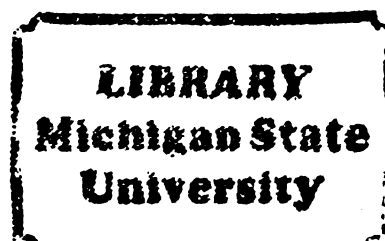


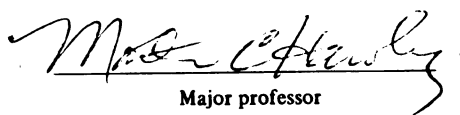
THESIS



This is to certify that the
thesis entitled
MICROWAVE HEATING OF POLAR LIQUIDS AND SOLIDS

presented by
Mark C. Finzel

has been accepted towards fulfillment
of the requirements for
M. S. degree in Chemical Engineering



Major professor

Martin Hawley

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MICROWAVE HEATING OF POLAR LIQUIDS AND SOLIDS

By

Mark Christopher Finzel

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemical Engineering

1985

DEDICATION

To all soldiers, Raiders, and spaceheads past,
present, and future, and to all symbiotic concepts
of man and nature.

"At one with the knowledge and magic of the source,
attuned to the majesty of music, we march as one
with the earth."

- Jon Anderson, 1974

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Abstract

Microwave Heating of Polar Liquids and Solids

By

Mark Christopher Finzel

A resonant microwave cavity was developed to couple microwave power to a series of dielectrics. The cavity operated in the TM_{012} mode so that the maximum amount of power possible could be coupled to the dielectric. Coupling efficiencies (percent input power absorbed) ranged from 90% for ethylene glycol to 18% for teflon. Power absorbed was found to depend on both the dielectric constant and the complex permittivity. A model based on ACT Theory and internal molecular rotation successfully predicts the dielectric absorption of hydroxide-containing liquids, particularly small glycols. The dielectric spectrum of Nylon 66 was also modeled using ACT Theory and parameters based on cooperative relaxation of dipoles in polymers. Additionally, a finite difference method was used to determine temperature distributions in a nylon rod. Both models for liquids and solids predict the change in coupling efficiency with time and temperature correctly.

INTRODUCTION:

It is well established that radio and microwave frequency radiation is absorbed by polar liquids and solids. Large amounts of dielectric data have been collected for a wide variety of materials.^[1,2,3,] This absorption of electromagnetic power by polar liquids and solids can be used to heat these materials. This is known as dielectric heating and is a method of affecting large increases in temperature in materials in a short period of time as anyone who has used a microwave oven for cooking purposes knows. The rapid heating possible using dielectric heating can be used for a variety of specialized applications. One such application is processing of composite materials. Composite materials are made of layers of ceramics, metals, fibers, and various polymers and have superior mechanical, chemical, and electrical resistance characteristics. The layers are joined together by adhesives (usually thermosetting resins such as epoxies). Since many thermosetting resins include polar groups they are candidates for dielectric heating. The work included herein is an exploratory investigation of dielectric heating in liquids and solids in order to develop a data base and a fundamental understanding of the absorption of microwave radiation by liquids and solids,

and to determine how much power can be coupled to various dielectrics.

First, a description of composite materials, thermo-setting resins, and microwave heating is given in order to show the advantage of the concept as it relates to composite processing. A summary of the important theoretical models for dielectric absorption is then given for both polar liquids and polymer systems. A description of the experimental system and measurements is then given, followed by a description of the modeling used to describe the fundamental factors influencing the experimental results. Finally, the experimental and modeling results are compared. Since this work was carried out in order to develop a data base for a proposal to the Defense Advanced Research Projects Agency (DARPA), suggestions for future work based on the enclosed information in this thesis are provided.

I. Composite Materials, Thermosetting Resins, and Microwave Dielectric Heating.

This discussion will focus on composite materials in military applications as well as the properties of the thermosetting resins used in the adhesive layer that are applicable to microwave heating.

A. Composite Materials

Composite materials are a broad classification of materials too extensive to be discussed in detail here. Generally speaking, they are composed of layers of materials including metals, fabrics, and ceramics which are joined together by an adhesive layer. These composite structures exhibit mechanical strength, temperature resistance, and chemical and electrical properties superior to those of the component materials.

One application of these materials is for ceramic composite armor.^[4] This type of personnel and vehicle armor has been in use since the end of World War II. It involves the use of a ceramic (alumina, boron carbide, and silicon carbide have been used) backed up by a fabric layer (often a glass-reinforced plastic). Adhesives used include epoxy and polyester resins. If the fabric back up layer does not provide adequate support, a projectile impacting on the ceramic surface will cause the opposite surface of the ceramic to fail. The backup must deflect in order to prevent high shear

stress. A notable current use of composite armor is the Chobham armor used in the latest tank used by the U. S. Army, the M-1 Abrams. The exact composition of Chobham armor is of course a secret. Composite armor is also used in personal body armor ("flak jackets") as well as underneath pilot seats in helicopters and aircraft for protection against ground fire.

Composites are also used in airframes of military aircraft due to their superior flexibility and lighter weight. Some of the fibre filaments used include boron and graphite fibres of various diameters, silicon carbide, alumina fibre, and even fiberglass. When used in conjunction with epoxy resins and aluminum honeycomb structures and titanium, lightweight airframes may be constructed. Parmley [5] provides several instances where composite structures are already in use, including the F-14 and F-15 fighters and the B-1 bomber. A great amount of the work in composites has occurred as a result of aerospace studies.

The above is by no means a complete summary of the uses of composite materials. References [4, 5, 6] include a wide variety of materials used and applications of those materials. In addition to the above, composites have been used in space vehicles, transportation equipment, pressure vessels, and boat and building construction.

B. Curing of Thermosetting Resins and Composite Processing

Thermosetting resins are materials which change irreversibly when heated from a fusible, soluble material to an infusible, insoluble material. Heating these resins causes crosslinking to occur within the material forming a stable, covalently-crosslinked network which is somewhat more resistant to chemical and physical change. Therefore, heating these materials causes a change in the chemical nature of the system by producing cross-linked networks. A brief discussion of some of these resins, their curing, and their use in composite processing follows.

The most common thermosetting resins commercially used are the phenolic resins. Initial monomers for production of these resins are formed by ortho- or para- condensation of phenol with formaldehyde. Subsequent crosslinking and polymerization of these materials also occur by condensation. Crosslinks are either methylene or ester bridges. These materials are notable for their thermal and electrical resistance. Fillers are often used to improve properties and reduce costs. Phenolic resins can withstand extremely high temperatures as they do not readily vaporize or melt. Instead phenolic resins carbonize forming a protective thermal barrier. In addition, they are used for laminating composites of wood (most plywood, in fact, is manufactured in this way), paper, glass, and others, and they are also used as bonding resins, varnishes, coatings, and adhesives, and as ion-exchange resins

for chromatographic separations.

Amino resins are formed by condensation between methylol compounds, which are formed by addition of formaldehyde to amino compounds such as urea and melamine (I). These resins are colorless and have superior tensile strength and hardness when compared to phenolic resins, but their heat, moisture and electrical resistance are lower. These resins can be heated by high frequency electric currents due to their high polarity. These resins are used to impregnate clothing to impart crease resistance, fire retardance, and stiffness control, and for laminating and other applications similar to phenols.

Epoxy resins are polyethers which contain epoxide groups and are formed by reaction of diphenylol (bisphenol A) propane and epichlorohydrin. While other compounds can replace bisphenol A, the resulting epoxides are much more expensive. Crosslinking (or curing) occurs by addition of many types of materials, including urea-formaldehyde and phenol-formaldehyde resins previously discussed. The mechanism of curing includes esterification of the secondary hydroxyl groups of the epoxy or of the epoxide group itself, or condensation of secondary hydroxyl groups. They can also be cured by using Lewis acids in cationic polymerization, which forms polyethers from the epoxide groups. Epoxy resins are primarily used in surface coating

applications, including highway surfacing and bridge building, and are also used in composite processing with glass-fiber reinforcing to produce articles with superior mechanical strength and high chemical and electrical resistance.

Unsaturated polyester resins include dibasic acids and glycols containing unsaturated carbon-carbon double bonds. Crosslinking occurs via radical chain polymerization involving these double bonds and a vinyl monomer, usually styrene, in the presence of a fibrous filler, usually glass. Curing is accomplished by using a radical-generating initiator, such as a peroxide. Depending upon the degree of unsaturation of the acid or glycol, the exothermicity of the cure and the stiffness of the product can be fixed to a controlled value. A large degree of unsaturation implies a high exothermicity and an extensively cross-linked rigid product. Applications include lamination and contact molding to produce reinforced plastics for use in boat hulls, autoparts, and for other uses. Epoxy resins are generally superior to unsaturated polyester resins in mechanical, chemical and electrical properties although they are more expensive. Other types of thermosetting resins include urethane foams, silicone polymers, alkyd resins, and several additional varieties. [7]

Curing of laminates or composites with these resins is a multi-stage process. First, the material to be laminated is impregnated with either a liquid or dissolved resin, at

which point the adhesive characteristics of the resin are used to assemble the sheets. Finally, the sheets are compressed and heated to affect the cure. One way of doing this has been to hold the sheets in place with an inflatable rubber mattress, which is filled with steam in order to provide both heat and pressure. It is proposed that microwave heating is an alternative method of providing heat input for thermosetting the impregnating resin. Following is a discussion on microwave heating mechanisms in epoxy systems.

C. Microwave Heating of Thermosetting Resins

The following discussion focuses on epoxy resins although the principles are generally consistent for systems of other thermosetting resins. Epoxides have been chosen as a basis for the discussion due to the large amount of current interest in the literature. First, the molecular structure of an epoxide resin is examined, and then the mechanism and heating at differing stages of curing is discussed. Thermosetting resins are similar to one another due to the large number of polar side chain groups at which condensation, esterification, and other cross-linkings occur.

Bearing in mind that relaxation occurs at polar side groups as well as over the length of the entire molecule, the following relaxation processes have been identified. Maxima in the loss tangent vs. temperature curve occur for

the $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}$ group, the epoxy group, supermolecular molecular structure reorientation and reorientation of associations of macromolecules. The $\text{CH}_2\text{CHOHCH}_2\text{O}$ group could be excited by rotation of the group about the chain axis or of the hydroxyl group itself. Systems that absorb in the microwave region generally tend to be highly polar and small in size. It is indeed fortunate that thermosetting resins contain large numbers of polar groups, and the fact that these groups are generally where the esterifications or condensations associated with crosslinking occur has led to investigations of microwave curing of epoxy systems. Gourdenne^[8,9] has investigated curing of a glass-filled epoxy system, and Williams^[10] has investigated curing of epoxy-impregnated pipe at 2450 MHz.

Gourdenne has also calculated thermal phenomena in microwave heating of both epoxies and polyesters and has calculated temperature vs time curves for these systems. Heating occurs slowly at first with no crosslinking as the activation energy for crosslinking has not been reached. Then, temperature increases rapidly as the resins undergo crosslinking since the condensation reaction is exothermic. The temperature increases until crosslinking is completed and a maximum equilibrium temperature is reached. Then, the temperature decreases slowly with heat being transferred to the system by microwave energy and to the surroundings by convection.

D. Desired Characteristics of Materials for Microwave Heating.

The most important characteristic is, of course, that the medium to be heated have a dipole moment, either locally (on the molecular chain) or for the entire molecule. The resins discussed do indeed have this property, ranging from phenolic resins containing hydroxide groups to epoxy resins containing epoxide groups, amino groups in amino resins, and others. Systems will not absorb in the microwave region without having a dipole moment.^[11]

A more subtle characteristic concerns the behavior of the dielectric loss with respect to temperature. As microwaves are absorbed the temperature of the dielectric increases. If it so happens that the dielectric loss of a material increases with increasing temperature, than such a system would be expected to exhibit an exponential increase in absorption with respect to time. This enables heating to be localized to an extremely narrow slot or interface without too much microwave power being absorbed by the surroundings. Variations of loss tangent with frequency and temperature are available in the literature for a variety of materials including resins, various fillers, and numerous other dielectrics.^[1,2,3]

The materials from which the composite is constructed would have to exhibit little dielectric loss in the microwave region or else they would interfere with local absorption by the resin to be crosslinked. While highly absorptive filler

materials would supply heating, energy transfer would occur with less efficiency. An advantage of microwave heating is the selective input of energy into the resin, and strongly absorbing fillers or composites removes this advantage.

