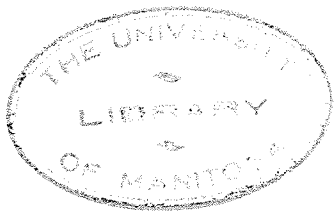
DIELECTRIC DISPERSION IN A SERIES OF SOLID POLYVINYL ACETALS

By

Thomas Hughes Sutherland, B. Sc. (Hons.)

McGill University



A Thesis submitted to the Faculty
of Graduate Studies and Research
in partial fulfilment of the
requirements for the degree of
Master of Science.

University of Manitoba

September 1952.

ACKNOWLEDGEMENTS

In appreciation of the guidance, valuable criticisms and constant interest, the writer expresses his sincere thanks to Dr. B. L. Funt, Assistant Professor of Chemistry, who directed this research.

Further thanks are extended to Mr. G. Trider and Mr. J. Atkinson for their cooperation in machining articles of apparatus.

TABLE OF CONTENTS

LIST OF TABLES

TABLE OF FIGURES

PREFACE

It was the object of this work to study the correlation between second order transition temperature as determined by the dielectric and mechanical methods. The polymers were chosen so that the effect termed "internal plasticization" could be studied and compared to "externally plasticized" systems. An insight into the basic mechanisms involved was afforded by the application of the Absolute Reaction Rate Theory to the dielectric data.

INTRODUCTION

GENERAL INTRODUCTION

Previous to 1930, very little theoretical work concerning the physical chemistry of high polymer systems had been undertaken. Styrene chemistry had been fairly well established by this time, and work on polyvinyl acetate was under way.

Due to the fact that polymer molecules were many times larger than any of those with which physical chemistry had had to deal with before, apparently anomalous results were obtained for physical properties (e.g. colligative properties, viscosity). This was partly due to the existence of a great multiplicity of molecular weights in a single polymer. Great variations in such properties as hardness could be obtained by changing the molecular weight. Indeed a large change in the molecular weight of a single polymer could produce a greater change than would be encountered in going from one polymer to another of the same molecular weight.

After 1930, a considerable amount of research clarified the situation considerably, and physical chemical theory was extended to include treatment of substances capable of having a wide range of molecular weights.

Due to the wide variations in the properties of a polymer, certain physical tests were needed to give an

indication of the properties of the material. Industry, on adoption of plastics for commercial purposes, devised a number of rapid tests for this purpose. Tests such as striking the sample with a hammer, bending a strip until it was doubled over, penetration of a needle, and others were usually quite crude and gave no insight into the actual processes taking place in the polymer. These tests are still used today because of their rapidity and simplicity.

More scientific tests, such as heat capacity, thermal conductivity, modulus of elasticity and refractive index, were studied in research laboratories in an effort to obtain more information of the basic mechanisms involved (3). A great advance in this direction came with the study of dielectric properties of polymers.

Curtis, McPherson and Scott (5) found that at fixed frequency and temperature, a vulcanized rubber displayed a maximum in the loss factor and dielectric constant with increasing sulphur content. They attributed this to the formation of stoichiometric compounds between sulphur and rubber. Khitchin (29) however, showed that this effect was dependent on temperature and frequency. He suggested that above the second order transition temperature the rubber-sulphur dipoles were free to respond to the electric field, while below this temperature the

dipoles were frozen in place.

Tuckett (36) clarified the relationship between dielectric and mechanical measurements. He indicated that the maximum in the loss factor occurred in the temperature range over which high elasticity developed, since both processes depend on a high degree of rotational freedom about the carbon-carbon bonds. Thus dielectric measurements would seem to give a more basic mechanism of the transition.

"In contrast to the method of study of mechanical properties in which deformation is applied to the outside of a matrix of molecules, and the resultant effect on individual molecules is assessed indirectly, application of an electric field to a polar polymer may be regarded as a direct application of a constraint to the molecules themselves." (2)

Since the mechanical and electrical properties are closely related, there should be some correlation of results between the two methods. Frith and Tuckett (14) compare values for the transition temperature obtained from electrical measurements and the mechanical brittle points of polyvinyl chloride, acetate and methyl acrylate, and the deviation or uncertainty between the two values obtained was about 7-9 C^{o}.

Transition temperatures obtained from mechanical

tests are subject to such diverse factors as heating rate, and rate of deformation. Because of this, discrepancies of 20 C° between different observers have been noted. Notwithstanding minor experimental difficulties, these effects are not encountered in electrical measurements,-- the only requirement being thermal equilibrium. Slight differences might be expected due to different methods of preparation and purification of the polymers. The literature does not give any comparison between electrical transition temperature and mechanical brittle or softening points of the same sample.

THEORETICAL INTRODUCTION

THEORETICAL INTRODUCTION

Dielectric Theory

The Debye Theory (7) originally put forth in 1912 (8) was derived for dispersion in polar liquids. This theory was not extended by him to include treatment of macromolecules.

The main difference between a polar liquid and a polar polymer is that in the former the dipoles are mechanically independent of the other dipoles in the system, whereas in the case of polar polymers the dipoles are joined together by covalent bonds. Thus, by slight changes it may be expected that the Debye Theory could be extended to cover polar polymers. Hence a general physical picture of the Debye Theory should give an indication of the mechanisms involved. (16)

The two types of electric current, alternating and direct, have different current carrying mechanisms. Direct current necessitates the actual transfer of particles, ions or electrons, but for alternating current a periodic displacement of bound charges is all that is necessary for the passage of current. Thus substances which are insulators for direct current can pass alternating current.

In an alternating field, the electrons of the atoms in the sample are displaced with respect to the nuclei. The maximum of current occurs at the zeros of voltage since

this is where the field is changing most rapidly. Thus the current is 90° out of phase with the voltage. This current is represented as a vector perpendicular to the voltage vector. The nature of the dielectric determines the magnitude of the electric displacement, the polarizability of the medium. This electron displacement current is present at all frequencies despite the presence of other current carrying mechanisms. The magnitude of this electronic displacement current is measured by the optical dielectric constant which theoretically is equal to the square of the index of refraction. It is the value obtained at relatively high frequencies or low temperatures with all substances.

Hydrocarbon polymers have lower polarizabilities than those containing halogen since the electrons in the former are more rigidly held.

Some substances at low frequencies have a higher dielectric constant than the optical value, which means another current carrying mechanism has been introduced. Substances showing this effect usually have an asymmetric structure with a centre of high electron density and are known as dipoles.

In an electric field the dipole experiences a torque tending to rotate it into alignment parallel to the field. If the polar molecule is suspended in a low

viscosity medium and a low frequency alternating field is applied, the dipole will oscillate in phase with the field. This periodic displacement of the dipole produces an alternating current which is superimposed on the electronic current. Thus many organic compounds have high dielectric constants. If the polar liquid is frozen, the molecules cannot oscillate and so polar crystalline solids usually have low dielectric constants.

In the absence of a field, a random dipole orientation and uniform distribution exists. In a d.c. field, each molecule tends to swing parallel to the field producing a component of polarization in the direction of the field. This orientation is affected by thermal motion but an average polarization will persist. If the field is removed, the orientation vanishes gradually due to thermal motion. The rate at which molecules return to uniform distribution will depend on the viscosity of the medium, the size of the molecule and the temperature (kinetic energy). The time, τ, required for a steady state orientation to decay to i/e, the value, is called the time of relaxation. According to Debye

$$\tau = \frac{4\pi\eta a^3}{k\,T} \qquad 1.$$

Where η is the viscosity, k is the Boltzmann constant, a the diameter of a sphere hydrodynamically equal to the

molecule and T is the absolute temperature. This is known as the Debye-Stokes equation.

For a definite system, a low frequency field is defined as one whose period is large compared to the relaxation time. In a low frequency field, there is equilibrium between orientation and the field at all times. Under these conditions, a system will exhibit its maximum dielectric constant ϵ_o called the static dielectric constant since it is the value obtained by d.c. methods.

If the frequency is increased, a condition will be reached where the molecules cannot follow the impressed field and the polarization will begin to lag. This lag is greatest when the period of the field is of the same order as the time of relaxation. At frequencies much greater than this, the dipole cannot follow the field at all, and as a result the dipole assumes a mean position in the field.

The lag in polarization produces two effects. First, since the dipole orientation decreases with increasing frequency, the dielectric constant decreases from the static value ϵ_o to the optical value ϵ_∞ when only electronic polarization is present. Secondly, polarization out of phase with the field means that the current is less than 90^o out of phase with the voltage. The current is then no longer purely reactive, but part of the current is

carried resistively. Since the current and voltage are in phase in a pure resistance, and current carried in this manner must dissipate energy as heat, there will be heat generated in the dielectric. This dissipation will be greater, the smaller the angle, between the voltage and current vectors. The dissipation factor is the tangent of the angle complementary to θ, known as δ.

$$\therefore \text{D.F.} = \tan \delta \qquad 2.$$

and from phasor diagrams

$$\tan \delta = \frac{G}{B} \qquad 3.$$

where G is the conductance and B is the susceptance of the dielectric.

The energy consumed in a dielectric is measured by ϵ'', the loss factor, while ϵ' the dielectric constant measures the capacity. These two entities are components of the generalized dielectric constant ϵ, given by Debye as

$$\epsilon = \epsilon' - j\epsilon'' \qquad 4.$$

where j is the operator for a 90° rotation and is equal to $\sqrt{-1}$.

The loss factor is zero at very low frequencies where the electronic and molecular polarization are in phase with the field, and also at very high frequencies where there is only electronic polarization which is

always in phase with the field. Between these high and low frequency limits, the loss factor reaches a maximum when the polarization is out of phase. This occurs when

$$\omega\tau = 1 \qquad 5.$$

where $\omega = 2\pi$ times the frequency. The dissipation factor or loss angle is determined by

$$\text{D.F.} = \tan\delta = \frac{\epsilon''}{\epsilon'} \qquad 6.$$

If the system has a single relaxation time, τ, the components of ϵ are given by

$$\epsilon' = \epsilon_\infty + (\epsilon_o - \epsilon_\infty) / (1 + \omega^2\tau^2) \qquad 7.$$

$$\epsilon'' = (\epsilon_o - \epsilon_\infty)\omega\tau / (1 + \omega^2\tau^2) \qquad 8.$$

The path of the vector ϵ in the ϵ'' - ϵ' plane is a semicircle terminating at ϵ_∞ and ϵ_o with its centre on the ϵ' axis where the ordinate is ϵ'' max (4)

Dielectric Relaxation and Absolute Reaction Rate Theory

The theory of absolute reaction rates was first applied to dielectric relaxation by Frank (13) and Eyring (10) (26) (33) and later by Kauzmann (28) and others.

Since the relaxation time is temperature dependent, and $\log\frac{1}{\tau}$ vs 1/T plots give straight lines, it would seem that an energy of activation were involved in the process. Whenever the rate of a process depends on temperature, it is quite certain that at some stage in the process a

molecule or other unit involved is forced to wait until it has acquired, by thermal fluctuations, a considerable amount of energy in excess of the average thermal energy of the medium. An insight into the mechanism might be gained by the application of this theory. Kauzmann criticizes the Debye theory for assuming that Stokes' law is valid and having to assume that viscosity is the controlling factor in the process of dipole orientation. Values of the macroscopic viscosity quite often did not give sensible values of a in equation 1. From experimental evidence presented in his paper, he assumes that there is a definite relation between the two processes involved, but that the mechanism of relaxation rates is a much simpler problem, the solution of which might help to clarify the viscosity mechanism.

According to the theory of absolute reaction rates, we can define a free energy of activation $\Delta F^{\ddagger}$ for dielectric relaxation by the equation

$$\frac{1}{\tau} = \frac{kT}{h} \exp\left(-\frac{\Delta F^{\ddagger}}{RT}\right) \qquad 9.$$

where k and h are the Boltzmann and Planck constants and T the absolute temperature. This equation can be written

$$\frac{1}{\tau} = \frac{kT}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \cdot \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) \qquad 10.$$

where $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are the entropy and enthalpy of activation respectively. The components of the equation

are easily determined if it is written in logarithmic form

$$\log \frac{1}{\tau} = \log \frac{kT}{h} + \frac{\Delta S^{\ddagger}}{2.303R} - \frac{\Delta H^{\ddagger}}{2.303\ RT} \qquad 11.$$

From the plot of $\log \frac{1}{\tau}$ vs $1/T$ the value of $\Delta H^{\ddagger}$ can be obtained from the slope of the line

$$\Delta H^{\ddagger} = -2.303 \times R \times \text{slope} \qquad 12.$$

and since $\Delta F^{\ddagger}$ can be determined from the relation

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad 13.$$

$$= -2.303\ RT \log \frac{h}{kT\tau} \qquad 14.$$

then $\Delta S^{\ddagger}$ is found from the relation

$$\Delta S^{\ddagger} = \frac{\Delta H^{\ddagger} - \Delta F^{\ddagger}}{T} \qquad 15.$$

When the free energies of the relaxation process and viscosity are nearly equal, it is assumed that there is a close relation between the two mechanisms. (33) (27) (34)

The value of the $\frac{1}{\tau}$ can be found from the maxima in the loss factor curves. It is equal to 2π times the frequency of maximum absorption at a given temperature.

