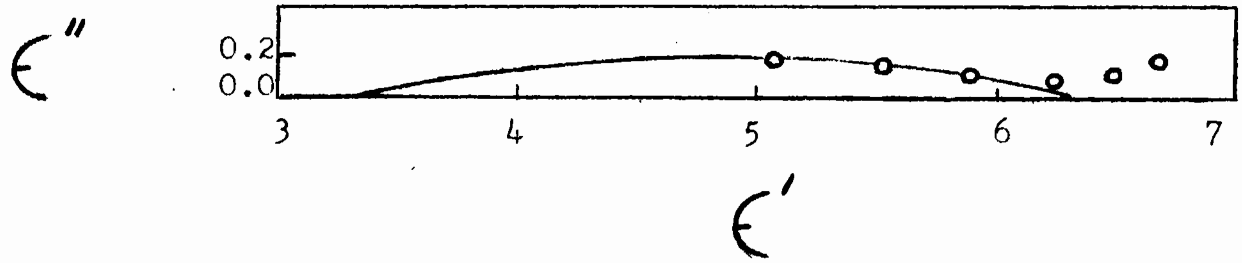
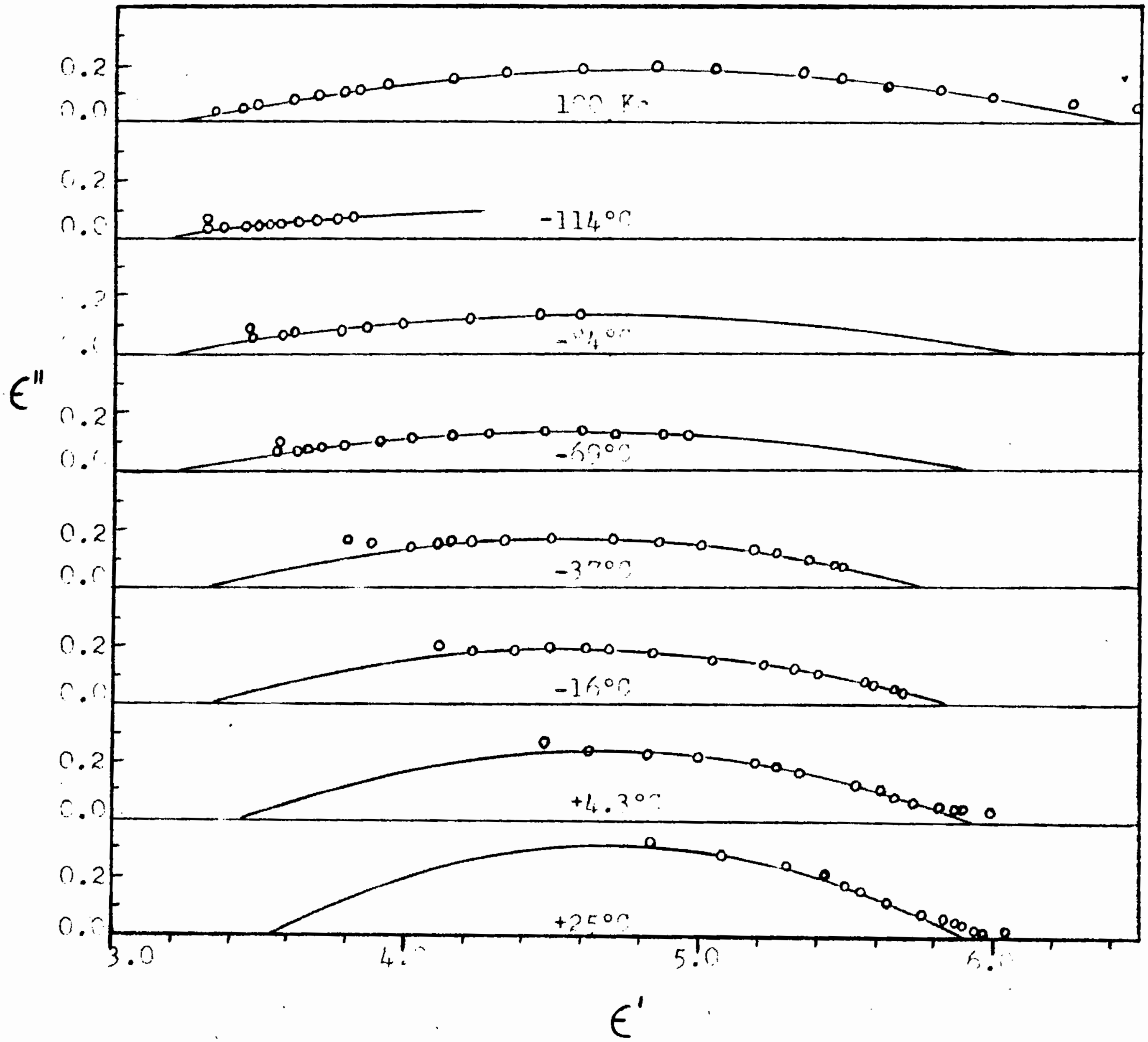


FIGURE 71

<u>FIGURE 71</u>

Cole-Cole plots for cellulose



0.2
0.0
100 Kc
-114°C
-94°C
-69°C
-37°C
-16°C
+4.3°C
+25°C
ε''
3.0
4.0
5.0
6.0
ε'