E. Advantages of Microwave Heating.

Consequences of the dielectric loss increasing with temperature have been previously discussed. If the dielectric exhibits this property, heating at interfaces without too much dissipation to the surroundings can be accomplished. This is useful for fusing two sheets into one, either surface-to-surface (composite processing) or edge-to-edge (sealing). White^[12] has discussed sealing plastics in this manner, and has sealed seams up to 24 meters long of a polyvinyl fluoride film, while Williams^[10] has sealed epoxy-impregnated pipe at 2450 MHz. Composite processing with microwaves is a comparatively new area, although sealing applications have been in use for a longer time.

Microwaves are able to heat these systems extremely rapidly. White carries out a brief calculation of the thermal time constant of a typical polymer film, and estimates it to be 20 to 100 milliseconds. This short time constant enables heat to be concentrated in a small area without heat transfer to the surroundings if the heating time is less than that of the value of the time constant. Longer heating times will heat the area surrounding the interface.

The basic advantage of microwave heating, then, is the ability to be able to concentrate heating of polymers or composites on a very small area. In addition, heating is expected to be much more rapid due to the high frequency of the radiation.

II. Dipolar Relaxation in Unassociated Liquids

This discussion will focus on the basic elements of dipole relaxation as presented in the Debye Theory and the ACT Theory. While intermolecular interactions in liquids are less complicated than in solids, the basic principles presented here are common to all dielectric materials. Results for an "ideal" Debye response (ethylene glycol) are included.

A. Debye Theory for Relaxation in Polar Liquids

The first modeling effort toward the explanation for absorption of electromagnetic power by polar liquids and solids was that of Peter Debye, who sought an explanation for the observation by Drude (1897) that dielectric constant decreased with increasing frequency for a variety of substances, particularly those containing hydroxyl or amino groups.^[13] Debye postulated that it was the polarity of the molecules that caused this effect. Debye also noticed that maximum absorption occurs at the frequency $\omega = \frac{1}{\tau}$ whose τ is defined as the relaxation time. The relaxation time is an indication of the amount of time required for a collection of dipoles in an electric field to revert to a random orientation once the field is removed.

Debye sought to model the randomization of dipoles in

a liquid by considering the randomization mechanism as thermal Brownian motion of a rotating sphere (the molecule) in a viscous medium (the liquid). By determining the time dependency of the angular distribution function for the rotating sphere, the time constant for the decay was found to be

$$\tau = \frac{\xi}{2kT}$$

where ξ is the friction factor for the sphere, k is Boltzmann's constant, and T is the absolute temperature. Substituting the friction factor found by Stokes for a rotating sphere in a viscous medium.

$$\xi = 8\pi\eta a^3$$

where η is the viscosity and a^3 is the molecular volume, the relaxation time is found to be

$$\tau = \frac{4\pi\eta a^3}{kT}$$

A medium will have a short relaxation time at high temperatures, low viscosities (low intermolecular attraction) and small molecular size (or small dipole size).

Absorption can be described by first breaking up the dielectric constant into a real and complex part as follows:

$$\epsilon^* = \epsilon' - j\epsilon''$$

with ϵ' being the dielectric constant associated with electromagnetic conduction and ϵ'' (the complex part) governing the strength of the absorption.^[11]

The electric displacement can be written as

$$\vec{D} = \vec{E} + 4\pi \vec{P}$$

where $\vec{P}$ is the polarization per unit volume and is a function of the motion of the dipole moments of the system.

If a sinusoidal field ($\vec{E} = \vec{E}_0 \cos \omega t$) has persisted for a time, the displacement will also be oscillating at a frequency but at a phase angle ϕ behind the motion of E .

This can be expressed by writing

$$\vec{D} = \vec{D}_0 \cos (\omega t - \phi) = \vec{D}_1 \cos \omega t + \vec{D}_2 \sin \omega t$$

$$\vec{D}_1 = \vec{D}_0 \cos \phi, \vec{D}_2 = D_0 \sin \phi$$

Since it is also true that

$$\vec{D} = \epsilon_s \vec{E} \quad (\epsilon_s \text{ static zero-frequency dielectric constant})$$

the above can be used to define a pair of dielectric constants.

$$\vec{D}_1 = \epsilon'(\omega) \vec{E}_0 \text{ and } \vec{D}_2 = \epsilon''(\omega) \vec{E}_0$$

The ϵ' and ϵ'' are, therefore, functions of frequency.

Debye developed relationships to describe the frequency dependency and these equations are included in a subsequent section.

Absorption can be thought of as a function of how the dipoles respond to the oscillating electric field of the incident radiation. At frequencies $\omega \ll 1/\tau$, the motion of the dipoles is more rapid than the motion of the electric field and absorption will not occur. At $\omega = 1/\tau$ the oscillatory motion of the dipoles is of the same frequency as the electric field although the motions are not in phase with one another. The response of the dipoles lags behind the forcing electric field causing energy transfer

from the field to the system. Finally at high frequencies ($\omega \gg 1/\tau$), the dipoles can no longer respond to the field quickly enough and absorption does not occur.

The ratio of $\vec{D}_2$ to $\vec{D}_1$ is

$$\frac{D_2}{D_1} = \frac{D_o \sin \phi}{D_o \cos \phi} = \frac{E''(\omega) E_o}{E'(\omega) E_o} = \frac{\sin \phi}{\cos \phi} = \tan \phi = \frac{\epsilon''(\omega)}{\epsilon'(\omega)}$$

The ratio of the absorbing part to the non-absorbing part is often called the loss tangent of the system for a particular frequency and absorption is often referred to as dielectric loss. A high loss tangent gives high absorption. [11]

B. Activated Complex Theory.

The Debye equation for dielectric relaxation of a spherical molecule

$$\tau = \frac{4\pi^2 \eta}{k_B T} = \frac{3V\eta}{k_B T} \quad V = \text{molecular volume}$$

has been discussed previously. Since the relaxation time τ is defined as the time necessary for the dipole correlation function to decay to $1/e$ of its initial value, the inverse of the expression for τ could be interpreted as a first order rate constant for dipole randomization. [16]

$$\frac{1}{\tau} = k_{\text{relax}} = \frac{k_V T}{3V\eta}$$

Comparing to the expression for the rate constant given by

activated complex theory (ACT), the same dependence on $(k_B T)$ is noted. Additionally, the $(V\eta)$ term in the denominator can be interpreted as proportional to an activation energy. An increase in either term leads to a greater amount of friction exerted on the rotating species, leading to an increase in activation energy $\Delta G^\ddagger$

$$k_{\text{relax}} = \sigma \frac{k_B T}{h} e^{-\Delta G^\ddagger/RT}$$

$$k_{\text{relax}} = \sigma \frac{k_B T}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

$\Delta G^\ddagger$ = free energy change of activated complex

$\Delta S^\ddagger$ = entropy change of activated complex

$\Delta H^\ddagger$ = enthalpy increase of activated complex

σ = transmission coefficient (generally set equal to one due to lack of better information).

Reinverting, the following expression for τ is obtained with $\sigma = 1$.

$$\tau = \frac{h}{k_B T} e^{-\Delta S^\ddagger/R} e^{\Delta H^\ddagger/RT}$$

This is the equation which will be used to interpret the experimental results.

Debye's equation was the first to attempt to correlate macroscopically observed dielectric phenomena with the actual molecular motions associated with relaxation. These

motions are extremely difficult to characterize theoretically, and a large amount of work has been done in this area without a conclusive theory being developed. The idea that dipole relaxation can be described as a rate process is an old one, and the literature abounds with results fitted to the Arrhenius rate law, with τ^{-1} as the rate constant

$$\tau^{-1} = A \exp (-Q/RT)$$

and where Q is the activation energy for dipole reorientation.

Activated complex theory was developed to describe chemical reaction rates but was also applied by Eyring (1936) and Kauzmann (1942) [14,15] to viscous flow, ionic conduction and dielectric relaxation.

C. Debye Equations.

Once the relaxation time is estimated from the activation energy for a particular relaxation, the real and imaginary parts of the dielectric constant, ϵ' and ϵ'' , associated with conduction and absorption can be calculated using the famous Debye equations. [17]

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

ϵ_0 = static (zero frequency dielectric constant)

$$\epsilon'' = \frac{\epsilon_0 - \epsilon_{\infty} \omega \tau}{\omega^2 \tau^2}$$

ω = excitation frequency
(radians/sec)

ϵ_0 = static (zero-frequency)
(dielectric constant)

ϵ_∞ = infinite frequency dielectric constant (n_D^2) where n_D is the index of refraction.

For systems with more than one relaxation mechanism, the following equations can be used [17]:

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \sum_{i=1}^n C_i \frac{1}{1 + \omega^2 \tau_i^2}$$

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \sum_{i=1}^n C_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2}$$

The subscript i denotes a particular relaxation mechanism, and the constant C_i is the weighting factor for the i -th mechanism with τ_i the relaxation time associated with the i th dipole reorientation.

If a plot of ϵ' and ϵ'' with frequency ω at constant T conforms even approximately to the above equations, the dipole relaxation is referred to as a Debye Relaxation. A typical Debye relaxation for ethylene glycol is shown in Figure 1.^[18] Materials exhibiting this behavior are generally either small molecules or molecules containing small polar groups in the liquid state where intermolecular attractions are relatively low. Water, various glycols, small-chain organic alcohols and others show dielectric relaxations conforming to the Debye equations.^[23] Using ACT Theory, the ΔH^* was determined to be 3.9 kcal/mol.

Highly viscous liquids containing high degrees of molecular association or solids do not exhibit normal Debye relaxations.^[25] While there is still a peak in the ϵ'' curve, the plot of ϵ'' versus ω for these materials gives a much broader curve than that of a Debye Relaxation. Modeling of these systems is described in the following section.

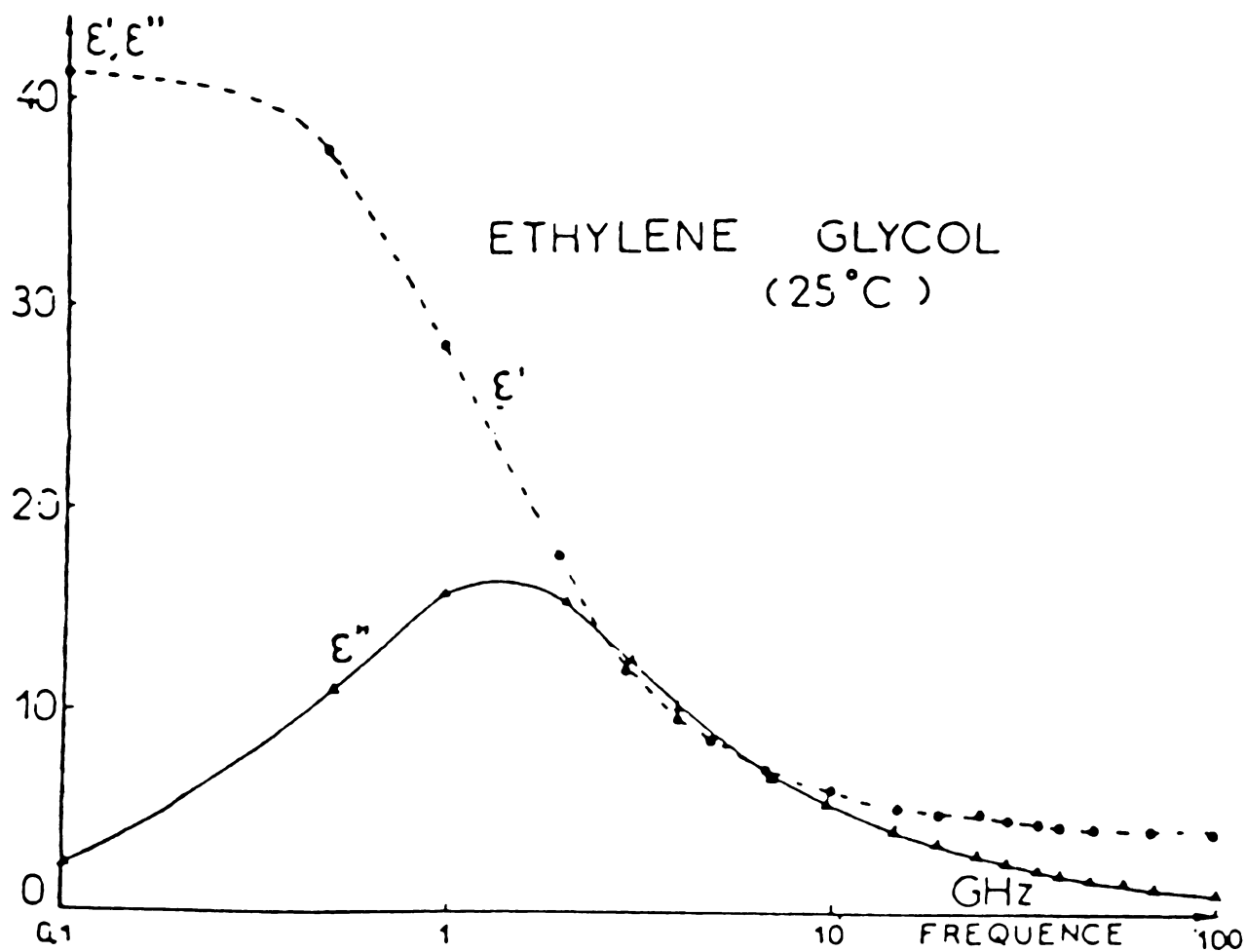


Figure 1. Example of Debye Relaxation. The dielectric spectrum of ethylene glycol shows a clear absorption peak around 1.5 GHz. (Ref. 18).