EXPERIMENTAL

EXPERIMENTAL

Electrical Apparatus

For the electrical measurements a Schering type capacitance bridge (General Radio, Model 716C) was used. The A.C. signal was supplied by a Hewlett-Packard oscillator, continuously variable from 20 c.p.s. to 200 kc. The bridge balance was detected by observing an amplified signal on an oscilloscope and a Simpson multirange voltohmmeter with a 5,000 ohms per volt rating.

The polymer samples were placed in a parallel plate condenser, (Fig.I.) consisting of two plane brass plates 4.000 inches in diameter which were silver plated. The bottom (high voltage) plate was mounted on a "micalex" plate, one inch thick, which in turn was mounted on a rigid stand. A precision micrometer, mounted on the supporting stand, was made to ride on a ballbearing contained in a cylindrical collar which was secured to the upper plate. The thickness of a sample placed between the plates could be read directly. The micrometer arrangement also served to centre the top plate over the lower one. (15)

The test condenser just described was placed in an insulated box measuring eighteen inches on all sides, equipped with a removable top. The interior of the box was

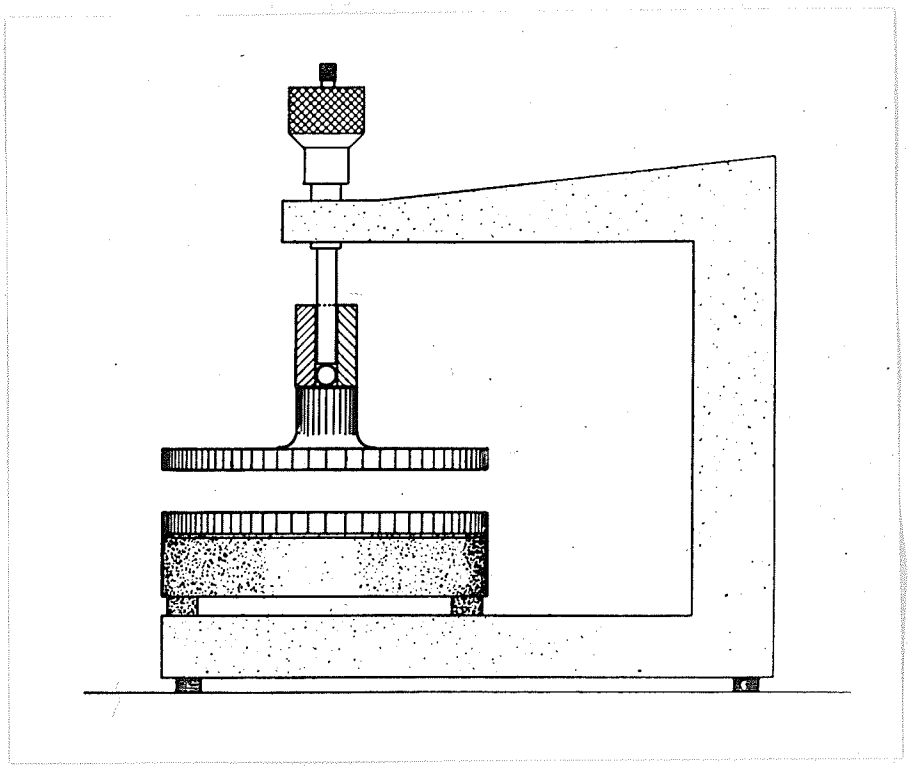


Fig. I Test Condenser

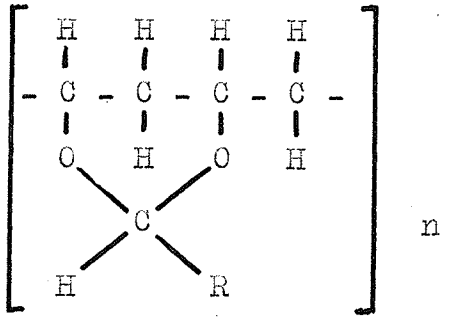
lined entirely with sheet aluminum to eliminate stray electrical effects.

A Fenwal "Thermoswitch" operating a Fisher-Serfass electronic relay provided temperature regulation to $\pm$ 0.1°C. A toaster element served as the heater, and stirring in this air thermostat was supplied by a 1/4 h.p. motor to the shaft of which a six-bladed fan, 7 inches in diameter, was attached.

Temperature measurement was effected by a five junction copper-constantan thermocouple embedded in the top grounded plate of the test condenser. The resulting voltage was multiplied by a resistor arrangement (acting as a reverse voltage divider) and read on a Leeds & Northrup Hydrogen Ion potentiometer variable from 0 to 1.6 volts. The thermocouple was calibrated against a standard thermometer which was in turn calibrated against a Platinum resistance thermometer by Dr. W. J. Bierman.

Materials

The polymers used were members of a group known as the polyvinyl acetals which have the general formula



Where R is - H for the formal

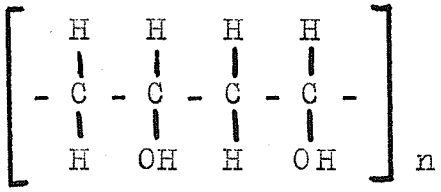
- CH_3 for the acetal
- $CH(CH_3)_2$ for the isobutyral
- C_5H_{11} for the hexanal
- $CH_2CH(C_2H_5)-C_3H_7$ for the 2-ethyl hexanal

The vinyl formal and acetal polymers were commercial samples obtained from Canadian Resins & Chemicals Company. These polymers were prepared by the hydrolysis and subsequent acetalization of polyvinyl acetate. The polyvinyl formal sample, known as Formvar 15/95E, was prepared from Gelva 15, a polyvinyl acetate having a molecular weight of 60,000, the replacement of acetate groupes being 95% complete. The polyvinyl acetal, Alvar 7/70, a high acetate content sample, was prepared from a polyvinyl acetate, Gelva 7, having a molecular weight of 35,000. In the hydrolysis of the latter, only 70% of the acetate

groups was removed.

The remaining three polymers were obtained from A. F. Fitzhugh of the Research Laboratory of the Shawinigan Resins Corporation, Springfield, Massachusettes. They are isobutvar (Polyvinyl isobutyral), hexvar (polyvinyl hexanal) and octvar (polyvinyl 2-ethyl hexanal). These were prepared by 99% hydrolysis of polyvinyl acetate, (Gelva 60) having a molar viscosity in benzene at 20°C. of approximately 60 centipoises (Molecular weight - 180,000), and subsequent acetalization with the corresponding aldehyde (isobutyraldehyde, n-hexaldehyde, 2-ethyl hexaldehyde). The polyvinyl alcohol contents for the isobutvar, hexvar and octvar were 13.3%, 12.2% and 12.8% respectively. (11)

The polyvinyl alcohol content is a measure of the number of hydroxyl groups that are not replaced in the acetalization step and is expressed as monomer unit



Procedure

The polymer samples were dried at 80°C. for eight hours in vacuo in a pistol drying apparatus. The polymer was then placed in a die which had previously been heated to about 100C° above the softening point of the polymer

(as determined by the dielectric method). In order to prevent permanent impairment of the pressing die, lubrication with silicone grease was required, since the lower members of this series are used commercially as bondings for glass and metals. (35)

The die was then placed on a hydraulic press and the polymer was subjected to a pressure of 1,000 p. s. i. for a period of five to ten minutes. The die was then allowed to cool to room temperature and the sample, previously granular, was then in the form of a transparent disk slightly greater than four inches in diameter and from 50 to 70 thousandths of an inch thick. Due to a slight amount of "play" in the piston of the die, the disk was not sufficiently uniform in thickness for the electrical measurements. This entailed the adoption of a grinding process which consisted of securing the disk horizontally on a plate of glass with stopcock grease, and placing a grinding powder, No. 100 or 120, on the exposed side of the disk. A few drops of water were added to this powder and a second piece of glass was placed over this. Grinding was accomplished by pressing down on the top plate of glass with concurrent horizontal motion.

The disk was removed periodically and the thickness measured at eight places with a micrometer. The disks were ground in this manner until the deviation from the mean was

± 0.0003 inches. A dilute suspension of aquadag (colloidal graphite) was applied to each surface of the disk and allowed to dry. (15) (18) (19) The sample was placed on a lathe between two rubber faced brass plates which had been accurately machined to a four-inch diameter. The disk was then cut down to a four-inch diameter with the lathe cutting tool. The polymer sample was then placed in the test condenser in the air bath and "conditioned".

In the process of heating the polymer, pressing the disk and cooling, certain strains are introduced in the sample just as in any casting or moulding. (19) On heating the disk above its softening temperature, there is a tendency to relieve these strains by distortion of the sample to a greater or lesser extent which could create erratic results and affect the reproducibility of the data. This distortion takes the form of an increase in thickness of about 3% (9) which becomes very noticeable at low values of dielectric constant. This is especially noticeable at high frequencies where the dielectric constant does not increase until a temperature much higher than the softening point is reached. (Fig.II.)

"Conditioning" means that these strains are largely removed by heating at about ten degrees above the softening point of the polymer for a period of twenty-four hours. At a temperature much higher than this viscous flow becomes

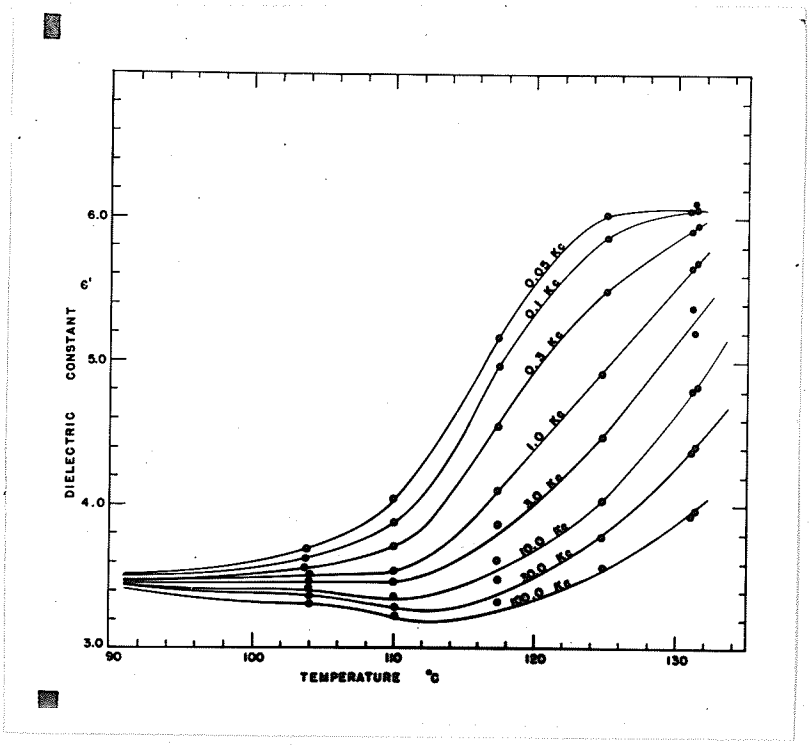


Fig. II Effect Produced by Distortion of Sample

an important factor and it is not desirable to leave the sample at an exceedingly high temperature for periods longer than those required for the attainment of the thermal equilibrium necessary for stable and reproducible bridge readings.

The General Radio capacitance bridge was adaptable to two different methods for the measurement of capacitance and dissipation factor. In the direct method, the unknown capacitance is placed in one arm and is balanced by a variable standard air capacitor in the adjacent arm. (Fig.III.) In the substitution method, a fixed condenser is placed in the arm occupied by the unknown condenser in the direct method, and the unknown capacitance is placed in parallel with the variable air capacitor. (Fig.IV.)