III. Dipolar Relaxation in Polymeric Systems

This section describes theories of dielectric relaxation in polymeric systems. After a brief discussion of dipole relaxation mechanisms in polymers, the concept of a dipole correlation function is introduced with several examples of these functions as developed by Williams and Watts.^[20] The idea of a "universal" high-frequency dielectric response as put forward by Jonscher and Ngai^[21,22] is discussed. Finally, relaxation mechanisms of a particular polymer, Nylon 66, are discussed in greater and more specific detail.

A. Dielectric Relaxation Processes in Polymers

Polymers often exhibit several distinct types of relaxation mechanisms.^[19] The first type of mechanism is called the α process in the literature. This mechanism randomizes the dipole moments through random Brownian motion of large segments of the polymer chain. These relaxations take place at low frequencies and therefore high relaxation times. The characteristic relaxation time is increased over that of the liquid state due to reduced molecular motion in the solid state.

Another type of mechanism occurs at higher frequency and is called the β process. This mechanism randomizes the dipole

moments by reorientation of individual dipoles in the chain, involving segmented motion of a small section of the polymer chain than the α relaxation. If absorption is caused by motion of dipolar groups in the chain backbone (polyvinyl chloride, then reorientation occurs by movement of the chain with respect to itself. On the other hand, dipolar side groups can reorientate essentially independently of the chain. A plot of the loss tangent versus temperature would yield a broad, flat distribution due to the fact that there are a number of different dipoles involved in a β -process each with its own characteristic absorption. These processes are higher frequency processes and as such might be expected to occur in or near the microwave region. As the relaxations occur at higher and higher frequencies, they are denoted γ , δ , etc. in order of increasing characteristic frequency. These relaxations involve successively smaller sections of the polymer chain in the relaxation.

B. Theory of Dielectric Relaxation in Polymers

The theory of dielectric (dipole) relaxation is based heavily on a quality known as a dipole correlation function the form of which for an i th dipole is given as^[20]

$$\Gamma_{ii}(t) = \frac{\langle \mu_i(0) \cdot \mu_i(t) \rangle}{\mu^2}$$

$\mu_i \rightarrow$ vector quantity
 $\mu \rightarrow$ magnitude squared, scalar

This function is meant to describe how the motion of the dipole moment and its orientation $\mu_i(t)$ at a given time $t=t$ is correlated to the initial orientation of the dipole $\mu_i(0)$ at $t=0$. Since all directions are considered to be equally probable initially

$$\langle \mu_i(0) \cdot \mu_i(t) \rangle = \mu_i(0) \cdot \langle \mu_i(t) \rangle.$$

The quantity $\langle \mu_i(t) \rangle$ is the average dipole orientation at time t given the dipole orientation $\mu_i(0)$ at $t=0$. The Fourier transform of the time derivative of the dipole correlation function $\Gamma_{ii}(t)$ is related to the complex permittivity in the following manner.

$$\frac{\epsilon^*(j\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = - \int_0^\infty \left[\frac{d\Gamma_{ii}(t)}{dt} \right] \exp(-j\omega t) dt \quad \begin{matrix} \epsilon_\infty = \epsilon(\infty) \\ \epsilon_0 = \epsilon(0) \end{matrix}$$

If the dipole motion is strongly correlated than $\Gamma_{ii}(t)$ is essentially constant in time and the complex permittivity is approximately zero, while if $\Gamma_{ii}(t)$ changes strongly with time then a strong absorption would be expected to occur.

Polymers exhibiting multiple relaxation processes would be expected to exhibit different decay regions at different times. Polymers exhibit dipole correlations along the polymer chain and as a result the correlation function contains cross terms involving correlations

between an i-th dipole and a j-th dipole in the same chain. For flexible chains only two or three nearby dipoles give terms which contribute significantly to the correlation function. The further apart the dipoles are separated, the less correlation between them. A suitable correlation function is given as

$$\Delta(t) = \frac{\langle \mu_i(0) \cdot \mu(t) \rangle + \sum_{j=1} \langle \mu_i(0) \cdot \mu_j(t) \rangle}{\langle \mu^2 \rangle}$$

which contains both an autocorrelation term ($\langle \mu_i(0) \cdot \mu_i(t) \rangle$) and cross terms. This function is used in the same manner as $\Gamma_{ii}(t)$ described earlier in order to find the complex permittivity.

The Debye Theory of relaxation in polar liquids assumes an exponential decay in time for the value of the correlation function.

$$\Gamma_{ii}(t) = \exp(-t/\tau)$$

Brownian motions in solids are different than in liquids due to the fact that there is more "cooperation" required in the reorientation of the dipole, and the decay process is therefore non-exponential. An empirical form uses β adjustable parameter.

$$\phi(t) = \exp [(-t/\tau_0)^\beta] \text{ with } 0 < \beta < 1$$

A correlation function for two decay processes, α and β , that occur in a polymer system has been given by Williams and Watts as

$$\Gamma_{ii}(t) = \phi_{\alpha}(t) \left[\sum_s P_s q_{\alpha s} + \sum_s P_s q_{\beta s} \phi_{\beta s}(t) \right]$$

$\phi_{\alpha}(t)$ - correlation function for α -process

$\phi_{\beta s}(t)$ - correlation time function for β -process in "s"

By considering a section of the chain as an environment "s", and assuming that dipoles in this environment can be relaxed by α - or β -processes only, the above function is constructed. The first term on the right hand side

$$\phi_{\alpha}(t) \sum_s P_s q_{\alpha s}$$

is the term dealing with relaxation of the environment "s" via the α relaxation with P_s being equal to the probability of being in the environment "s" and $q_{\alpha s}$ being equal to $(\langle \mu^2 \rangle_s / \mu^2)$ where $\langle \mu \rangle_s$ is the net dipole moment obtained for environment "s" by averaging over a time scale long compared with the local β -processes but short compared to the α -processes. The second term on the right.

$$\phi_{\alpha}(t) \sum_s P_s q_{\beta s} \phi_{\beta s}(t) \quad q_{\beta s} = 1 - q_{\alpha s}$$

contains both decay terms, while the first term only contains a decay term for the α -process. This model predicts two separate decay regions for low temperatures since $\phi_{\beta s}(t)$ decays much more quickly than $\phi_{\alpha}(t)$. The high frequency end is characterized by $q_{\beta s}$ and the range of values associated with this quantity will produce a broad β -peak.

At high temperatures the $\phi_{\alpha}(t)$ decays so quickly that the effects of the motions arising from the local dipole motions are dominated by Brownian relaxation. [20]

Discussion of the Williams-Watts model is included for the sake of completeness. Due to its greater simplicity, the model proposed by Jonscher and Ngai (next section) will be used to predict the complex permittivity ϵ'' as a function of frequency and temperature. In spite of the fact that the Williams-Watts model was not used to interpret the experimental results, a description of it is useful as it serves to show how fundamental processes contribute to dipolar relaxation.

C. The "Universal" Dielectric Response

It may be recalled that the Debye Equation for the absorptive part of the dielectric constant is given by

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

where all terms have been defined previously. If τ is held constant it can be seen that

$$\epsilon'' \propto \frac{1}{\omega} = \omega^{-1}$$

for a Debye relaxation at high frequencies.

While Debye relaxations are rare, it has been noted by Jonscher and Ngai [21,22] (1977, 1979) that the high-frequency behavior of ϵ'' for practically all materials

follows the form

$$\epsilon'' \propto \omega^{n-1} \text{ with } 0 < n < 1$$

The value of n depends on the type of interaction between the dipoles in the solid (or associated liquid). Extremely low values of n are characteristic of "ideal" Debye responses and are extremely rare. Values this low imply virtually no interaction between neighboring Dipoles. When $n \approx 0.3$ or thereabouts nearest neighbor interactions dominate. Typical examples include liquids, polymers and glasses above the glass transition temperature, liquid crystals, etc. As n increases ($n = 0.5 - 0.7$) many body interactions become more important as the material becomes more lattice-like. Finally, a value of n near unity indicates an extremely well-developed highly pure lattice.

It can be expected that at the high frequencies associated with microwave radiation, this model would be useful for describing how ϵ'' varies with frequency for a given relaxation time. Relaxations in Nylon 66 will now be discussed with the ideas of this section in mind.

D. Relaxations in Nylon 66

There are three distinct relaxation mechanisms in Nylon 66 polymer. The α -relaxation is associated, as usual, with the random Brownian motion of a large segment of the polymer chain. It does not occur below the glass transition

temperature ($T_g = 50^\circ \text{C}$). Data taken by Boyd^[24] (1959) show that n for this relaxation is equal to 0.676, implying a strong many-body interaction between neighboring chains.

The β -relaxation is associated with segmental motion of small elements of the polymer chain involving an amino group. It has a broad, flat peak over several decades of frequency. Data presented by von Hippel^[3] (1954) indicates that the value of n is 0.896 which is very large indicating strong interactions among these chain segments. Its maximum magnitude of ϵ'' is much smaller than that of the α -relaxation, and it possesses a shorter relaxation time.

Finally, the γ -relaxation occurs at the highest frequency and has the lowest peak magnitude of the three. Data taken by Starkweather^[26] (1981) indicates that it conforms approximately to a Debye relaxation with a narrow peak indicating that the relaxation occurs "independently" and probably only involves a very small part of the polymer chain.

Activation energies for these relaxations have been found in the literature and we presented below along with the peak values of ϵ'' for each particular relaxation. It seems that the more "difficult" the relaxation, the higher the peak value of ϵ'' .

Relaxations in Nylon 66.

Relaxation	ϵ'' max	$\Delta H^\ddagger$	Ref
α	2.15	46 kcal/mol	24
β	0.0880	15 kcal/mol	3, 26, 19
γ	0.0180	9 kcal/mol	19, 26

Depending on the water content, these values can change. The values above are given for dry Nylon 66. Increasing values of water content lower the value of $\Delta H^\ddagger$ and increase the value of ϵ'' max. Water molecules are thought to absorb at amide groups in the polymer, although the exact nature of this involvement is not certain. The exact amount of water present in the Nylon 66 used to obtain the experimental results in Section IV is not known. Since changes in $\Delta H^\ddagger$ and ϵ'' max for the relaxation are small with respect to water content in any case, the nylon rod was assumed to be dry for the purposes of the modeling in Section V.

Data taken by Boyd^[24] (1959) concerning the α -relaxation and the effect of frequency and temperature on ϵ'' are presented in Figure 2. It can be seen from this data how the α -relaxation has a much higher loss associated with it than do the β - or γ - relaxations, as well as how the α -relaxation "turns on" at temperatures above 50°C. Data by Starkweather and Barkley^[26] (1981) show the peak heights of ϵ'' for the β - and γ - relaxations. While their data is taken over a different temperature range, it can be assumed that ϵ'' max does not change appreciably since a "maximum" value of ϵ'' at 25°C is 0.0880 (von Hippel, 1954)^[3] which is similar to their data for ϵ'' at lower temperatures. Temperature dependency of the loss peaks for the various relaxations is included in Figure 3^[19]. It is obvious from this figure that at microwave frequencies (10^9 Sec^{-1}), the peaks for all three relaxations occur at very high temperatures, indicating that at room temperature the relaxations are far away from a resonant peak. The value of ϵ'' at $3.0 \times 10^9 \text{ sec}^{-1} = f$ and $298^\circ \text{K} = T$ is 0.0390.

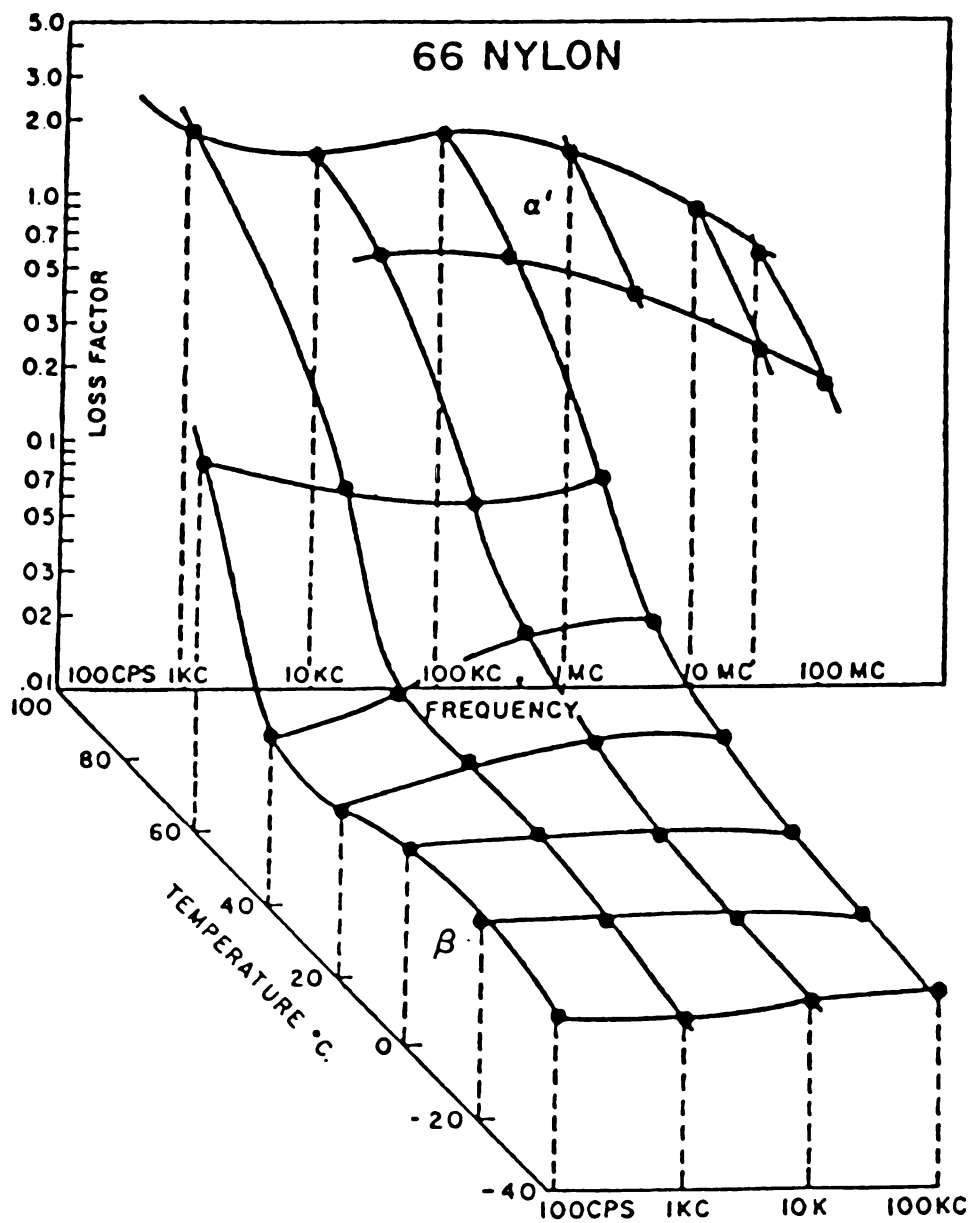


Figure 2. Complex permittivities for Nylon 66 for various frequencies and temperatures. (Ref. 24).

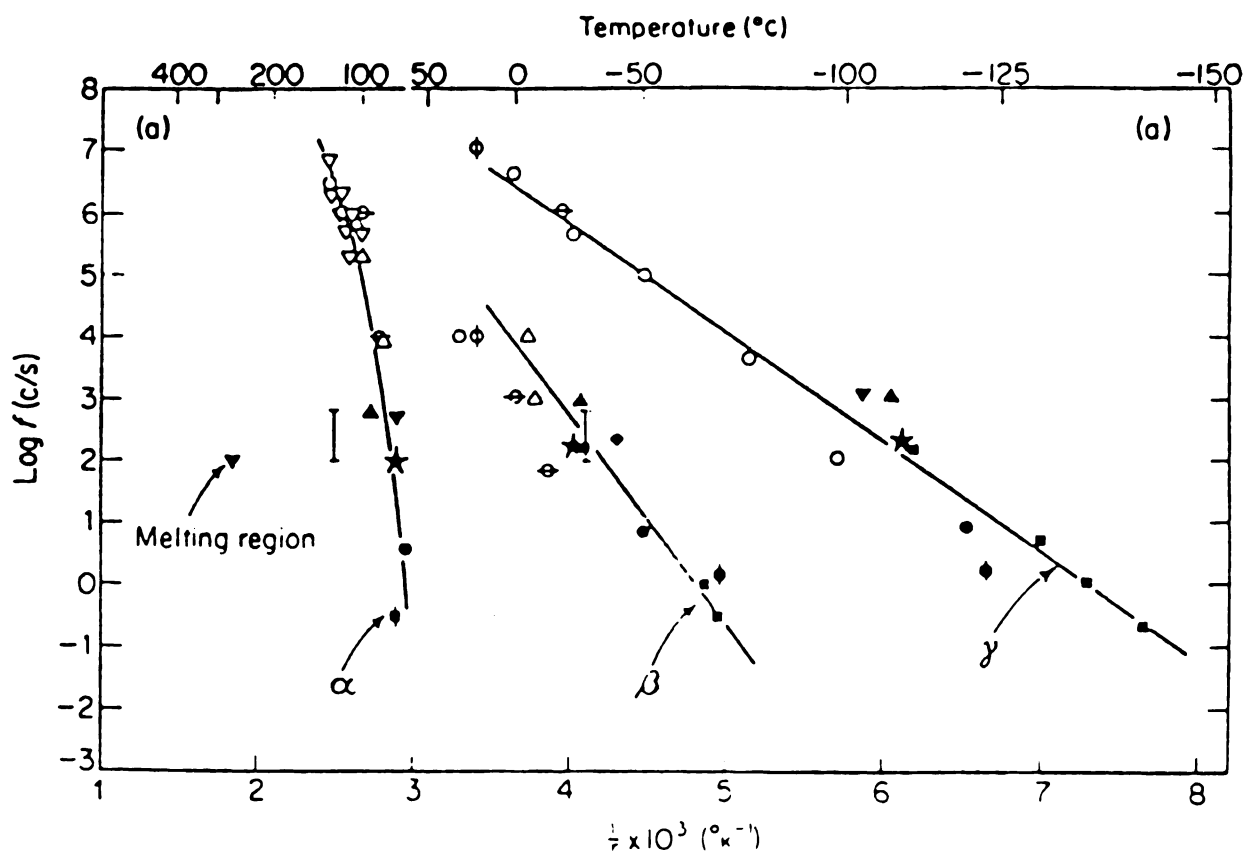


Figure 3. Dependence of frequency of loss peak for different relaxations in Nylon 66 on Temperature. (Ref. 19).

IV. Resonant Coupling and Cavity Diagnostics.

The following describes the important features of a cylindrical resonant cavity in the TM_{012} mode that are applicable to coupling electromagnetic energy to liquids and solids for electromagnetic processing.

A. Absorption of electromagnetic energy by loss of dielectives in the TM_{012} mode.

Electromagnetic power absorbed per unit volume by a dielectric is given by the following equation.

$$P(\omega/\text{cm}^3) = \frac{1}{2} \omega \epsilon'' E^2$$

ω - excitation frequency
(rad/sec)
 ϵ - Complex part of dielectric
constant
 E^2 - electric field strength
inside dielectric.

The amount of power absorbed is dependent therefore on the three factors listed above. If ω is held constant, power absorbed per unit volume is dependent on the loss-ness of the dielectric material and the electric field inside the material. If the material is not very lossy but E^2 is very large, or vice versa, an appreciable amount of energy can be absorbed by the dielectric. If both factors are large, a great amount of power can be absorbed.

Resonant cavities are potentially useful for electromagnetic coupling to liquids and solids due to the fact that very large electric fields may be generated in these cavities.^[27] It is, therefore, possible to couple large

amounts of energy to materials with low loss tangents. If the electromagnetic power can be focused into the volume where the dielectric material is placed, the efficiency of coupling would be further increased.

The TM_{012} mode was chosen for cavity excitation due to the fact that it possesses the property that the strongest E-field components are radially centered in the cavity. A diagram of the field lines in the TM_{012} mode is presented in Figure 4.

The electric field in both the z- and r- directions is given by

$$E_z(r, z) = AJ_0(k_c r) \cos \beta z$$

$$E_r(r, z) = AJ_1(k_c r) \frac{\beta}{k_c} \sin \beta z; k_c = \frac{2.405}{R}, \beta = \frac{2\pi}{L}$$

where J_n are cylindrical Bessel functions of the first kind. [27]

Consequences of the above equations are:

(1) There is no E_z component at $r = R$ and therefore $|E|^2$ at the wall is dependent on E_r only.

(2) $E_r = 0$ along the axial center of the cavity and if the dielectric is positioned in the center $|E|^2$ in the dielectric will essentially depend on E only.

(3) $E_r = 0$ at any r when $z = \frac{1}{2}L$, or when $z = 0$ or L .

(4) $E_z = 0$ when $z = \frac{1}{4}L$ or $\frac{3}{4}L$.

(5) The field is rationally symmetric ($E_\phi = 0$ everywhere).

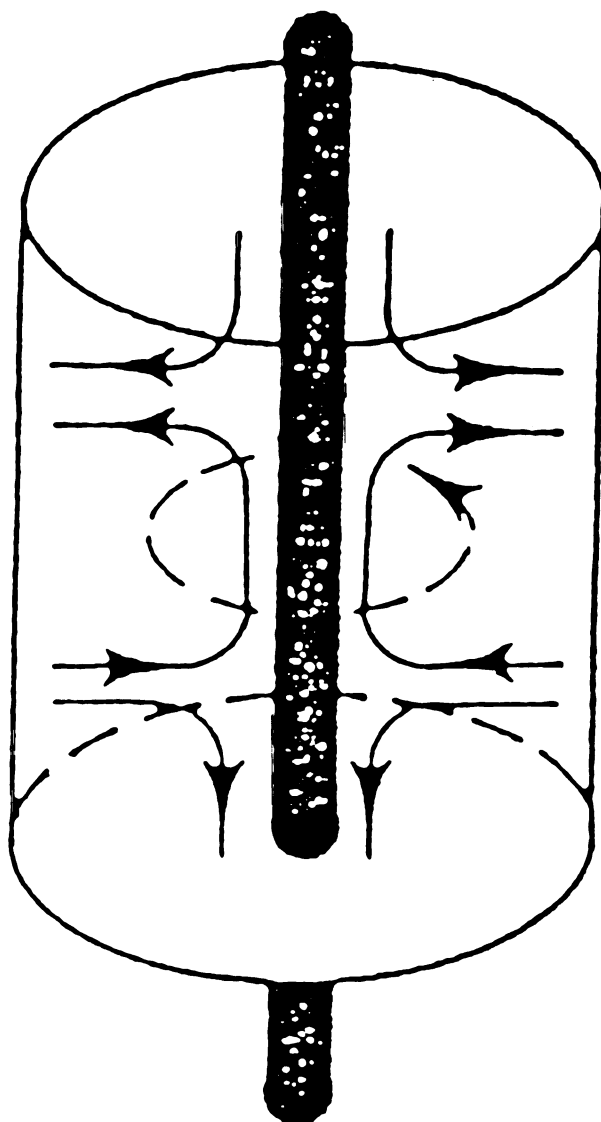


Figure 4. Field lines in a resonant cavity in the TM_{012} mode. (Ref. 27).