Since the formulae contained in the manual for the capacitance bridge did not include any correction for leads, it was necessary to derive these expressions from the given formulae.

A poor condenser can be treated as an ideal capacitance in parallel with a resistor. If the cell, containing the sample, and the leads, are considered as two such combinations, in parallel, the treatment is as follows:

Capacitances in parallel are additive and so the capacitance of the sample is determined by subtraction of

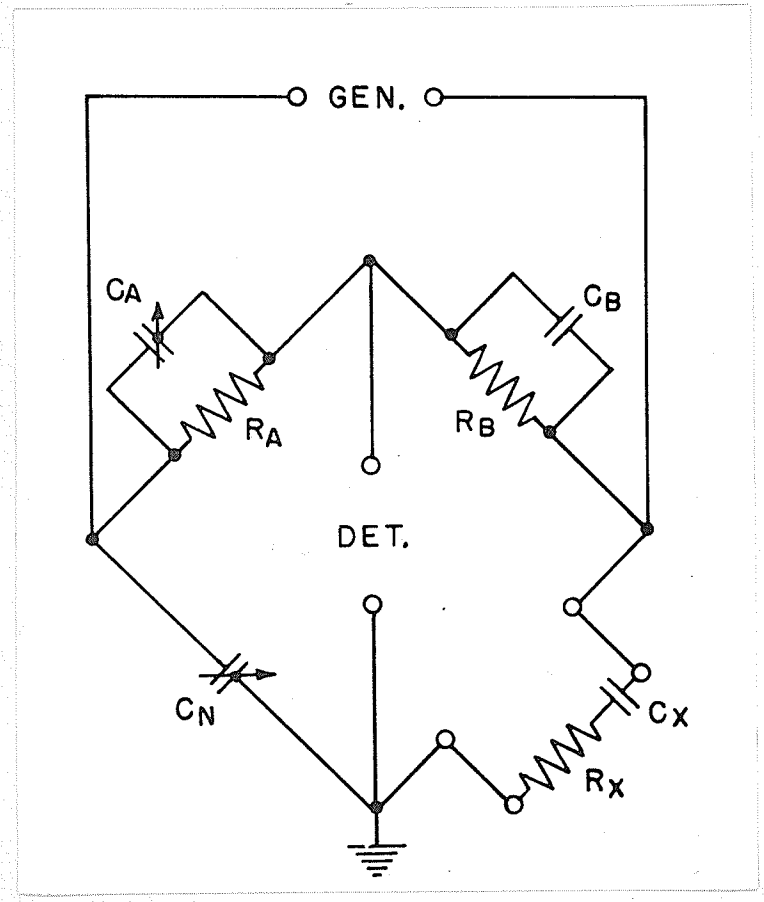


Fig. III

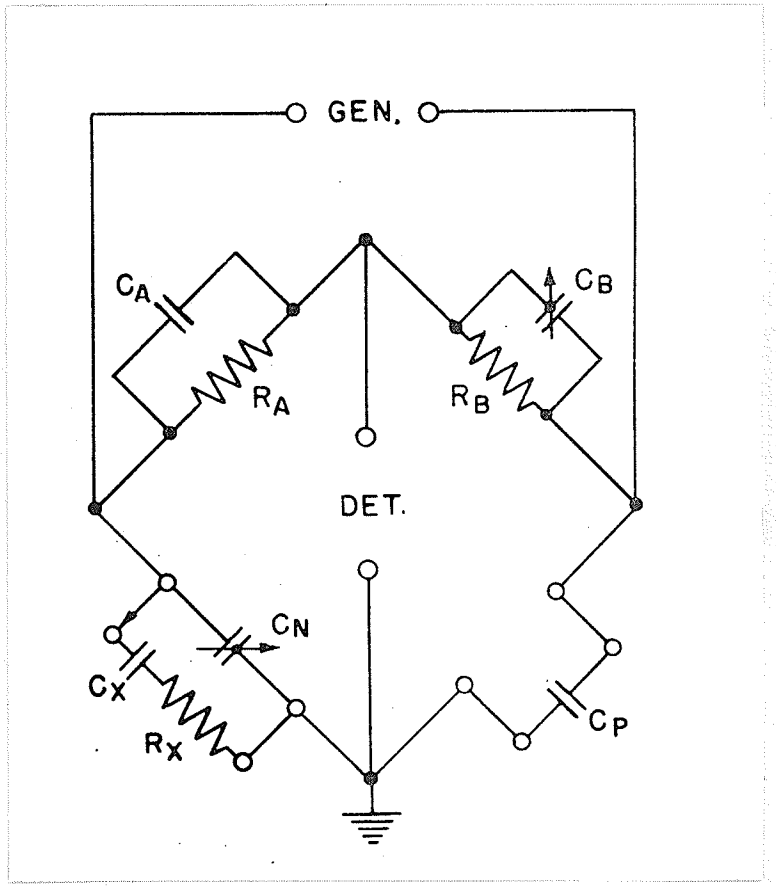


Fig. IV

Schematic Diagrams of the Schering Bridge for Direct Method (Fig. III) and Substitution Method (Fig. IV) (25)

Subscripts: x denotes the unknown; n denotes standard variable Air Condenser; p denotes precision condenser; a and b are the two ratio arms of the bridge.

the leads capacitance from the total capacitance. This holds for both "substitution" and " direct" methods of the bridge.

The dissipation factor is a ratio of conductance to susceptance (24)

$$D.F. = \frac{G}{B} \qquad 3.$$

Since the resistive components are in parallel, their conductances are additive, hence

$$G \text{ total} = G \text{ leads} + G \text{ sample} \qquad 16.$$

which is the same as

$$\frac{1}{Rp \text{ total}} = \frac{1}{Rp \text{ leads}} + \frac{1}{Rp \text{ sample}} \qquad 17.$$

where Rp is the equivalent parallel resistance.

$$\therefore \frac{1}{Rp \text{ sample}} = \frac{1}{Rp \text{ total}} - \frac{1}{Rp \text{ leads}} \qquad 18.$$

By the substitution method, the formula given is (25)

$$\frac{1}{Rp} = \omega C' \Delta D \qquad 19.$$

where ω is the angular frequency (2π x frequency).

C' is the capacitance dial reading with the leads out. (It is the "zero" reading of the bridge by this method.)

$\Delta D = D - D'$ where D represents the reading of the dissipation factor dial with the unknown across the terminals (which may be leads only, or leads + sample) and D' is the "zero" reading of the dissipation factor

dial and is taken concurrently with C'.

By substitution in 18 from 19

$$\frac{1}{Rp \text{ sample}} = \omega C' (D \text{ total} - D' - D \text{ leads} + D')$$
$$= \omega C' (D \text{ total} - D \text{ leads}) \qquad 20.$$

Combining this with 3

$$D.F. = \frac{G}{B} = \frac{1/Rp \text{ sample}}{\omega C \text{ sample}} = \frac{\omega C' (D \text{ total} - D \text{ leads})}{\omega C \text{ sample}}$$
$$= \frac{C' (D \text{ total} - D \text{ leads})}{C \text{ sample}} \qquad 21.$$

where C sample is the capacitance due to the sample alone corrected for stray capacitances.

By the direct method, the theory is the same, the formula for the equivalent parallel conductances being the only difference. It is (25)

$$\frac{1}{Rp} = D\omega C \qquad 22.$$

where D is the reading on the dissipation factor dial,

ω is again the angular frequency and

C is the equivalent parallel capacitance of the unknown

$$\therefore \text{ Dissipation Factor (D.F.)} = \frac{G}{B} = \frac{\omega [(DC) \text{ total} - (DC) \text{ leads}]}{\omega C \text{ sample}}$$
$$= \frac{(DC) \text{ total} - (DC) \text{ leads}}{C \text{ sample}} \qquad 23.$$

RESULTS

RESULTS

The numerical results are presented in this section in tabular form. The graphical plots from these values will follow in the discussion since references will be made to them in that section.

Sample Calculations

These calculations are taken from typical sets of data obtained by the direct and substitution methods of the bridge (General Radio Company, Form 681-B).

a Direct Method: the data presented here are the 300 cycle, 94.8°C. readings for polyvinyl acetal.

C Total (including leads)	457.2 $\mu\mu$f.
C Leads	156.1 $\mu\mu$f.
D Total (including leads)	2.29%
D Leads	0.047%

The D readings given on the bridge are expressed as a per centage and depend on the frequency. The bridge is direct reading at frequencies which are multiples of 10 from 100 cycles to 100 kilocycles. The D readings of the bridge must be multiplied by a factor of $0.01 \frac{f}{fo}$ where f is the frequency used in the determination and fo is the frequency setting of the range selector switch. On applying

this correction, using the 100 cycle range

$$D \text{ Total} = 0.03 \times 2.29 = 0.0687$$

$$D \text{ Leads} = 0.03 \times 0.047 = 0.0014$$

The equivalent parallel capacitance is given by the equation

$$Cxp = \frac{C}{1 + D^2} \cdot \frac{1}{1 + DD_o} \qquad 24.$$

Where C is the capacitance reading of the bridge and D is the reading of the dissipation factor dial corrected as above. Do is given by the expression

$$Do = 0.026 \times \frac{f}{fo}$$

$$Do = 0.078 \text{ for this example}$$

$$\therefore (C\,xp)\ \text{Total} = \frac{457.2}{1 + (0.0687)^2} \cdot \frac{1}{1 + (0.0687 \times 0.078)}$$

$$= 454.4\ \mu\mu f.$$

Since the value of D for the leads is very small, the (Cxp) Leads value is the same as the C reading.

The residual or stray capacitance of the cell was determined by measuring the capacitance of the empty cell at different spacings and extrapolating to infinite thickness of the sample (air in this case) (15) (17)

The geometric capacitance of the condenser obtained from the slope of this line and was found to agree well with standard formulae for parallel plate condensers.

$$(Cxp)\ \text{sample} = (Cxp)\text{Total} - (Cxp)\text{Leads} - Co$$

$$= 454.4 - 156.1 - 18.0$$

$$= 280.3\ \mu\mu f. \qquad 25.$$

where Co is the stray capacitance of the cell.

The geometric capacitance is given by

$$Cg = \frac{2.825}{t''}\ \mu\mu f \qquad 26.$$

where t is the thickness of the sample or separation of the plates. The value 2.825 was determined from the slope of the calibration plot as mentioned previously.

$$Cg = \frac{2.825}{0.06159} = 45.87\ \mu\mu f.$$

the value of t being determined from the mean of eight readings as described in the experimental section.

$$\therefore\ \epsilon' = \frac{(Cxp)\ \text{sample}}{Cg} \qquad 27.$$

$$= \frac{280.3}{45.87} = 6.110$$

The value of the dissipation factor was calculated by equation 23

$$D.F. = \frac{[(D \times Cxp)\text{Total} - (D \times Cxp)\text{Leads}]}{(Cxp)\ \text{sample}}$$

$$= \frac{[(0.0687 \times 454.4) - (0.0014 \times 156.1)]}{280.3}$$

$$= 0.1102 \qquad 6.$$

$$\therefore \text{since D.F.} = \tan\delta = \frac{\epsilon''}{\epsilon'}$$

$$\text{then } \epsilon'' = \epsilon' \times \tan\delta = \epsilon' \times D.F.$$

$$= 6.110 \times 0.1102$$

$$= 0.6733$$

b Substitution Method

The following values are taken from the 122.6°C., 300 cycle data of polyvinyl formal where C and D denote the readings of the capacitance and dissipation factor dials respectively.

C Total = 413.6 μμf.

C Leads = 813.2 μμf.

C' (without leads or sample) = 968.6 μμf.

D Total = 1.75%

D Leads = 0.051%

$\Delta C = C' - C$ and

$\Delta D = D - D'$

The D values must be corrected as in the direct method by the factor $0.01 \frac{f}{fo}$.

Since the 100 cycle range was chosen, the correction factor will be again 0.03.