Assuming that E_r can be neglected inside the dielectric, the magnitude of E_z is inversely proportional to the real part of the dielectric constant ϵ' . It is expected that E^2 will be lower in systems with high ϵ' than in systems with low ϵ' . However the exact nature of this dependency is not known a priori and experimental results will have to be used to correlate ϵ' with E^2 for these cavities.

B. Significance of Measurements of Q and $E_{r\omega}^2$

The Q of a resonant cavity is given by the following expression:

$$Q = 2\pi f_0 \times \frac{\text{energy stored in cavity}}{\text{power dissipated in cavity}}$$

f_0 - excitation frequency, cycles/sec.

If the numerator of this expression is held constant (a reasonable assumption) Q is then dependent on the changing value of the denominator. A cavity's Q value will decrease proportionately with an increase in absorbed power. By way of example, a cavity containing a dielectric that absorbs 50% of the incident power would expect to have a Q half as long as that of the corresponding empty cavity. Similarly, the value of E_r^2 at the wall (where $E_z^2 = 0$) can be used to obtain the coupling efficiency.

$$1 - \frac{E_{r\omega}^2}{E_{r\omega}^2 \text{ (empty)}} = \text{coupling efficiency}$$

The methods used to obtain these quantities for various dielectrics are outlined in the next section.

The Q values and the coupling efficiency are related in the following manner:

$$1 - \frac{Q}{Q_{\text{empty}}} = \text{coupling efficiency}$$

This equation will be used to determine coupling efficiencies if $E_{r\omega}^2$ data is not available. [27]

V. Description of Experimental Apparatus

The experimental system used in these experiments is discussed in the following section. The basic components of the experimental set-up are the microwave circuit for generation and transmission of microwave power, a vertically-mounted cavity for transferring microwave energy to the material and the dielectric material itself requiring the use of a quartz tube for containing liquids. The dielectric materials used are discussed in a separate section. This section focuses on the microwave circuit used, the performance of the cavity in the TM_{012} mode, and methods used for the cavity diagnostic measurements.

A. Microwave Circuit and Resonant Cavity

The power source used for the low-power experiment to the RF output of a HP8620C sweep oscillator. If low-level amplification (1-15w) was required, the signal was amplified using a Varian TWT amplifier. After the generated signal passes through a unidirectional coupler (isolater), another directional coupler is necessary to isolate the incident power from the reflected power. Neither the isolater or the directional coupler attenuates the microwave signal. A 10 dB attenuator and a power meter were attached to each directional coupler. For the high-power measurements, 20 dB attenuators were used. An effort

was made to reduce the amount of flexible coaxial cable used in order to eliminate circuit noise.

A stand was constructed so that the cavity could be mounted vertically. Additionally, a clamping system was devised that held the dielectric vertically which allowed for easy insertion and removal of the dielectric from the cavity. A horizontal platform was constructed to mount the directional coupler in order to fix it in a horizontal position. The directional coupler was not attached to this platform so that the coupling probe depth could be adjusted.

The cavity itself is formed by the 17.8 cm diameter cylindral brass pipe and two transverse brass shorting planes, here after referred to as "shorts." One of the shorts was adjustable so that the cavity length could be varied from 6 to 16 cm. While the power levels used in this experiment were low enough so that cooling was not necessary, water flow through copper tubing attached to the exterior of the cavity would provide cooling for higher-power experiments. An E-field diagnostic probe was mounted directly opposite the coupling probe on an adjustable sliding track. The probe used in this case was a 2 mm diameter micro-coaxial waveguide.

Brass collars were attached to either end of the cavity in order to reduce microwave leakage. The collars had holes drilled at the center to accommodate the two

different sized dielectrics, 6 mm O.D. for liquids and 12 mm O.D. for solids. While brass screens were not used in the experiments, these could be attached to either end of the cavity in order to further reduce leakage. The two different size collars used necessitated two separate sets of measurements for liquids and solids.

B. Low- and High-Power Measurements

Since the primary information required from these measurements is the amount of microwave power absorbed in the dielectric, this discussion will focus on the measurement of Q for the cavity and how it changes with the inclusion of the various dielectrics. The Q value for a cavity is defined as

$$Q = 2\pi f_o \times \frac{\text{stored energy in cavity}}{\text{power dissipated in cavity}}$$

$$Q = f / \Delta f_o$$

where f_o is the resonant frequency and Δf_o is the frequency width at the half power point on the cavity resonance curve.

The cavity resonance curve is obtained using an oscilloscope in X-Y mode. The cavity length (L_s) and the coupling probe depth (L_D) were adjusted until the reflected power was at a minimum. Resonance is strong enough so that the reflected power is neglected in all subsequent calculations. Since the experiment is conducted in the TM_{012}

mode, L_s must be somewhere near its theoretical value of 14.48 cm. Once a resonant cavity is formed, the cavity resonance curve is obtained using an oscilloscope in X-Y mode, and Δf is obtained from this curve.

For the high-power experiments, this procedure was slightly modified. Absorption of high powered microwaves causes the temperature of the dielectric to increase, therefore changing the absorption characteristics of the dielectric. Periodic adjustment of L_s and L_p is required until temperature equilibrium is obtained and the reflected power can be maintained at a constant level. When the point of temperature equilibrium was reached, the TWT amplifier was quickly unhooked from the circuit (delay would upset the temperature equilibrium and the Q was then measured in the usual manner. It was interesting to note that, in the high loss materials, the linewidth of the cavity resonance curve visibly changes as the dielectric cools, indicating that Q is indeed sensitive to temperature. Either unhooking the TWT too quickly or taking too long a time to make the Q measurement once the TWT is removed from the circuit leads to experimental error.

The E-field probe could be placed virtually anywhere axially by using a slide adjustment similar to that used for varying L_s . Care was taken not to allow the probe to come within 0.5 cm of either the fixed or sliding short

in order to prevent damage to the probe. Additionally, the probe depth of the microcoax tube could not be altered once set since the E-field measurements are extremely sensitive with respect to probe depth. The E-field measurements are uncalibrated, meaning that only relative field strengths (proportional to power) were determined and compared to one another. All measurements taken show the existence of the axially centered node for the TM_{012} mode. Coupling efficiency was determined on the basis of this E-field probe, as it was felt that this measurement is more accurate and repeatable than that of the Q measurement.

The E-field measurements were carried out only for the low-power circuit. For the high-power circuit, it was found that the measurement took too long, therefore introducing error due to the temperature change. Results of these experiments, both high- and low-power, are discussed and interpreted in the following section.

Therefore, measurements taken consisted of measuring the power density at the wall of the cavity using an uncalibrated measurement system, measuring Q (power stores in cavity/power dissipated in cavity) by using a resonance line width method, and measuring Q as a function of incident power for each material. The power density measurements were not repeated in the latter case. These measurements enabled the loss tangent of the more lossy materials to be determined.

The power density at the wall is proportional to $|E|^2$.

Therefore, this measurement gives knowledge of the electric field in the cavity in regards to relative magnitude only, as the power measurements were uncalibrated with electric field strength. The results are those expected for the TM_{012} mode, with an axial node in $|E|^2$ at the center of the cavity. Relative peak heights for each experimental system measured are given in Table 1.

The Q values of each system were found by tuning the cavity to resonance at 2.45×10^9 Hz, obtaining a picture of absorption versus frequency on a oscilloscope, and taking the resonance peak width at half peak height and dividing it into the resonance frequency. This Q represents the ratio of power absorbed in the cavity vs. power dissipated in the cavity. Results of these measurements are given in Table 2. The more absorbent the system, the lower the Q of the cavity. Also, coupling probe depth increased with absorption, while the cavity length decreased from its empty cavity length of 14.35 cm.

Finally, Q values for each system at higher power levels were measured. An apparent pattern can be seen for Nylon 66 that is not observed in the other materials. The Q value decreases with increasing temperature indicating that the loss increases with temperature and that the % power absorbed increases from 55% to 85%. The inconsistent nature of some of the other results [particularly poly propyleneglycol] could results from measurements being

taken within the time constant of the system. Since precise knowledge of the temperature is not known (it is assumed, of course, that temperature within the dielectric increases with increasing power level) the temperature dependency of the loss tangent and ϵ'' on temperature is not quantitatively modeled from these results at this time. These results are given in Table 3.

Results in Table 2 were determined using an incident power level of $1.5 \times 10^{-3} \text{ W}$. The column in Table 3 of results at $1.5 \times 10^{-3} \text{ W}$ were low power measurements taken at the same time as the high power measurements, and their inconsistency with the results in Table 2 is indicative of a certain amount of experimental error.

The materials chosen for processing were selected with regard to generating a wide range of experimental results. Liquids chosen were ethylene glycol, which is polar and is expected to absorb strongly, propylene glycol (1, 2-propanediol) which is of an essentially similar chemical and physical nature to ethylene glycol except for the molecular size, and polypropylene glycol ($M_{\text{avg}} = 4,000$), a polymer liquid which has a very high viscosity (913 cp) and therefore greater hindrance on the molecular motion, so that it should not absorb as strongly as either of the glycols.^[25] Water was also chosen for measurement but it absorbed so strongly that the $|E|^2$ measurements and Q measurements were of such low values that they were not

possible to make accurately with the experimental apparatus. Solids chosen were two polymer rods, poly tetrafluoroethane (teflon) which is essentially lossless, and Nylon 66, a polymer with polar groups which should be absorptive.^[24] The polymer rods were of a different size than the quartz tube used to contain the liquids necessitating two separate sets of measurements for liquids and solids.

The liquids were processed in a quartz tube, 4.5 mm ID and 6.0 mm OD. "Empty" cavity measurements for the set of liquids measured were taken with an empty quartz tube at these dimensions in the cavity. The solid polymer rods were 12.0 mm in diameter and empty cavity measurements were carried out for a cavity with 12.0 mm ID collars. Each of the Tables of Results is therefore divided into two sections, liquids (A) and solids (B).

TABLE I. Relative Peak Heights

A. Liquids ($P=1.52 \times 10^{-3} \omega$)		
Material	$ E ^2$ (Relative Units)	z, cm
Empty	0.03250	3.3
Ethylene Glycol	0.00325	3.3
Propylene Glycol	0.00725	3.3
Polypropylene Glycol ($m\omega = 4,000$)	0.02480	3.3
B. Solids ($P = 1.50 \times 10^{-3} \omega$)		
Empty	0.0593	3.4
Polytetrafluorethane (Teflon)	0.0480	3.4
Nylon 66	0.0289	3.4

TABLE II. Q Values and Cavity Parameters

Material	Q	Cavity Length cm	Coupling Probe Depth, cm
A. Liquids			
Empty	662	14.35	+0.50
Ethylene Glycol	76	14.275	+2.00
Propylene Glycol	126	14.30	+1.35
Polypropylene Glycol	490	15.35	+0.75
B. Solids			
Empty	1800	14.35	-0.10
Teflon	1600	14.31	0.00
Nylon 66	980	14.28	+0.25

Table III. Q Values at Various Incident Powers

Material	$1.5 \times 10^{-3} \omega$	1ω	3ω	10ω	12ω
A. Liquids ($Q_{\text{Empty}} = 770$)					
Ethylene Glycol	84	66	84	---	116
Propylene Glycol	150	129	122	---	129
Polypropylene Glycol	580	580	---	580	---
B. Solids) ($Q_{\text{empty}} = 3,000$)					
Teflon	2880	---	---	2880	2880
Nylon 66	1400	1400	1200	600	---

NOTE: --- Indicates measurement not taken.

Following is a series of Figures designed to show the various aspects of the experimental system. First, Figure 5 shows the design of an experimental microwave cavity, with the coupling probe structure also shown. Figure 6 is a representation of the microcoax probe used to determine the $E_{r\omega}^2$ values at the cavity wall. A diagram of the experimental apparatus is shown in Figure 7. Finally, the measured values of $E_{r\omega}^2$ are given in Figures 8 and 9.

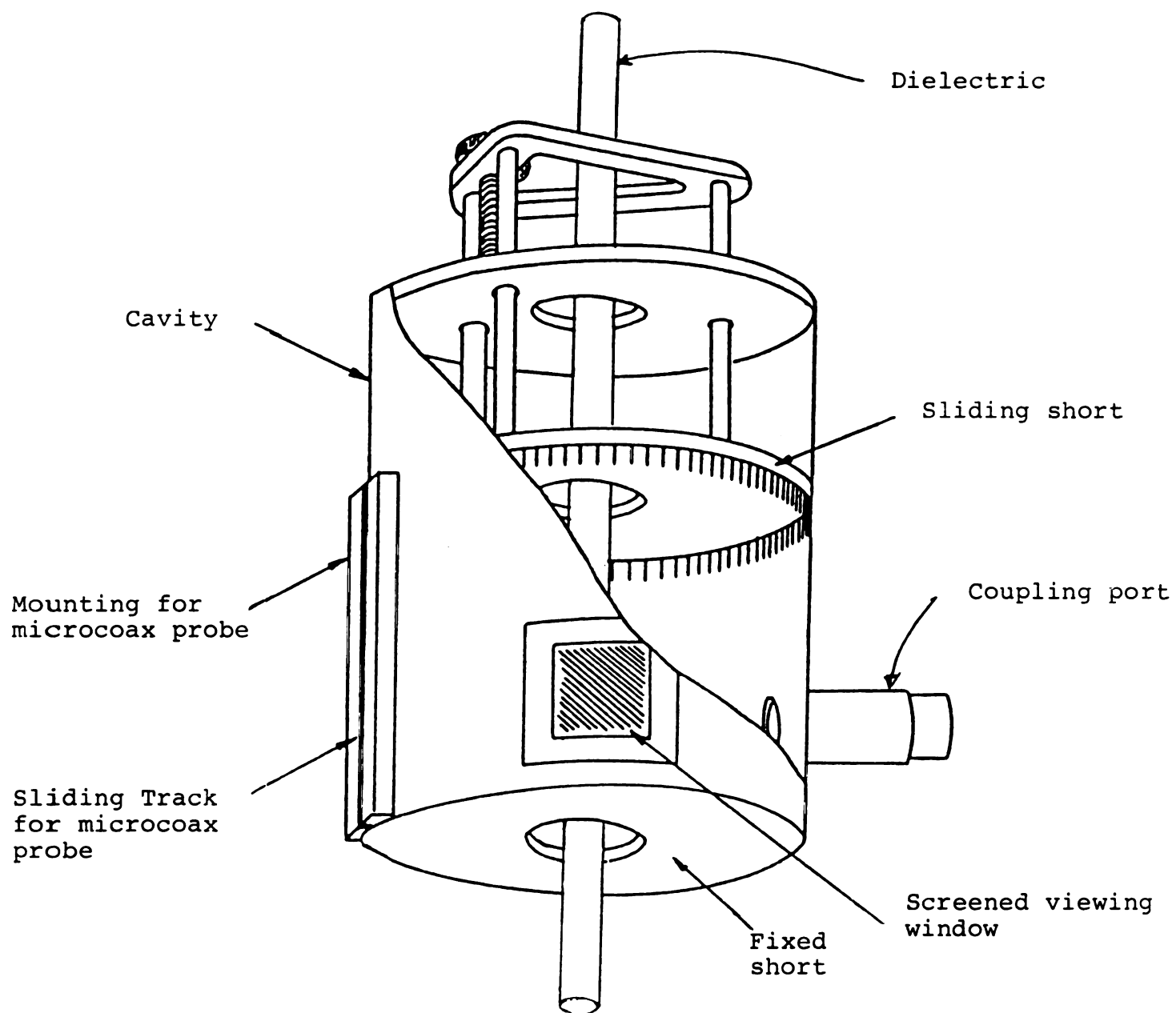


Figure 5. Diagram of microwave cavity. (Ref. 27).

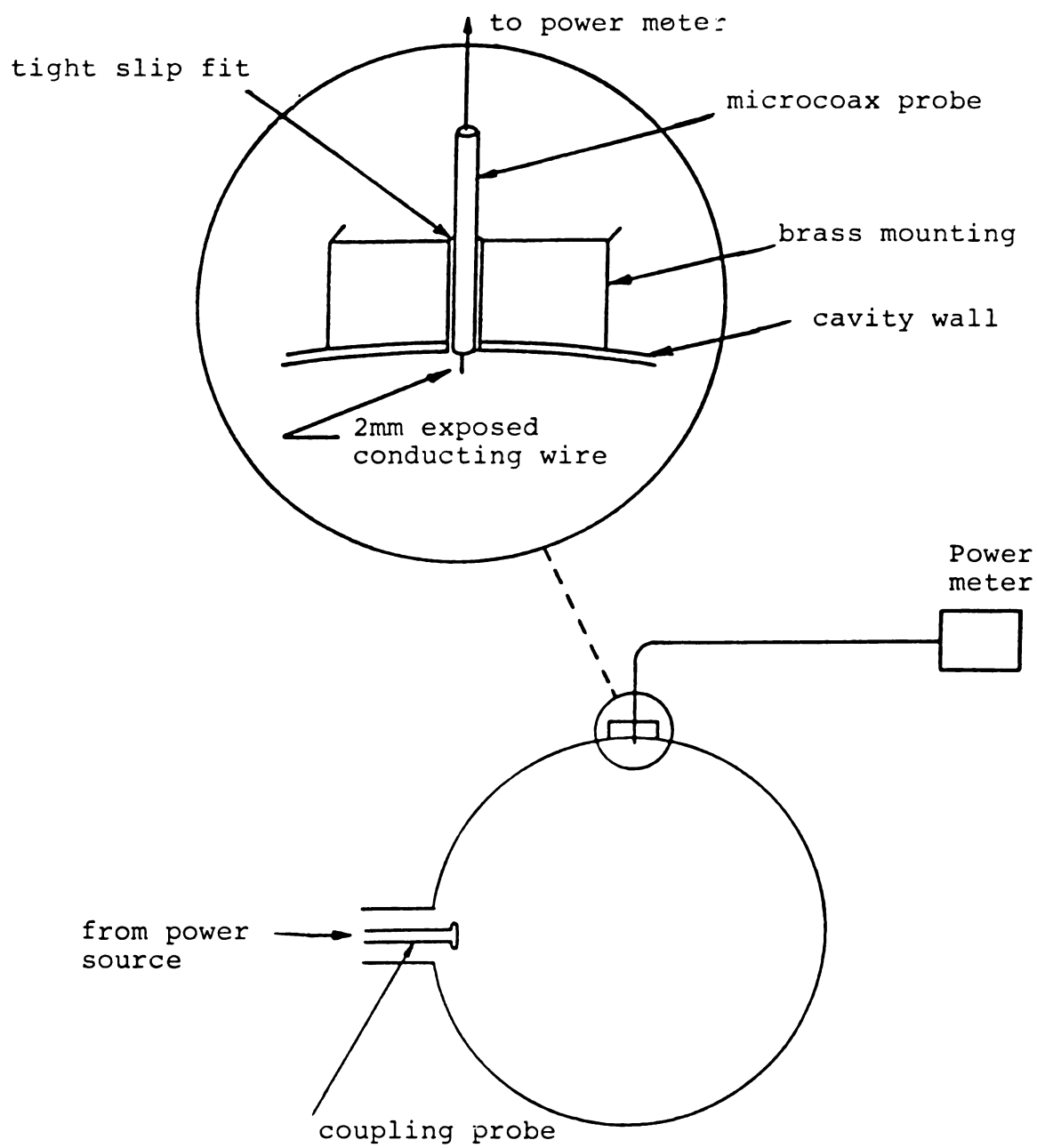


Figure 6. Design of microcoax probe. (Ref. 27).

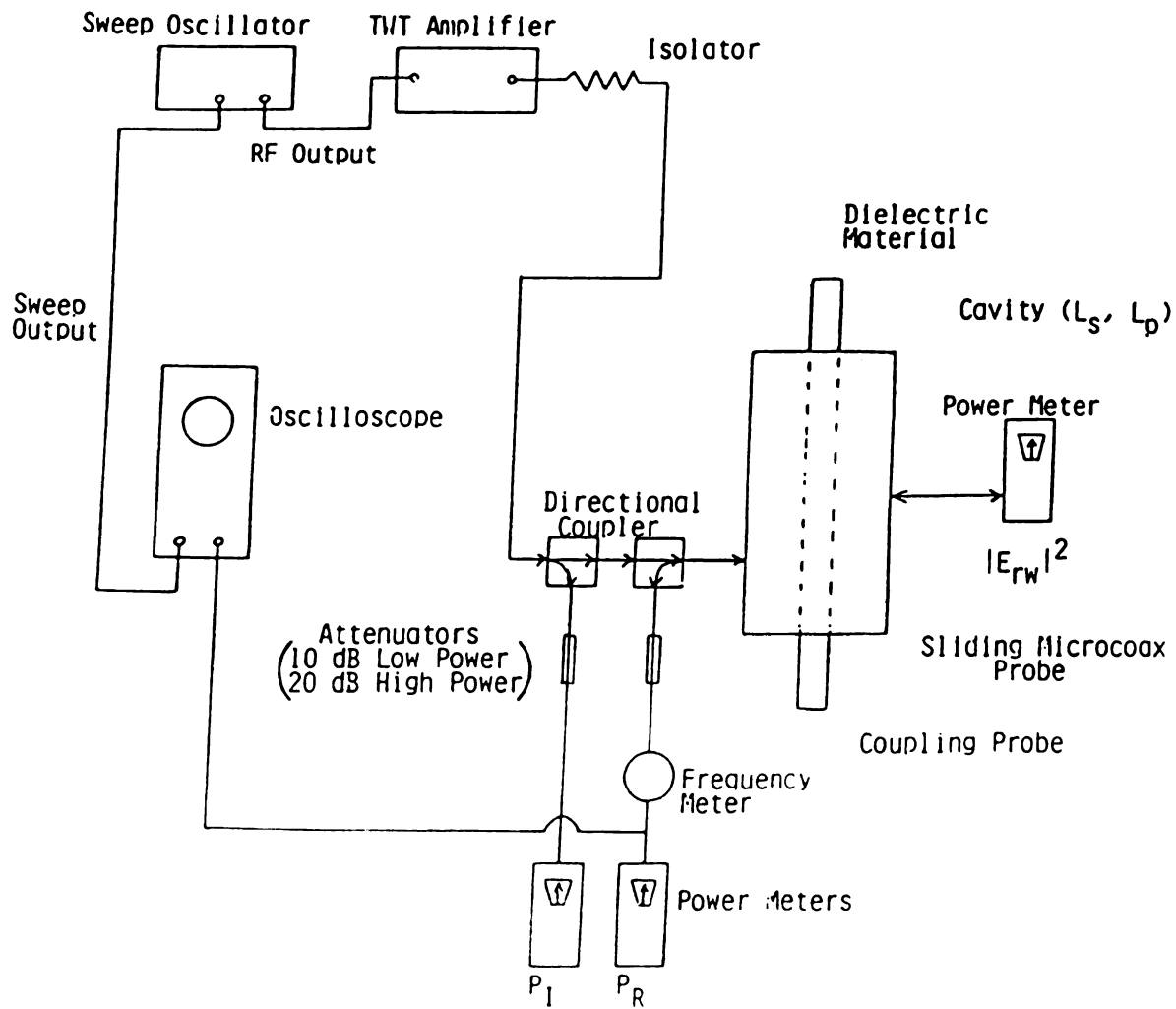


Figure 7. Overall design of experimental apparatus.