$\therefore$ (D Total - D Leads) = 0.03 (1.75 - 0.05)

= 0.0510

The equation for the equivalent parallel capacitance is given by

$$Cxp = \Delta C \times \frac{1 - (\Delta D)^2 \frac{C}{\Delta C}}{1 + (\Delta D)^2} \qquad 28.$$

when the total dissipation factor reading of the bridge is less than 10%, the correction factor is negligible and so

$$Cxp = \Delta C$$

$$\therefore \quad (Cxp)\ \text{sample} = (C' - C\ \text{Total}) - (C' - C\ \text{Leads}) - Co$$

$$= C\ \text{Leads} - C\ \text{Total} - Co \qquad 25.$$

$$= 813.2 - 413.6 - 18.0 = 381.6\ \mu\mu f.$$

For this sample

$$Cg = \frac{2.825}{0.04101} = 68.89\ \mu\mu f.$$

$$\therefore \quad \epsilon' = \frac{(Cxp)\ \text{sample}}{Cg} = \frac{381.6}{68.89} = 5.539$$

Using equation 21

$$D.F. = \frac{C'}{(Cxp)\ \text{sample}} \times (D\ \text{Total} - D\ \text{Leads})$$

$$= \frac{968.6}{381.6} \times 0.0510 = 0.1295$$

$$= \tan \delta$$

$$\therefore \epsilon'' = \epsilon' \times \tan \delta$$

$$= 5.559 \times 0.1295$$

$$= 0.7173$$

TABLE I

DIELECTRIC CONSTANTS AND LOSS FACTORS OF POLYVINYL FORMAL

Frequency kc.											
0.05			0.10			0.30			1.00		
t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''
23.9	3.221	0.0358	23.9	3.199	0.0339	23.9	3.178	0.0362	23.9	3.146	0.0447
41.8	3.270	0.0343	41.8	3.246	0.0318	41.8	3.227	0.0342	41.8	3.199	0.0406
62.4	3.294	0.0356	62.4	3.272	0.0334	62.4	3.254	0.0329	62.4	3.227	0.0219
83.9	3.343	0.0635	83.9	3.320	0.0465	83.9	3.298	0.0392	83.9	3.268	0.0399
91.9	3.358	0.0722	91.9	3.333	0.0570	91.9	3.307	0.0430	91.9	3.275	0.0413
101.2	3.445	0.1199	101.2	3.407	0.0719	101.2	3.372	0.0593	101.2	3.331	0.0506
105.8	3.662	0.2186	105.8	3.600	0.1577	105.8	3.529	0.1108	105.8	3.458	0.0871
111.3	4.287	0.5470	111.3	4.091	0.4304	111.3	3.876	0.2957	111.3	3.684	0.2081
117.0	5.477	0.8626	117.0	5.124	0.7701	117.1	4.654	0.6283	117.1	4.197	0.4638
122.4	6.172	0.6981	122.4	5.954	0.6776	122.6	5.539	0.7173	122.6	4.922	0.6886
128.1	6.255	0.7575	128.1	6.155	0.4062	128.3	5.965	0.4933	128.4	5.577	0.5973
133.3	6.285	1.3701	133.3	6.192	0.7944	133.6	6.014	0.4426	133.6	5.793	0.3904
139.7	6.303	2.5918	139.7	6.195	1.4106	139.3	6.063	0.6202	139.3	5.844	0.3752

TABLE I (Continued)

DIELECTRIC CONSTANTS AND LOSS FACTORS OF POLYVINYL FORMAL

Frequency kc.											
3.0			10.0			30.0			100.0		
t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''
23.9	3.121	0.0534	23.9	3.079	0.0813	23.9	3.038	0.1379	23.9	2.931	0.2685
41.8	3.176	0.0489	41.8	3.140	0.0722	41.8	3.106	0.1239	41.8	2.996	0.2571
62.4	3.205	0.0442	62.4	3.173	0.0647	62.4	3.146	0.1114	62.4	3.051	0.2459
83.9	3.247	0.0442	83.9	3.212	0.0620	83.9	3.188	0.1058	83.9	3.108	0.2319
91.9	3.252	0.0429	91.9	3.223	0.0561	91.9	3.196	0.0882	91.9	3.141	0.1853
101.1	3.304	0.0489	101.1	3.269	0.0582	101.1	3.238	0.0839	101.1	3.189	0.1630
105.8	3.410	0.0764	105.8	3.352	0.0717	105.8	3.310	0.0738	105.8	3.256	0.0876
111.3	3.572	0.1611	111.3	3.461	0.1308	111.3	3.385	0.1168	111.3	3.297	0.1154
117.1	3.944	0.3467	117.1	3.706	0.2557	117.1	3.569	0.2024	117.1	3.418	0.1699
122.6	4.487	0.5730	122.6	4.059	0.4372	122.6	3.816	0.3358	122.6	3.593	0.2601
128.5	5.152	0.6703	128.5	4.574	0.6239	128.6	4.189	0.5140	128.6	3.813	0.3893
133.6	5.574	0.4933	133.6	5.110	0.6270	133.6	4.660	0.6366	133.6	4.134	0.5283
139.4	5.706	0.3521	139.7	5.432	0.4737	139.5	5.088	0.6029	139.5	4.526	0.6269

TABLE II

DIELECTRIC CONSTANTS AND LOSS FACTORS OF POLYVINYL ACETAL

Frequency kc.											
0.1			0.3			1.0			3.0		
t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''
39.9	2.963	0.0599	40.0	2.940	0.0532	40.0	2.912	0.0547	40.0	2.888	0.0595
50.5	3.000	0.0831	50.4	2.967	0.0638	50.4	2.939	0.0611	50.4	2.912	0.0644
59.5	3.091	0.0881	59.4	3.047	0.0725	59.4	3.000	0.0699	59.4	2.975	0.0669
70.4	3.362	0.2165	70.0	3.267	0.1578	70.0	3.163	0.1287	70.0	3.102	0.0993
79.5	4.205	0.6652	79.4	3.845	0.4979	79.4	3.536	0.3589	79.4	3.361	0.2571
85.1	5.252	0.9811	85.2	4.621	0.7717	85.2	4.044	0.6276	85.2	3.701	0.4589
88.7	5.733	0.8640	88.4	5.049	0.9144	88.4	4.349	0.7511	88.2	3.897	0.5674
95.1	6.414	0.4227	94.8	6.110	0.6733	95.1	5.424	0.8944	95.1	4.770	0.8834
102.0	6.527	0.1919	102.1	6.448	0.2682	102.1	6.213	0.5039	101.9	5.770	0.7945
109.4	6.555	0.1698	109.1	6.500	0.1398	109.1	6.431	0.2051	109.1	6.322	0.3774
117.6	6.440	0.3065	117.3	6.413	0.1475	117.3	6.375	0.1135	117.3	6.296	0.1530
122.3	6.363	0.4511	122.4	6.269	0.1937	122.4	6.194	0.0161	122.4	6.221	0.1120

TABLE II (Continued)

DIELECTRIC CONSTANTS AND LOSS FACTORS OF POLYVINYL ACETAL

Frequency kc.								
10.0			30.0			100.0		
t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''
40.0	2.844	0.0833	40.0	2.793	0.0972	40.0	2.721	0.0952
50.4	2.862	0.0861	50.4	2.812	0.0962	50.4	2.736	0.1094
59.4	2.926	0.0878	59.4	2.875	0.0966	59.4	2.808	0.1129
70.0	3.032	0.1007	70.0	2.976	0.0967	70.0	2.908	0.0980
79.4	3.207	0.1953	79.4	3.115	0.1579	79.4	3.017	0.1300
85.2	3.421	0.3305	85.2	3.263	0.2441	85.2	3.122	0.1858
88.4	3.540	0.4039	88.4	3.351	0.2932	88.4	3.163	0.2138
95.1	4.101	0.7144	95.1	3.713	0.5298	94.8	3.381	0.3682
102.1	4.953	0.9218	101.7	4.297	0.8087	102.1	3.739	0.5713
109.1	5.941	0.7088	109.1	5.308	0.9576	109.1	4.454	0.8752
117.3	6.246	0.3210	117.3	6.006	0.6192	117.3	5.310	0.9303
122.4	6.161	0.2027	122.4	6.052	0.3904	122.4	5.627	0.7422

TABLE III

DIELECTRIC CONSTANTS AND LOSS FACTORS OF POLYVINYL ISOBUTYRAL

Frequency kc.

0.05			0.10			0.30			1.0		
t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''
23.4	2.874	0.0328	23.4	2.852	0.0165	23.4	2.843	0.0171	23.4	2.829	0.0178
43.3	2.921	0.0275	43.3	2.900	0.0232	43.3	2.888	0.0165	43.3	2.874	0.0167
50.5	2.974	0.0404	50.5	2.949	0.0310	50.5	2.931	0.0229	50.5	2.911	0.0218
54.7	3.028	0.0587	54.7	3.000	0.0459	54.7	2.974	0.0342	54.7	2.949	0.0289
62.1	3.205	0.1253	62.1	3.157	0.1010	62.1	3.100	0.0732	62.1	3.047	0.0576
67.9	3.459	0.2373	67.9	3.362	0.1930	67.9	3.260	0.1454	67.9	3.159	0.1080
71.2	3.693	0.3166	71.2	3.565	0.2274	71.2	3.413	0.2072	71.2	3.272	0.1535
77.9	4.220	0.4237	77.9	4.045	0.3936	77.9	3.805	0.3428	77.9	3.545	0.2726
84.8	4.681	0.3235	84.8	4.545	0.3500	84.8	4.311	0.3889	84.9	3.972	0.3853
90.5	4.744	0.2035	90.5	4.677	0.2025	90.5	4.559	0.2672	90.7	4.301	0.3566
96.4	4.683	0.1892	96.5	4.640	0.1452	96.5	4.583	0.1512	96.7	4.459	0.2287
100.5	4.652	0.2163	100.8	4.602	0.1463	100.8	4.553	0.1138	101.1	4.478	0.1505
106.8	4.577	0.2613	106.6	4.530	0.1653	106.8	4.488	0.0969	106.6	4.439	0.0937
112.9	4.516	0.2908	112.9	4.469	0.1743	112.9	4.427	0.0881	112.9	4.386	0.0623
120.5	4.498	0.4619	120.9	4.443	0.2657	120.9	4.392	0.1195	120.5	4.344	0.0669

TABLE III (Continued)

DIELECTRIC CONSTANTS AND LOSS FACTORS OF POLYVINYL ISOBUTYRAL

Frequency kc.											
3.00			10.0			30.0			100.0		
t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''
23.4	2.819	0.0200	23.4	2.805	0.0250	23.4	2.789	0.0321	23.4	2.748	0.0305
43.3	2.866	0.0160	43.3	2.852	0.0185	43.3	2.843	0.0210	43.3	2.815	0.0304
50.5	2.900	0.0188	50.5	2.884	0.0205	50.5	2.872	0.0207	50.5	2.862	0.0209
54.7	2.933	0.0252	54.7	2.913	0.0248	54.7	2.900	0.0258	54.7	2.878	0.0210
62.1	3.016	0.0452	62.1	2.984	0.0394	62.1	2.963	0.0350	62.1	2.941	0.0306
67.9	3.100	0.0812	67.9	3.043	0.0636	67.9	3.010	0.0521	67.9	2.974	0.0401
71.2	3.189	0.1132	71.2	3.106	0.0857	71.2	3.063	0.0680	71.2	3.006	0.0535
78.1	3.392	0.2134	78.1	3.246	0.1565	78.1	3.161	0.1173	78.1	3.079	0.0782
84.9	3.726	0.3361	84.9	3.470	0.2651	84.9	3.325	0.1995	84.9	3.189	0.1448
90.7	4.043	0.3893	90.7	3.709	0.3509	90.7	3.494	0.2827	90.7	3.295	0.2096
96.7	4.287	0.3292	96.7	3.967	0.3796	96.7	3.705	0.3542	96.7	3.431	0.2820
101.2	4.384	0.2367	101.4	4.148	0.3414	101.4	3.890	0.3769	101.6	3.575	0.3357
106.6	4.398	0.1407	106.5	4.266	0.2538	106.3	4.049	0.3519	106.1	3.709	0.3720
112.9	4.366	0.0685	112.9	4.317	0.1235	112.9	4.238	0.2272	112.9	3.998	0.3450
120.5	4.325	0.0515	120.5	4.295	0.0661	120.5	4.266	0.1177	120.5	4.152	0.2346

TABLE IV

DIELECTRIC CONSTANTS AND LOSS FACTORS OF POLYVINYL HEXANAL

Frequency kc.											
0.05			0.10			0.30			1.0		
t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''
24.5	2.995	-----	24.5	2.987	0.0117	24.5	2.973	0.0178	24.5	2.904	0.0256
31.1	3.040	-----	31.1	3.026	0.0207	31.1	3.010	0.0236	31.1	2.937	0.0294
36.1	3.123	0.0390	36.1	3.105	0.0396	36.1	3.080	0.0397	36.1	2.997	0.0405
44.1	3.455	0.1734	44.1	3.384	0.1497	44.1	3.305	0.1150	44.1	3.171	0.0951
50.7	3.940	0.3696	50.7	3.789	0.3263	50.7	3.605	0.2491	50.7	3.378	0.1868
56.7	4.558	0.4613	56.7	4.343	0.4608	56.7	4.042	0.4054	56.7	3.683	0.3230
66.0	5.039	0.2288	66.0	4.950	0.2880	66.0	4.738	0.3994	66.0	4.301	0.4568
70.6	5.046	0.1539	70.6	5.001	0.1775	70.6	4.894	0.2701	70.6	4.574	0.4011
75.6	4.995	0.1464	75.6	4.961	0.1290	75.6	4.906	0.1639	75.6	4.712	0.2790
80.4	4.936	0.1614	80.4	4.906	0.1182	80.4	4.869	0.1139	80.4	4.740	0.1792
85.8	4.884	0.2095	85.8	4.855	0.1384	85.8	4.819	0.0920	85.8	4.718	0.1161

TABLE IV (Continued)

DIELECTRIC CONSTANTS AND LOSS FACTORS OF POLYVINYL HEXANAL

Frequency kc.											
3.0			10.0			30.0			100.0		
t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''	t°C	ϵ'	ϵ''
24.5	2.884	0.0300	24.5	2.856	0.0388	24.5	2.833	0.0459	24.5	2.805	0.0614
31.1	2.918	0.0309	31.1	2.888	0.0378	31.1	2.866	0.0430	31.1	2.837	0.0613
36.1	2.969	0.0401	36.1	2.933	0.0437	36.1	2.910	0.0471	36.1	2.876	0.0633
44.1	3.117	0.0804	44.1	3.054	0.0712	44.1	3.012	0.0660	44.1	2.971	0.0671
50.7	3.275	0.1448	50.7	3.175	0.1143	50.7	3.109	0.0948	50.7	3.054	0.0883
56.7	3.501	0.2472	56.7	3.329	0.1834	56.7	3.232	0.1435	56.7	3.143	0.1245
66.0	3.987	0.4234	66.0	3.655	0.3388	66.0	3.465	0.2574	66.0	3.291	0.1859
70.6	4.266	0.4509	70.6	3.870	0.4114	70.6	3.621	0.3273	70.6	3.398	0.2375
75.6	4.491	0.3988	75.6	4.100	0.4403	75.6	3.801	0.3945	75.6	3.513	0.3123
80.4	4.616	0.2963	80.4	4.305	0.4133	80.4	3.995	0.4279	80.4	3.643	0.3625
85.8	4.655	0.1918	85.8	4.463	0.3271	85.8	4.200	0.4166	85.8	3.829	0.4082
----	-----	------	92.5	4.525	0.2068	92.4	4.364	0.3360	92.3	4.011	0.4159

TABLE V

DIELECTRIC CONSTANTS AND LOSS FACTORS OF POLYVINYL 2-ETHYL HEXANAL

t	Frequency kc. 0.05		0.10		0.30		1.0	
°C	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
23.4	2.792	------	2.778	0.0094	2.761	0.0326	2.744	0.0277
32.4	2.959	------	2.932	0.0305	2.901	0.0444	2.867	0.0416
39.0	3.169	0.1043	3.114	0.0959	3.046	0.0914	2.976	0.0762
45.9	3.568	0.2494	3.449	0.2311	3.304	0.1939	3.164	0.1509
51.5	3.981	0.3292	3.819	0.3311	3.587	0.3053	3.357	0.2400
57.0	4.319	0.2751	4.174	0.3218	3.925	0.3615	3.618	0.3267
63.8	4.495	0.1483	4.418	0.1997	4.261	0.2983	3.973	0.3596
70.4	4.493	0.0899	4.457	0.1092	4.382	0.1731	4.208	0.2752
77.3	4.440	0.0799	4.411	0.0750	4.372	0.1019	4.290	0.1639
82.8	4.384	0.0978	4.353	0.0753	4.321	0.0761	4.268	0.1041

TABLE V (Continued)

DIELECTRIC CONSTANTS AND LOSS FACTORS OF POLYVINYL 2-ETHYL HEXANAL

t	Frequency kc. 3.0		10.0		30.0		100.0	
°C	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
23.4	2.729	0.0308	2.705	0.0357	2.686	0.0414	2.657	------
32.4	2.816	0.0408	2.807	0.0452	2.783	0.0479	2.742	------
39.0	2.935	0.0640	2.884	0.0629	2.850	0.0618	2.804	0.0070
45.9	3.082	0.1180	2.995	0.1000	2.944	0.0877	2.884	0.0234
51.5	3.222	0.1853	3.089	0.1452	3.014	0.1188	2.930	0.0539
57.0	3.420	0.2668	3.222	0.2062	3.114	0.1610	3.000	0.0867
63.8	3.725	0.3468	3.440	0.2903	3.273	0.2347	3.111	0.01406
70.4	3.998	0.3166	3.676	0.3466	3.457	0.2997	3.239	0.1921
77.3	4.176	0.2535	3.920	0.3448	3.674	0.3420	3.401	0.2462
82.8	4.208	0.1658	4.039	0.2718	3.826	0.3137	3.517	0.2648

DISCUSSION

DISCUSSION

The enthalpies of activation were determined from the slope of the log $\frac{1}{\tau}$ vs 1/T graph (Fig. V) and equation 12. (The log term containing the temperature did not change appreciably since the range of temperatures involved was fairly small.) Values of the free energy and entropy of activation were calculated from equations 14 and 15 respectively. The values are presented in Table VI together with extrapolated values for the relaxation time at 25° C. and values of the temperature (T_τ) for which τ = 1 second.

The Debye theory, which was originally derived for polar liquids, was extended to polar polymers due to the great similarity of the current carrying mechanism. However, the analogy to polar liquids has been carried further. Fuoss (20) has compared the softening point or transition temperature of polymers to an actual "internal melting". Below this temperature, the dipoles are "frozen" into position, as in a solidified polar liquid, displaying the properties of a three-dimensional solid. At the transition temperature, the polymer becomes a one-dimensional solid. Along the chain axis the molecules behave like those in a solid while perpendicular to the chain they behave like liquids. Superficially they are solids while with regards to molecular motion they are in many respects like liquids.

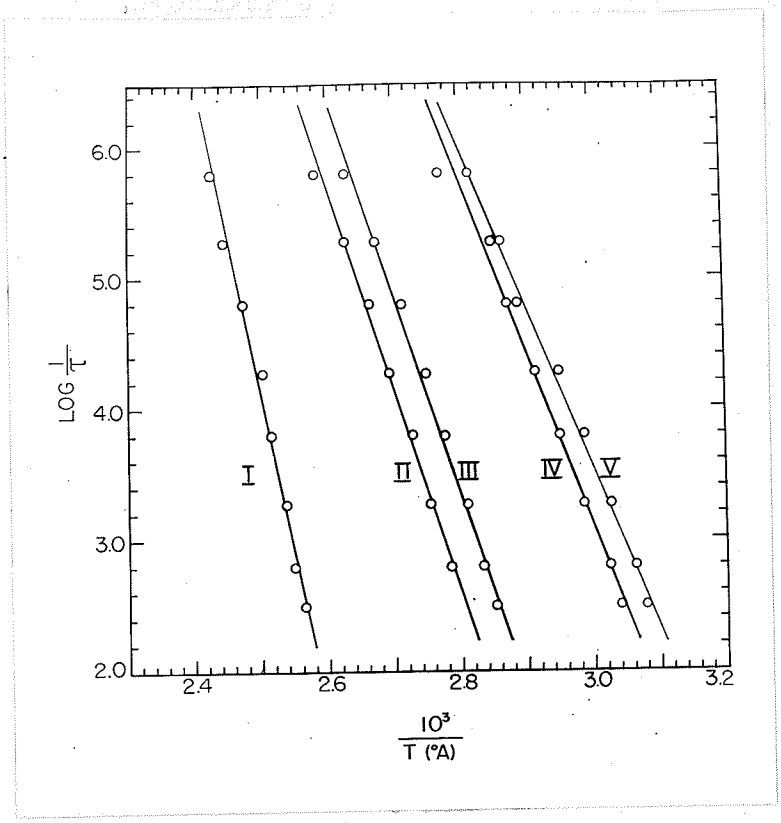


Fig. V Plot of Log $\frac{1}{\tau}$ vs. $\frac{1}{T}$ for;

I Polyvinyl Formal

II Polyvinyl Acetal

III Polyvinyl Isobutyral

IV Polyvinyl Hexanal

V Polyvinyl 2-Ethyl Hexanal

TABLE VI

VALUES OF ENTHALPIES, ENTROPIES, FREE ENERGIES, RELAXATION TIMES AND T_{χ} FOR:

Frequency kc.	Polyvinyl Formal			Polyvinyl Acetal			Polyvinyl Isobutyral			Polyvinyl Hexanal			Polyvinyl 2-Ethyl Hexanal		
	T °A	$\Delta S^{\ddagger}$ e.u.	$\Delta F^{\ddagger}$ Kcal.	T °A	$\Delta S^{\ddagger}$ e.u.	$\Delta F^{\ddagger}$ Kcal.	T °A	$\Delta S^{\ddagger}$ e.u.	$\Delta F^{\ddagger}$ Kcal.	T °A	$\Delta S^{\ddagger}$ e.u.	$\Delta F^{\ddagger}$ Kcal.	T °A	$\Delta S^{\ddagger}$ e.u.	$\Delta F^{\ddagger}$ Kcal.
0.05	389.9	237.2	18.70	-----	-----	-----	350.7	151.7	16.75	329.0	138.4	15.67	324.9	126.6	15.46
0.10	392.1	236.9	18.27	359.2	151.8	16.66	353.3	151.4	16.46	330.8	138.8	15.30	326.7	127.0	15.10
0.30	394.2	237.7	17.50	363.2	151.8	16.07	356.0	152.1	15.81	335.0	138.7	14.76	330.3	127.2	14.55
1.00	397.5	237.9	16.68	366.6	152.3	1534	360.3	152.1	15.13	339.0	138.9	14.13	334.9	127.3	13.95
3.00	400.2	238.1	15.94	371.3	152.1	14.73	363.7	152.5	14.48	343.2	138.9	13.56	339.0	127.4	13.39
10.00	404.2	237.8	15.13	375.2	152.5	13.99	368.7	152.3	13.80	348.2	138.7	12.93	346.4	126.2	12.86
30.00	408.4	237.0	14.40	380.7	151.9	13.37	374.2	151.7	13.19	355.2	137.4	12.42	349.2	127.1	12.20
100.00	412.2	236.8	13.55	387.2	151.1	12.68	380.5	150.9	12.51	362.2	136.4	11.81	355.2	126.7	11.57
$\Delta H^{\ddagger}$ Kcal.		111.2			71.19			69.94			61.22			56.58	
T_{χ} °C		100.6			63.6			58.1			36.4			31.0	
τ sec.(25°C)		3.0×10^{16}			1.0×10^{6}			1.3×10^{5}			4.0×10^{1}			6.7×10^{0}	

(T is the temperature (°A) at which the maxima occurs in the loss factor curve.)

At the transition temperature the polar side groups obtain enough kinetic energy to overdome the Van der Waal's forces holding them in place, and in this respect an "internal melting" takes place (31). Due to the nature of the polymer, the chains can rarely become disentangled and although the chains may have enough kinetic energy, a true melting cannot take place. Instead, the polymer becomes soft and exhibits a tendency to flow. This analogy has been borne out, to some extent, by density-temperature measurements (21). The temperature coefficient of density was found to be twice as great above the transition temperature as below. Fuoss (21) has also found a second maximum in the low temperature region which would tend to show that the polymer exists in two different states above and below the transition. This second maximum was found to disappear with increasing content of plasticizer (a plasticizer is a low molecular weight substance which when incorporated in the polymer may be thought of as forcing polymer chains apart and thus accomplishing the same effect as an increase in temperature). This second maximum was also quite noticeable (at high frequencies) in our polyvinyl formal sample (Fig. VII.), and to a lesser extent in our polyvinyl acetal sample (Fig. IX.).