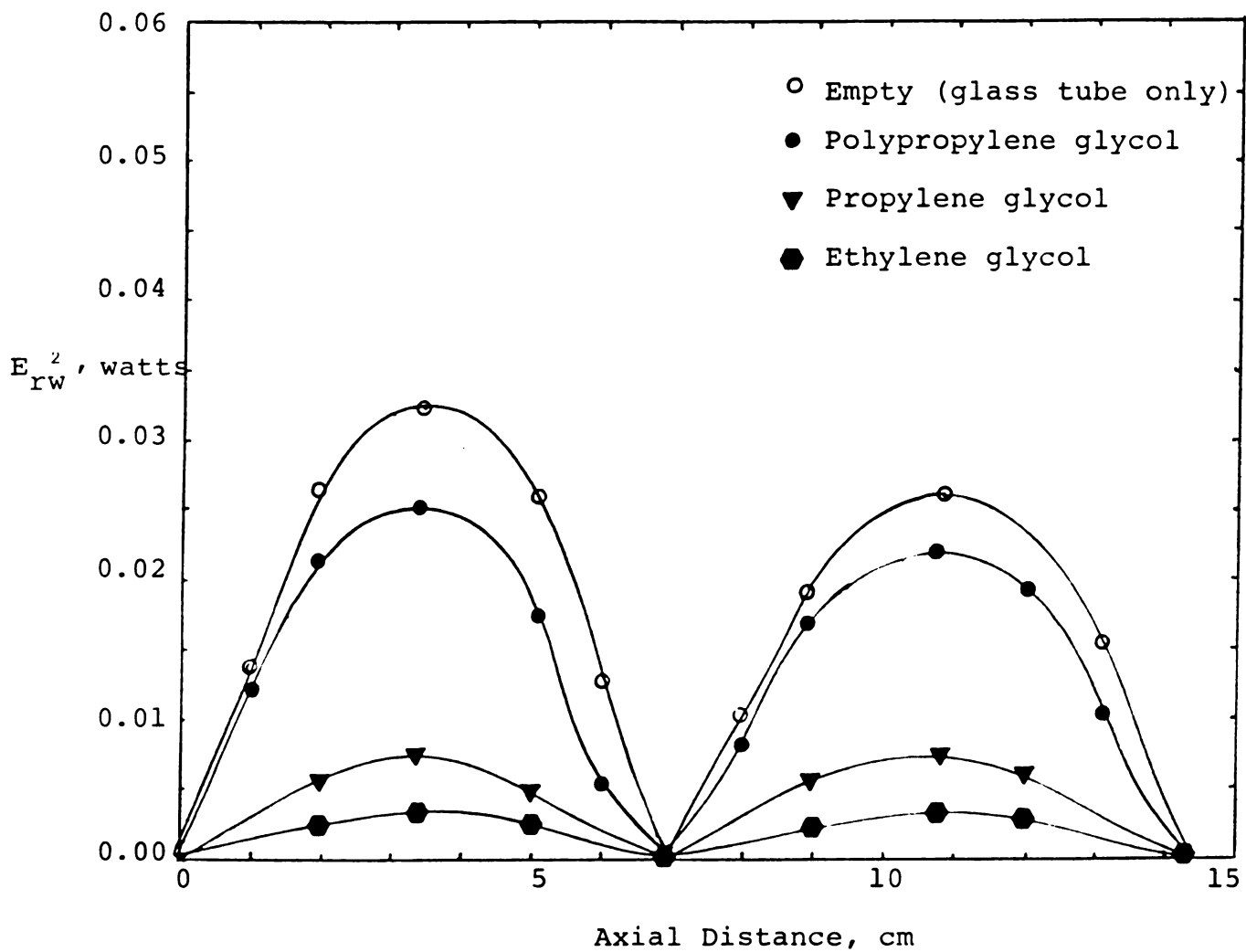


Figure 8. E_{rw}^2 in Watts vs. Axial Distance for various liquids.

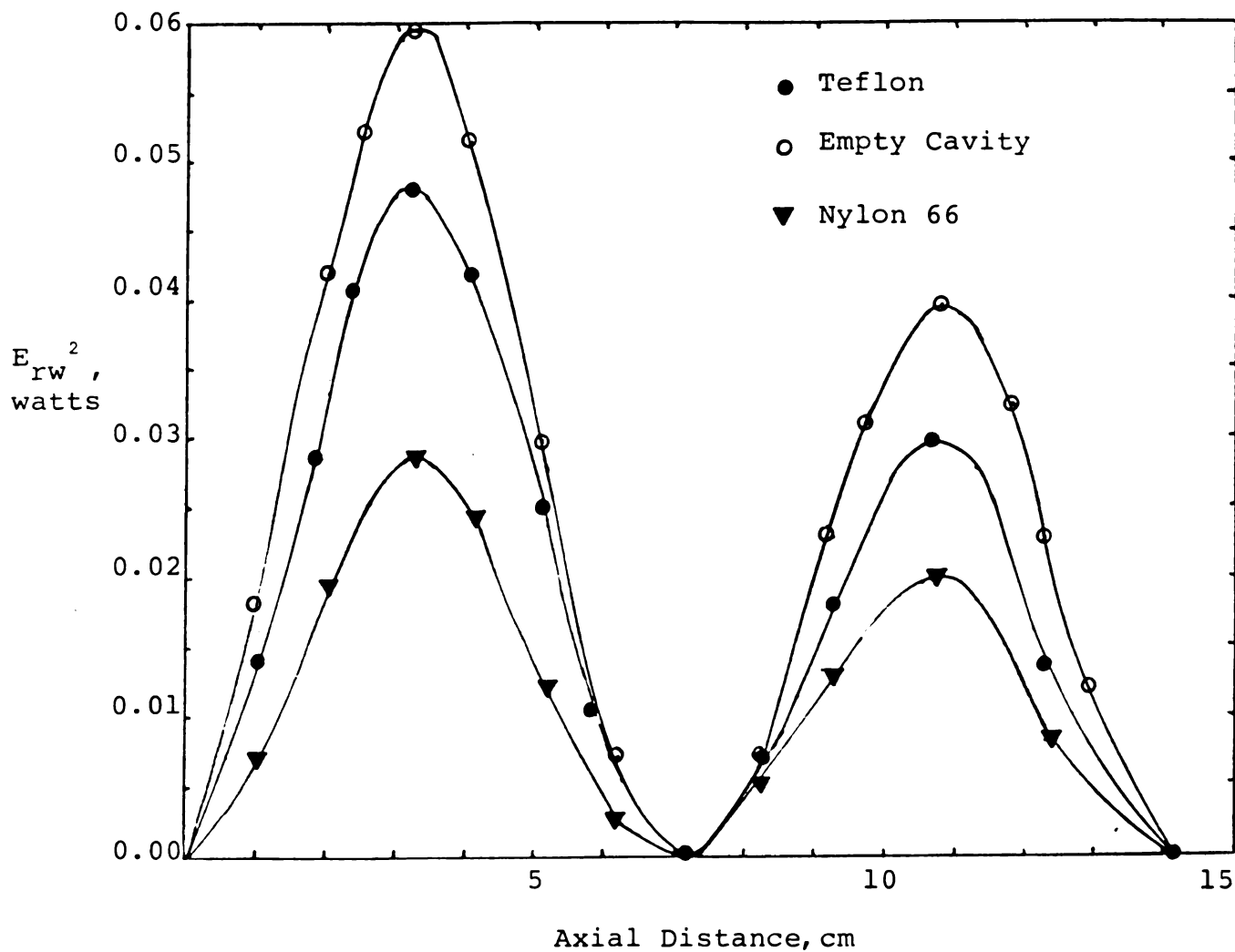


Figure 9. E_{rw}^2 in watts vs. Axial Distance in Cavity for various solids.

VI. Modeling of Dielectric Relaxations.

In this section, various models of dielectric relaxations will be considered with the goal of explaining and correlating some of the experimental measurements. First, liquids containing hydroxide groups (glycols, alcohols, water) will be modeled using the -OH group rotation about its bond as a method of estimating the relaxation time by estimating the activation energies as a sum of interactions with other molecules in solution and internal rotational barriers. Secondly, a calculation will be demonstrated to assess the dependence of E^2 on ϵ' that was monitored in the previous section. Finally, the temperature distribution in a nylon 66 rod in the TM_{012} mode will be determined numerically at a number of different incident power levels by first modeling the nylon 66 relaxations and then utilizing the explicit method along with an absorption term to determine the evolution of the temperature field with spatial position and time.

A. Relaxations in -OH containing liquids

To begin with, the relaxation of the simplest -OH containing liquid of all, water, was examined by taking data presented by von Hippel (1954)^[3] at four different temperatures and attempting to fit it to a Debye relaxation curve

(ϵ'' vs. ω), and estimating the relaxation times at each of the fair temperatures in the study. These τ 's were then plugged into an ACT expression to find $\Delta H^\ddagger$. (A value of zero is assumed for $\Delta S^\ddagger$ since, in a liquid of this nature with a great deal of rapid random Brownian motion, one orientation is no more "favorable" than another.)^[16] Very good agreement with the ACT model was obtained with $\Delta H^\ddagger$ 2.37 kcal/mol. (This calculation is demonstrated in greater detail in the Appendix). If the assumption is made that this $\Delta H^\ddagger$ is associated with the amount of energy required to "move" an -OH dipole, the assumption can be tested by fitting various alcohols of the form R-OH (R=CH₃, C₂H₅, C₃H₇, C₄H₉) to the Debye model and estimating τ 's and $\Delta H^\ddagger$'s in the same manner, with the results shown in Table 4. The data is sparse, particularly for ethanol, so that there may be some errors associated with these estimated values.^[3]

The value for the rotational barrier to a rotation of -OH about a -CH₃ bond is 1.1 kcal/mol^[17] If this value is subtracted along with the activation energy for water relaxation from the values of $\Delta H^\ddagger$ for this series of alcohols, the amount of energy associated with "additional" potential barrier can be found. A series of a similar nature for rotations of -CH₃ groups in hydrocarbons shows a similar dependency. Since an -OH groups is of similar size to a -CH₃ group, it is assumed

that substituents in hydrocarbon chains have a similar additive effect on rotational barriers in alcohols. Comparing results shown in Table 5 indicates that for such a simple model, the assumptions above work fairly well. It is, therefore, possible for relaxations of this type to be modeled using an "interaction" potential barrier of 2.3 kcal/mol for the -OH group's interaction with the environment along with an appropriate internal rotational barrier as an additional interaction. These considerations will now be applied to glycol molecules, particularly ethylene glycol and (1, 2)-propylene glycol.

Table 4. Relaxation Times and Activation for Various Alcohols

Alcohol	$\tau_{\text{est}} \times 10^{11} \text{ sec}$	$\Delta H^{\ddagger} \text{ kcal/mol}$
CH_3OH	5.3	3.4
$\text{CH}_3\text{CH}_2\text{OH}$	12.7	4.0
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	33.3	4.5
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	46.8	4.7

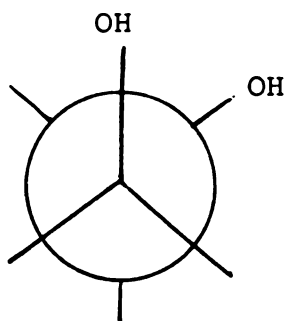
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Table 5. Comparison of Additive Rotational Barriers

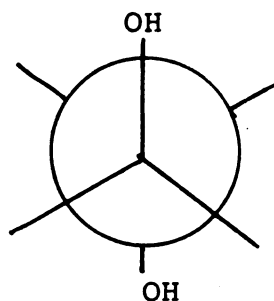
R	$\Delta H^{\ddagger}, \text{ R-OH}$ (-3.4 kcal/mol)	$\Delta H^{\ddagger}, \text{ R-CH}_3$ (-2.9 kcal/mol)
$-\text{CH}_3$	0	0
$-\text{CH}_2\text{CH}_3$	0.6	0.5
$-\text{CH}_2\text{CH}_2\text{CH}_3$	1.1	1.0
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	1.3	1.8

$\Delta H^{\ddagger}$ values for R-CH_3 taken from Carey and Sundberg^[28].