Much work has been done by various investigators on plasticized polymers (6), (9), (21), (23). Plasticization reduces the interchain potential barriers to

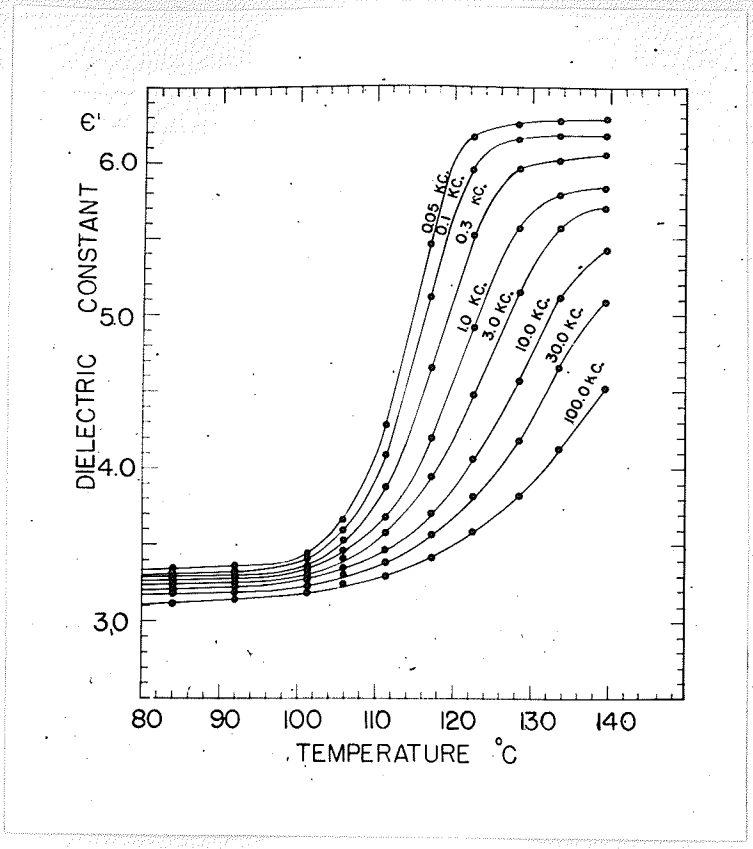


Fig. VI Dielectric Constants of Polyvinyl Formal

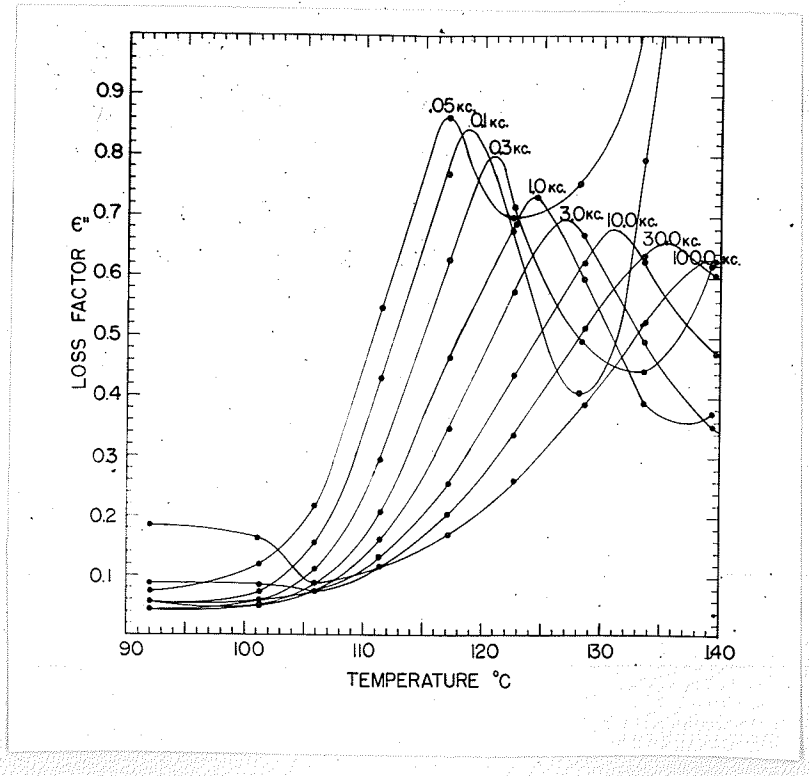


Fig. VII Loss Factors of Polyvinyl Formal

rotation. This facilitates the uncoiling of chains in elastic deformation, lowering the time of relaxation at a given temperature with increasing plasticizer content (1). In this investigation the same effect has been produced by introducing alkyl groups of increasing size (from the formal to the 2-ethyl hexanal) on to the polar side group. This can be considered as "internal plasticization". As can be seen from Table VI, the relaxation on times decrease from the formal to the 2-ethyl hexanal polymers, as well as the transition temperatures obtained.

Since this field of research is comparatively new, the method of calculating enthalpies, free energies and entropies of activation sometimes varies from one author to the other. The method of Kauzmann (27) has been employed in this work and Frank (13) agrees that this is the most reliable.

From the results of the plasticized systems of Fuoss (21) and Davies, Miller and Busse (6), a decrease in the enthalpy of activation and also the entropies of activation was observed with increasing amount of plasticizer. The values shown on Table VI, to which may be added the values for polyvinyl butyral (15) (i.e. $\Delta H^{\ddagger}$ = 65.2 Kcal., $\Delta S^{\ddagger}$ = 139 e.u., τ = 10^4 sec., Tx = 56°C) also tend to bear out the similarity between "externally" plasticized systems (ones to which plasticizers have been added) and "internally" plasticized systems (in which the "plasticizer"

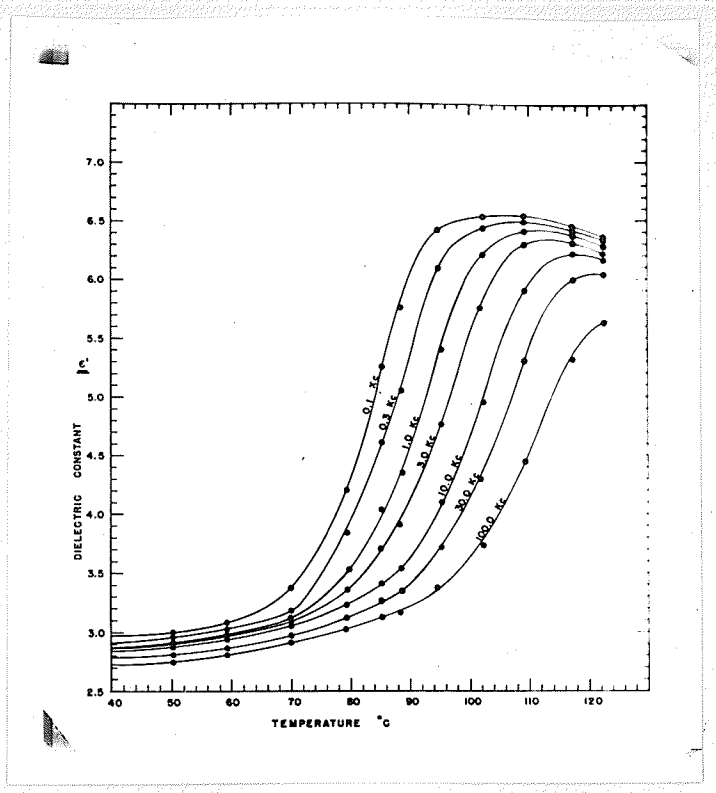


Fig. VIII Dielectric Constants of Polyvinyl Acetal

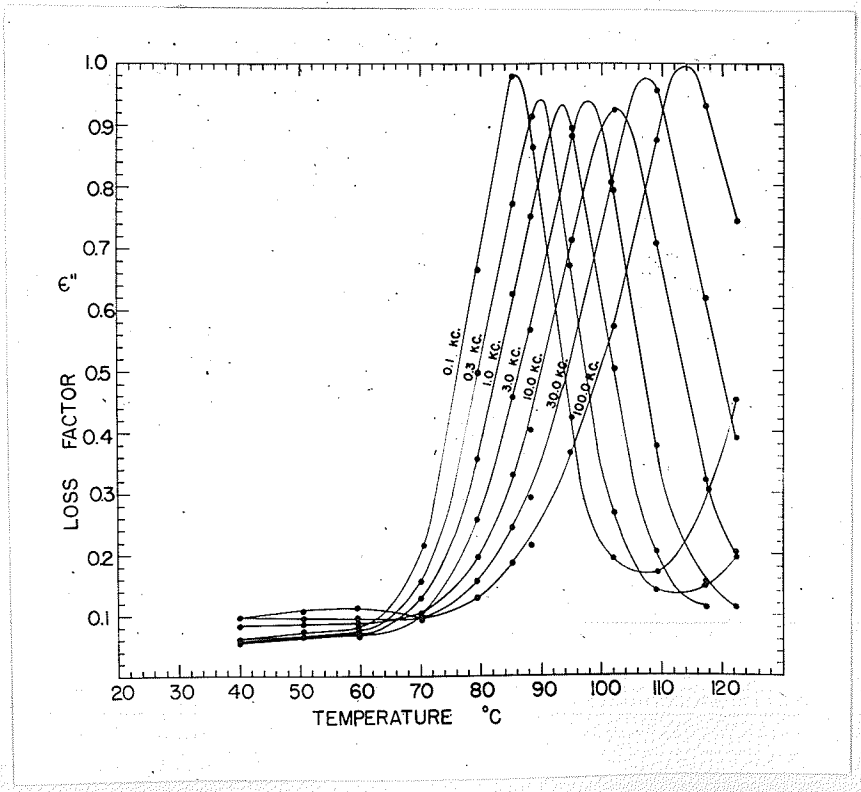


Fig. IX Loss Factors of Polyvinyl Acetal

is chemically combined with the polymer). In most cases, the greatest decrease in these "externally" plasticized systems occurs with the addition of the first few per cent of plasticizer (23a) (6). From Table VI, the greatest decrease occurs in passing from the polyvinyl formal to the polyvinyl acetal, which would correspond to the addition of a few per cent of plasticizer (polyvinyl acetal is the least plasticized sample that is possible in this series if we consider the polyvinyl formal as the unplasticized sample). With further plasticization, the change is not so pronounced.

On comparison of the work of Fuoss (21) and Davies, Miller and Busse (6) on polyvinyl chloride, it was found that, although the two samples of polyvinyl chloride were of different molecular weights, the energies of activation were nearly identical. Davies, Miller and Busse concluded that due to the hindrance of rotation of individual dipoles of the chain (because of the "kinky nature" of the chain) there was a rotation of whole segments of the chain. Since the activation energy seemed to be independent of molecular weight, then the size of the rotating units must be less than the length of the chains. Flory (12) found from a study of linear polyesters, that the energy of activation for viscous flow was independent of the molecular weight over the range he investigated (1,000 - 7,000). This would also seem to indicate a segmented flow of the polymers, and since the time

of relaxation and viscosity appear to be related in some manner, this would add support to the theory of segmented rotation in polar polymers (28) subjected to electric fields.

Another factor to consider is the entropy of activation. It would seem, from their frequent occurrence in the literature, that the high positive values are characteristic of linear polymers. Hence they would seem to be an essential feature in determining the mechanism for these types of materials.

If each monomer unit is able to rearrange itself in r alternative configurations when in the excited state, the total number of configurations available to the n monomer units is r^n and the entropy of activation is $R\ln(r^n)$ according to Kauzmann's definition, where R is the gas constant (9) (27)

$$\Delta S^{\ddagger} = Rn \ln r$$

An increase in the entropy of 50 e.u. implies an increase in the number of configurations available to a molecule or molecules in an activated complex of $\exp(50/2) = 10^{11}$. In order that there can be a positive entropy of activation, some more or less rigid structure containing the dipole must become free to move. For the large values of entropy encountered, the activation must involve more than a single dipole and its immediate attachments, another indication of segmental rotation.

Kauzmann compares the process in which a dipole suffers

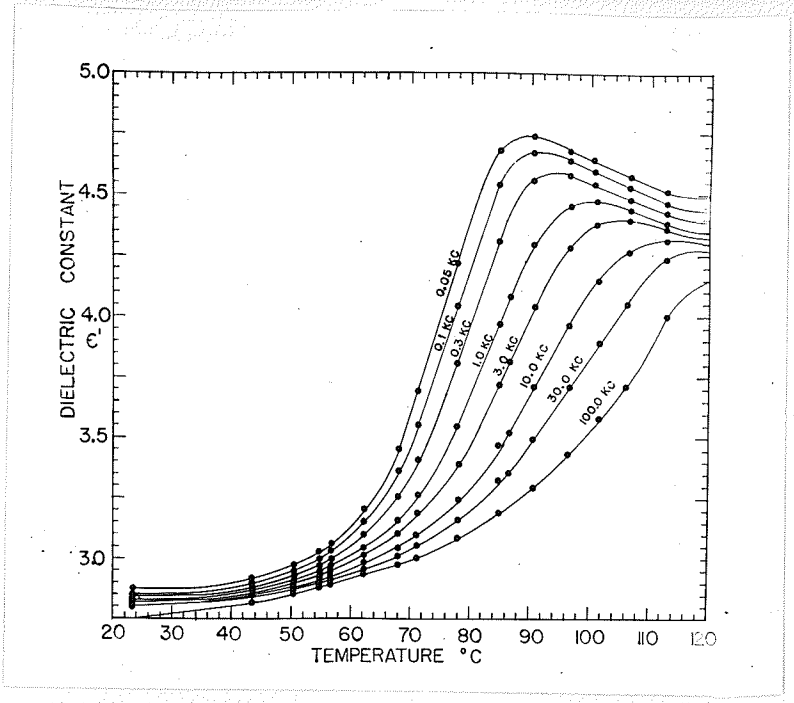


Fig. X Dielectric Constants of Polyvinyl Isobutyral

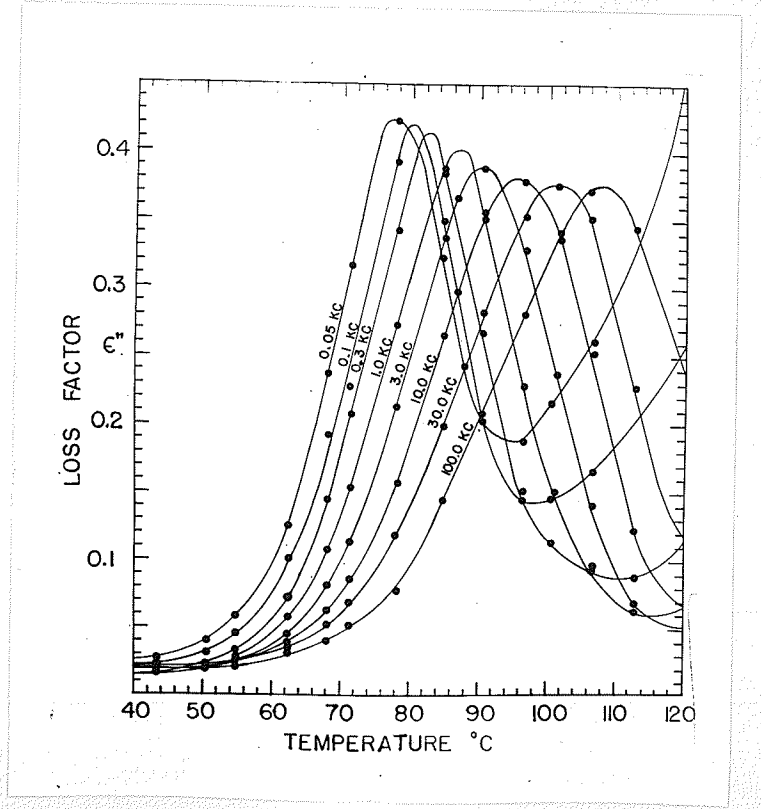


Fig. XI Loss Factors of Polyvinyl Isobutyral

a displacement to a vaporization process, since the activated polar group may be compared to a gas so far as forces tending to cause intermolecular orientation are concerned. This can also be seen by a comparison of the enthalpies of activation for the relaxation process and viscous flow. The latter are usually in the order of 2-3 Kcal. and rarely exceed 10 Kcal. In terms of the physical picture, this means that a molecule undergoing dipole rotation must break more bonds to its neighbor than a flowing molecule (33).

From Trouton's rule, Kauzmann derives a value of 10 e.u. for the entropy change involved in the "vaporization" of a polar unit witha molecular weight of 100. Thus, by dividing the entropies of activation by this value, the approximate number of monomer units rotating in a segment can be calculated.

The values of n calculated by this method for the series of polymers studied are as follows:

Polyvinyl Formal	25
Polyvinyl Acetal	15
Polyvinyl Isobutyral . . .	15
Polyvinyl Butyral (15) . .	14
Polyvinyl Hexanal.	14
Polyvinyl 2-Ethyl Hexanal.	13

Since plasticization is a solution effect (dilution of the polymer), it might be expected that at infinite dilution of the dipoles themselves the value of n would approach unity. This effect could be studied in dilute

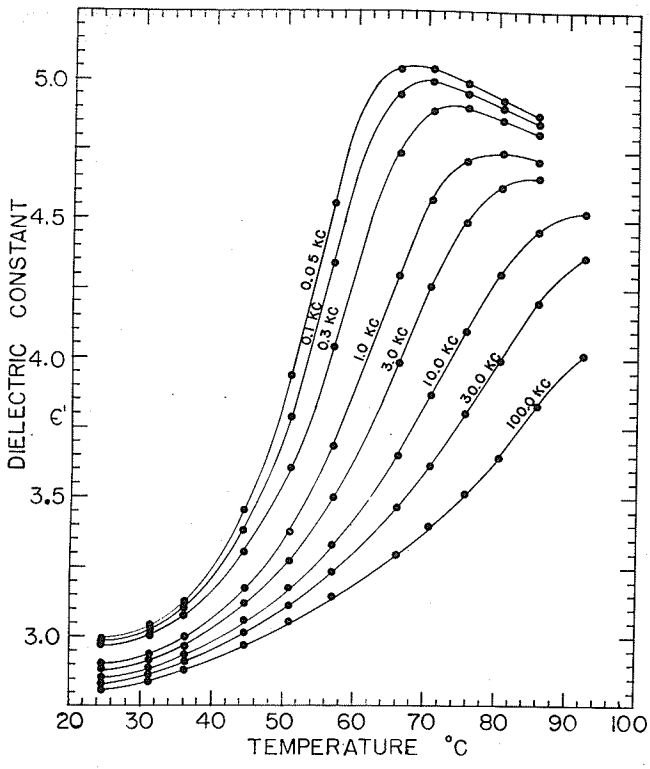


Fig. XII Dielectric Constants of Polyvinyl Hexanal

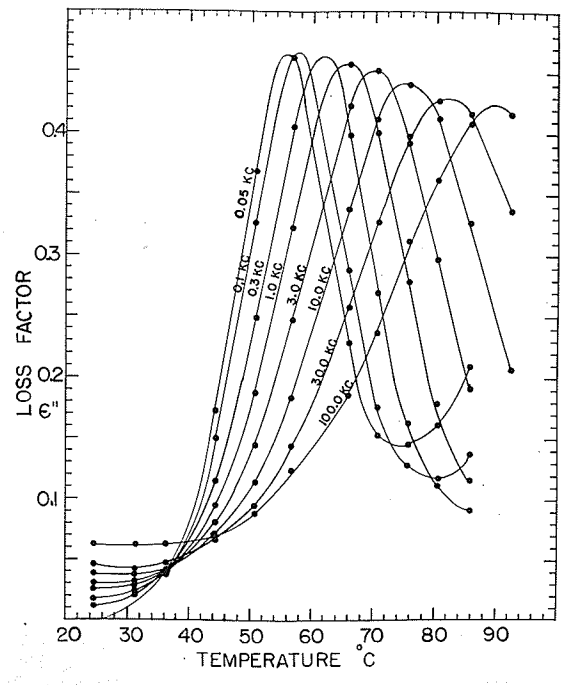


Fig. XIII Loss Factors of Polyvinyl Hexanal

solutions of polymers in which the dipoles are separated by a relatively long carbon-carbon chain.

Since the polymer molecules are entangled in a completely random fashion, it may be expected that all molecules will not be influenced to exactly the same extent by an alternating field. Because of this, a spread of relaxation times has been postulated and various mathematical distributions have been derived (22) (30) (27) (37, 38). As the investigation of this effect is not the primary object of this thesis a qualitative, rather than a mathematical discussion of the effects produced should suffice.

It can be seen from equation 8 that the maximum value of ϵ'' should $= \frac{1}{2}(\epsilon_o - \epsilon_\infty)$. As can be seen from Figs. VII, IX, XI, XIII and XV, the values are approximately 50% of the theoretical value. On comparison with the values obtained from other polymers, this value is quite high, and so the distribution of relaxation times is a relatively minor effect in this series of polymers.

The distribution of relaxation times is also responsible for the broadening of the bell-shaped loss factor curves at high frequencies, or high plasticizer content.

Since the "plasticizer" in our case is attached directly to the polar group, it is evident that due to the increased bulkiness of this non-polar side group, the loss factors and dielectric constants are lower than for a very highly polar

side group as in the case of polyvinyl acetate (20) where ϵ' reaches a value of 8.5 and ϵ'' a value of 1.8 at 60 cycles. There is an even greater effect if the chloroacetate polymer is used (23b). Since the longer hydrocarbon substituents are quite bulky, it might be expected that there will be a larger amount of tangling than in the case of the shorter side groups with the subsequent increase in the spread of relaxation times. Hence much broader loss factor curves and a more gradual increase in the dielectric constant curves is obtained for the 2-ethyl hexanal than for the acetal or formal. Figure XVI shows a comparison of the loss factor and dielectric constant curves for the various polymers at 1 kc.

There is another effect which is not predicted by theory. The loss factor curves after reaching their major maximum, approach a minimum and then increase very steeply. According to the Debye theory, the bell-shaped curves should be symmetrical about the bisector of the apex. This increase has been partially accounted for on the basis of ionic conductance, which can increase with the decrease in viscosity at these relatively high temperatures. Davies, Miller and Busse added stabilizers to prevent or retard the evolution of ionic materials or to neutralize them. Fuoss (19) studied the extent of pyrolysis with time and temperature of heating in an effort to account for this increase. However after correcting for d.c. conductance, the loss factor

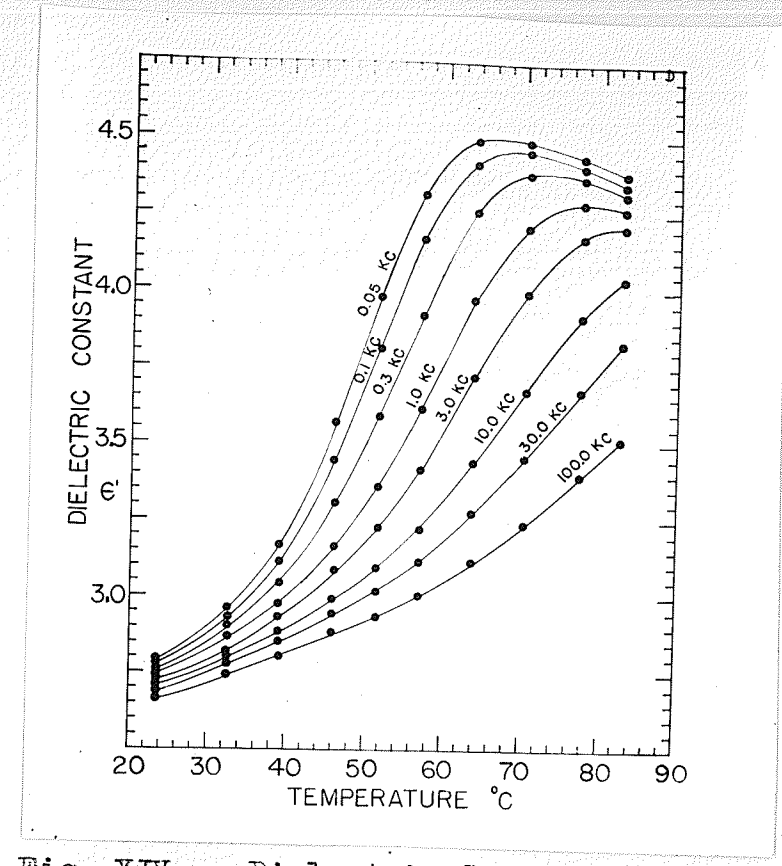


Fig. XIV Dielectric Constants of Polyvinyl 2-Ethyl Hexanal

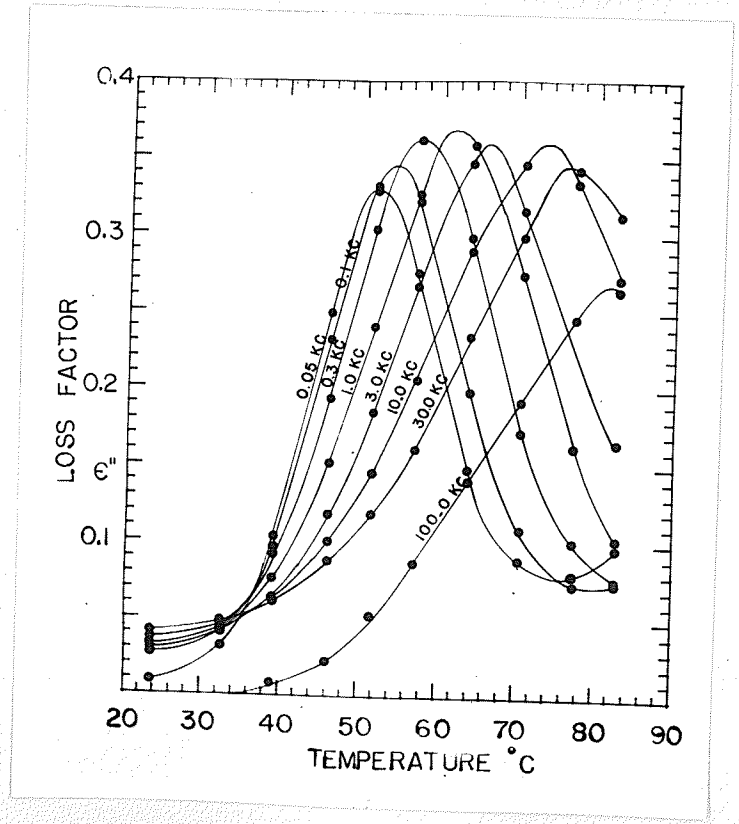


Fig. XV Loss Factors of Polyvinyl 2-Ethyl Hexanal

curves were still not symmetrical. This might be explainable on the basis of actual translational motion of the macromolecules since at these high temperatures there is a greater tendency to flow. In other words, the dipoles, which were restricted to rotation about the carbon-carbon bonds, might be able to drag the polymer chain itself, producing an effect similar to that of ionic conductance.

The effect of molecular weight on transition temperatures and relaxation time should be discussed. Very little literature on this particular subject, in connection with transition temperatures as determined by the dielectric method, has been presented. Kirkwood and Fuoss (30) have predicted that a plot of log fmax (where fmax is the frequency of maximum absorption) against log M (where M is the molecular weight) is linear and found some correlation although the evidence (16) is not conclusive. Frith and Tuckett (14) have stated that $\underline{\tau}$ varies linearly with chain length. Other investigations (3) by mechanical methods have shown that the brittle point (the temperature at which the polymer breaks without prelininary stretching) is linear with the reciprocal of the square root of molecular weight ($1/\sqrt{M}$). Tuckett (14) has found a similar relation from the study of brittle points.

The qualitative results presented do not seem to be affected by this difference. The similar values of $\Delta S^{\ddagger}$,

$\Delta H^{\ddagger}$, Tx and τ for polyvinyl acetal and polyvinyl isobutyral are partially due to the large percentage of acetate groups present in the acetal polymer. The dispersion range for polyvinyl acetate is much lower (23b) and the presence of acetate would tend to shift the dispersion range to lower temperatures.

The acetate groups would begin to rotate at a lower temperature than the acetal groups and it would be expected (from the concept of segmented rotation) that the oscillating acetate groups would assist in the rotation of the acetal groups, bringing about a lower transition temperature.

One of the main objectives in this research was to correlate the transition temperatures found by mechanical methods with those determined by electrical methods. For this purpose the temperature at which $\log \frac{1}{\tau} = 0$ is chosen. Since the mechanical methods used depend on a test which lasts for approximately one second (the relaxation time of the polymer will then be about one second), the extrapolation is made to a relaxation time of one second. In Table VII, the values of Tx, Tm (a second order transition at which rapid change of the elastic modulus occurs with increasing temperature (3)) and Ts, the softening temperature at which the elastic modulus has a value of 10,000 pounds per square inch. Tm and Ts are the values given by Fitzhugh and Crozier (11) for the same samples used in this work.

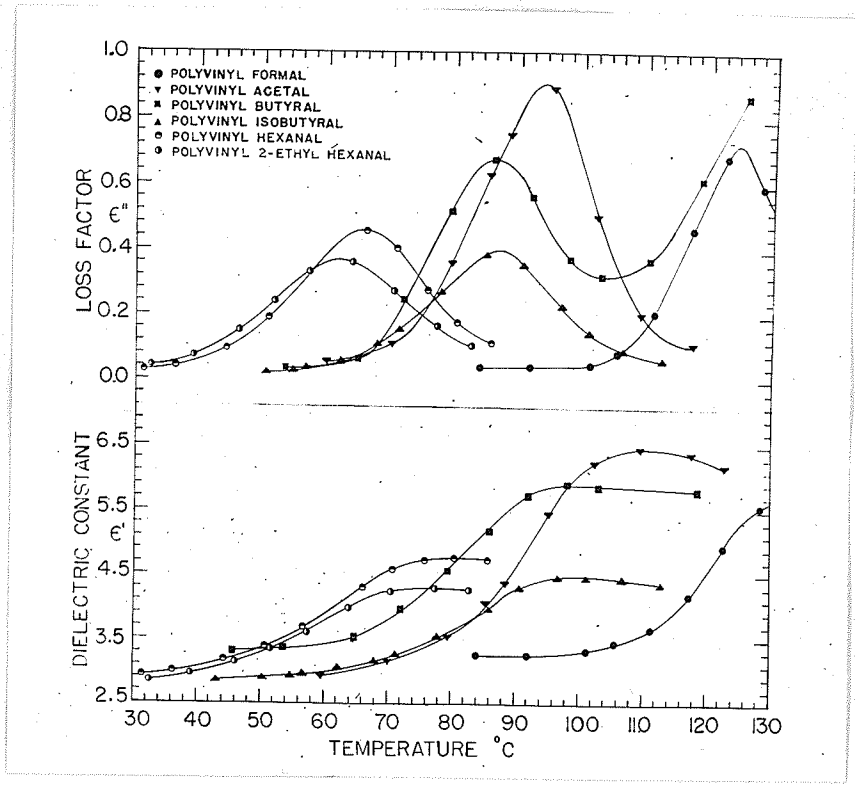


Fig. XVI Loss Factors (top) and Dielectric Constants (bottom) at 1 kc. for the series of Polymers studied.

TABLE VII

Comparison of Values of Transition Temperatures by Electrical and Mechanical Methods

	Tx °C	Tm °C	Ts °C
Polyvinyl Isobutyral. . . .	58.1	--	56
Polyvinyl Hexanal	36.4	39	39
Polyvinyl 2-Ethyl Hexanal .	31.0	35	35

These results are in excellent agreement, indeed, better than those which have appeared in the literature to date (cf. Frith and Tuckett (14) published in 1951). These values are inclined to be slightly low due to the nature of the extrapolated curve (Fig. V.) which shows a tendency to be concave downwards (i.e. the intercept at $\log \frac{1}{\tau} = 0$ strikes the 1/T axis at a higher value than if the concavity were taken into account).

From this evidence, it may be said that the dielectric method could be employed with success in the characterization of polymers.

SUMMARY

SUMMARY

The dielectric properties of a series of polyvinyl acetals have been studied and the results are in qualitative agreement with the Debye Theory of Dielectrics. The effect referred to as "internal plasticization" has been compared to plasticization in the usual sense and the analogy was found to hold. The data were discussed from the point of view of the Absolute Reaction Rate Theory, and the concept of segmented rotation about carbon-carbon bonds followed from this treatment. Also mentioned were the effect of the distribution of relaxation times and molecular weight on the values of the transition temperature. These were found to be of minor importance relative to the phenomenon of "internal plasticization". Of major importance was the close agreement between the extrapolated transition temperatures, (at which $\omega\tau = 1$), and mechanical softening points, Ts or Tm., found for identical samples of polymers.

In conclusion it might be said that the study of the electrical properties of polymers would give an insight into the basic mechanisms governing the behaviour of macromolecules.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. ALEXANDROV, A. P., and Lazurkin, IU. S., Acta Physicochim, U.R.S.S. 12, 647. (1940)

2. BAWN, C. E. H., Chemistry of High Polymers, Interscience (1948)

3. BOYER, R. F., and Spencer, R. S., Advances in Colloid Science, Vol. II, Interscience (1946)

4. COLE, R., and Cole, K., J. Chem. Phys. 9, 341. (1941)

5. CURTIS, H. L., McPherson, A. T., and Scott, A. H., National Bur. Standards Sci. Paper No. 560, 22, 398 (1927)

6. DAVIES, J. M. Miller, R. F., and Busse, W. F., J. Am. Chem. Soc. 63, 361 (1941)

7. DEBYE, P., Polar Molecules, Chemical Catalogue Co. (1929)

8. DEBYE, P., Physik. Zeits., 13, 97 (1912)

9. DYSON, A., J. Pol. Sc. 7, 133 (1951)

10. EYRING, H., J. Chem. Phys. 4, 283 (1936)

11. FITZHUGH, A. F., and Crozier, R. N., J. Pol. Sc. 8, 225 (1952)

12. FLORY, P. J., J. Am. Chem. Soc., 62, 1057 (1940)

13. FRANK, F. C., Trans. Faraday Soc., 32, 1634 (1936)

14. FRITH, E. M. and Tuckett, R. F., Linear Polymers Longmans (1951)

15. FUNT, B. L., Can. J. Res., 30, 84 (1952)

16. FUOSS, R. M., The Chemistry of Large Molecules, Interscience New York (1943)

17. FUOSS, R. M., J. Am. Chem. Soc., 59, 1703 (1937)

18. FUOSS, R. M. J. Am. Chem. Soc., 60, 451 (1938)

19. FUOSS, R. M., J. Am. Chem. Soc., 61, 2329 (1939)

20. FUOSS, R. M., J. Am. Chem. Soc., 63, 369 (1941)

21. FUOSS, R. M., J. Am. Chem. Soc., 63, 378 (1941)

22. FUOSS, R. M., and Kirkwood, J., J. Am. Chem. Soc., 63, 385 (1941)

23. FUOSS, R. M., J. Am. Chem. Soc., 63, 2401 (1941)

(23a) FUOSS, R. M., J. Am. Chem. Soc., 63, 2410 (1941)

(23b) FUOSS, R. M., J. Am. Chem. Soc., 63, 2832 (1941)

24. GENERAL RADIO COMPANY, Catalogue L (1948)

25. GENERAL RADIO COMPANY, Form 681-B

26. GLASSTONE, S., Laidler, K. J., and Eyring, H., The Theory of Absolute Reaction Rates, McGraw-Hill, New York (1939)

27. KAUZMANN, W., Rev. Mol-Phys., 14, 12 (1942)

28. KAUZMANN, W., and Eyring, H., J. Am. Chem. Soc., 62, 3113 (1940)

29. KHITCHIN, D. W., Ind. Eng. Chem., 24, 549 (1932)

30. KIRKWOOD, J., and Fuoss, R. M., J. Chem. Phys., 9, 329 (1941)

31. MACK, E. Jr., J. Phys. Chem., 41, 221 (1937)

32. MEAD, D. J., and Fuoss, R. M., J. Am. Chem. Soc., 63, 2832 (1941)

33. POWELL, R. E., and Eyring, H., Advances in Colloid Science, Interscience, New York (1942)

34. SCHOLLANACH, A., Trans. Faraday Soc., 42, 180 (1946)

35. SHILDKNECKT, C. E., "Vinyl and Related Polymers", Wiley, New York (1952)

36. TUCKETT, R. F., Trans. Faraday Soc., 40, 448 (1944)

37. WAGNER, K. W., Ann. d. Physik., 40, 817 (1913); Archiv. f. Electrotechnik, 3, 83 (1914)

38. YAGER, W. A., Physics 7, 434 (1936)