In solution, ethylene glycol can exist in two conformations, gauche or anti, diagrams of which are shown below.



gauche ($\mu_D=0$)



anti ($\mu_D=0$)

Using bond dipole moments and considering the literature value of μ_D , the relative contributions of the two gauche and the single anti conformations can be determined.

Using Boltzmann's equation for relative distributions.^[17]

$$\frac{f_1}{f_2} = e^{-(\epsilon_1 - \epsilon_2)/k_B T}$$

$$T = 298^\circ\text{K}$$

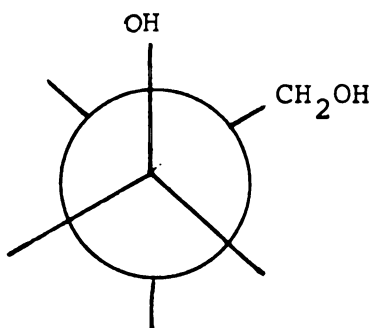
(1,2) denote states 1 and 2

($\epsilon_1 - \epsilon_2$) = difference in
energy between two states

and adjusting for the fact that there are two gauche conformations for each anti conformation, it was found that ($\epsilon_1 - \epsilon_2$) = 0.3 kcal/mol which corresponds to the order of magnitude of a hydrogen bond. For a hydroxide group

gauche to another an additional 0.3 kcal/mol must be added to $\Delta H^\ddagger$ as this hydrogen bonding interaction inhibits the rotational relaxation of the dipole. This interaction parameter is not added in the case of the anti conformation.

Additionally, the -OH dipoles have their internal rotation barriers increased by an additional substituent leading to steric hindrance. Looking down the O-C bond axis, it can be seen that the increased barrier to internal rotation arises from the -CH₂OH group.



It is assumed that this interaction is on the order of that for -CH₃ rotation about a C-CH₃ bond (0.5 kcal/mol) since the C-C and O-C bond lengths as well as the C-H and O-H bond lengths are somewhat similar. A summary of the interaction parameters discussed above are presented in Table 6. Using these values in the Debye equation for ϵ' , a value of $\epsilon'' = 14.57$ is calculated which compares favorably with the literature value of 14.60.

Modeling of 1,2-propanediol is similar, but more

complicated as the addition of a single extra -CH_3 group increases the number of possible relaxation mechanisms to six and increases the activation energy for rotation. These values are also presented in Table 6. The value of ϵ'' calculated is 10.29. Poly (propylene glycol) has a kinematic viscosity of 913 centistokes at 25°C indicating that an extensive hydrogen bonding network is present in the liquid. Results in the literature show that the relaxation is essentially independent of chain length, indicating that the -OH group "sees" only a small section of the chain. Applying the ACT expression for τ to the literature results ($\tau = 4.5 \times 10^{-9}$ sec at 0°C) gives $\Delta H^\ddagger = 5500\text{kcal/mol}$. This is approximately 1500 cal/mol above the value of propylene glycol indicating that there is an additional amount of rotational hindrance.^[25] Care must be taken when applying this model to solutions at very high viscosity or solids due to extensive hydrogen bonding networks or intermolecular attractions.

TABLE 6. Interactions in Glycol Systems

Material	Description of i Relaxation	C_i	Internal H-Bonding (0.3 kcal/mol)	Number of Rotational Barriers (0.5 kcal/mol)	$\Delta H^\#$ kcal/mol	τ_i^{10} ($\times 10^{10}$ sec)
Ethylene Glycol	-OH Rotation H-Bonded	1	0.768	yes	1	4.0
	-OH Rotation non-H-Bonded	2	0.232	no	1	3.7
Propylene Glycol	-OH Rotation H-Bonded	1	0.285	yes	2	4.5
	Extra Internal Barrier					3.216
	-OH Rotation H-Bonded	2	0.592	yes	1	4.0
	No Extra Internal Barrier					1.382
	-OH Rotation No H-Bonding	3	0.046	no	2	4.2
	Extra Internal Barrier					1.938
	-OH Rotation No H-Bonding	4	0.107	no	1	3.7
	No Extra Internal Barrier					0.833

The three glycol liquids have the modeling results summarized in Table 7. The mean relaxation time is defined as that calculated in the model using the Debye equations for a single relaxation process. Likewise, the mean activation energy is defined as the value of $\Delta H^\ddagger$ calculated from the mean relaxation time using activated complex theory. Temperature is 298°K unless otherwise specified.

Table 7. Summary of Glycol Relaxations

Material	$\tau_{\text{mean}}, (x10^{10} \text{ sec})$	$\Delta H^\ddagger, \text{ kcal/mol}$
Ethylene Glycol	1.254	3.940
Propylene Glycol	1.637	4.100
Polypropylene Glycol	17.410	5.500

B. Modeling of Relaxation in Nylon 66.

The nature of the relaxations in Nylon 66 has been discussed previously. The following is not an attempt to review the relaxations themselves but to model them so that the temperature field of a nylon rod in a resonant microwave cavity can be predicted.

All three relaxations were first fitted to expressions of the form (T-absolute temperature).

$$\tau_i = \frac{A}{T} e^{\Delta H^*/RT}$$

by taking the slope of an Arrhenius plot ($\ln \tau$ vs. $-E_a/R$) to find ΔH^* , and solving for A at a given temperature knowing ΔH^* , and τ_i . Results are given below.

Table 8. ACT parameters for Nylon 66 Relaxations

Relaxation	ΔH^*	A
α	46 kcal/mol	2.044×10^{-32}
β	15	3.219×10^{-15}
γ	9	3.482×10^{-12}

These relaxations were fitted to data in the literature for each relaxation using the following equations based on the "universal" response. (Jonscher &

Ngai) [21,22]

$$\epsilon_i'' = k_i \left[\frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \right]^{1-n}$$

$$\approx k_i \left[\frac{1}{\omega \tau_i} \right]^{1-n} \text{ at high } \omega$$

Table 9 includes the values of k and i for each relaxation.

Table 9. Debye Parameters for Nylon 66.

Relaxation	k_i	n
γ	0.0180	0
β	0.1184	0.8962
α	3.9115	0.676

Finally, the three ϵ_i'' 's are added and ϵ'' determined

$$\epsilon'' = \epsilon_{\beta}'' + \epsilon_{\alpha}'' + \epsilon_{\gamma}''$$

While adding them seems a bit simple, there are several justifications for it. First, the α -relaxation does not exist below $T = 50^{\circ}\text{C}$ and tends to dominate above it. The large value of k_i for the α -relaxation would swamp the β - and γ -relaxation at higher temperatures.

Also, the γ -relaxation is not strongly cooperating with the other relaxations, so it may be separated out. At 25°C , it appears as a small shoulder at around $f = 3 \times 10^7 \text{ Hz}$.

The alpha relaxation is written in a slightly different form for the calculation. In order to make the ϵ'' vs. (ω, T) curve smooth, the value of ϵ''_{α} at $T = 50^{\circ}\text{C}$ is subtracted out

$$\epsilon''_{\alpha}(T) - \epsilon''_{\alpha}(50^{\circ}\text{C}) = \epsilon''_{\alpha}(\text{final})$$

Now that $\epsilon''(\omega, T)$ is unknown, the value of E^2 in the dielectric must be found so that the equation

$$P/V = 1/2 \omega \epsilon'' E^2$$

may be used to determine the amount of absorbed power. A plot of $\ln E^2$ vs $\ln \epsilon'$ for both liquid and solid experimental systems is constructed in order to find the dependence of E^2 on ϵ' . This plot is shown in Figure 10. It is now possible to calculate P/V given the above parameters and use it in an finite difference calculation using the explicit method.^[29] FORTRAN implementation of this method is discussed in greater detail in the Appendix.

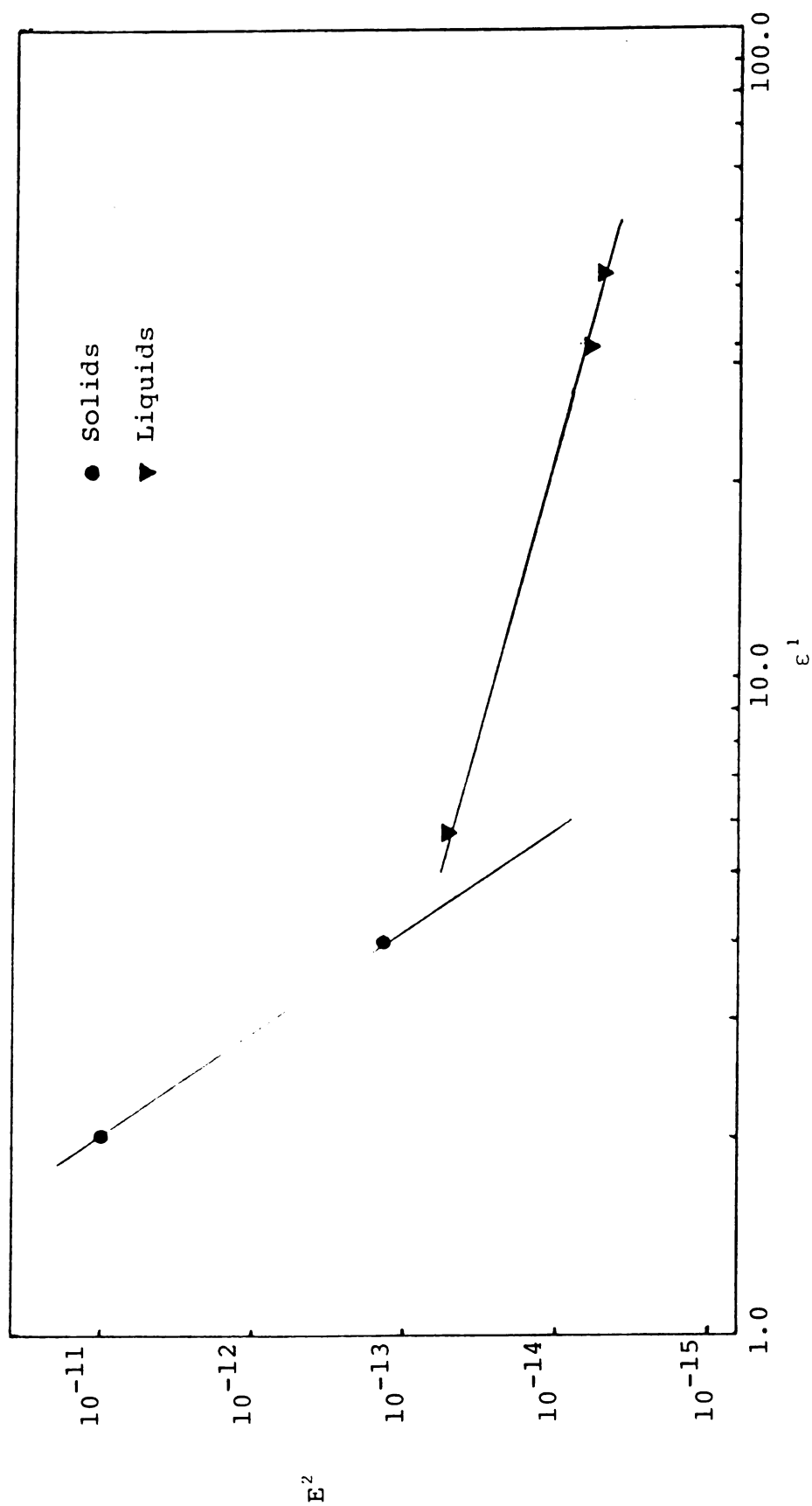


Figure 10. Log-log Plot of E^2 in Dielectric vs. ϵ^1 for liquids and solids.

The partial differential equation used is of the form:

$$k \nabla^2 T + [P/V] = \rho C_p \frac{\partial T}{\partial t}$$

(conduction) (absorption) (accumulation)

The set of grid points in this solution can be greatly reduced in size by invoking symmetry and using the fact that E_z is symmetric about the axial center of the cavity and $E_\phi = 0$ everywhere. A schematic is shown in Fig. 11. The rod to be modeled has a radius of 0.6 cm, with a length of 7.2 cm inside the cavity and 9.0 cm outside the cavity. The grid points were selected to be 0.2 cm apart.

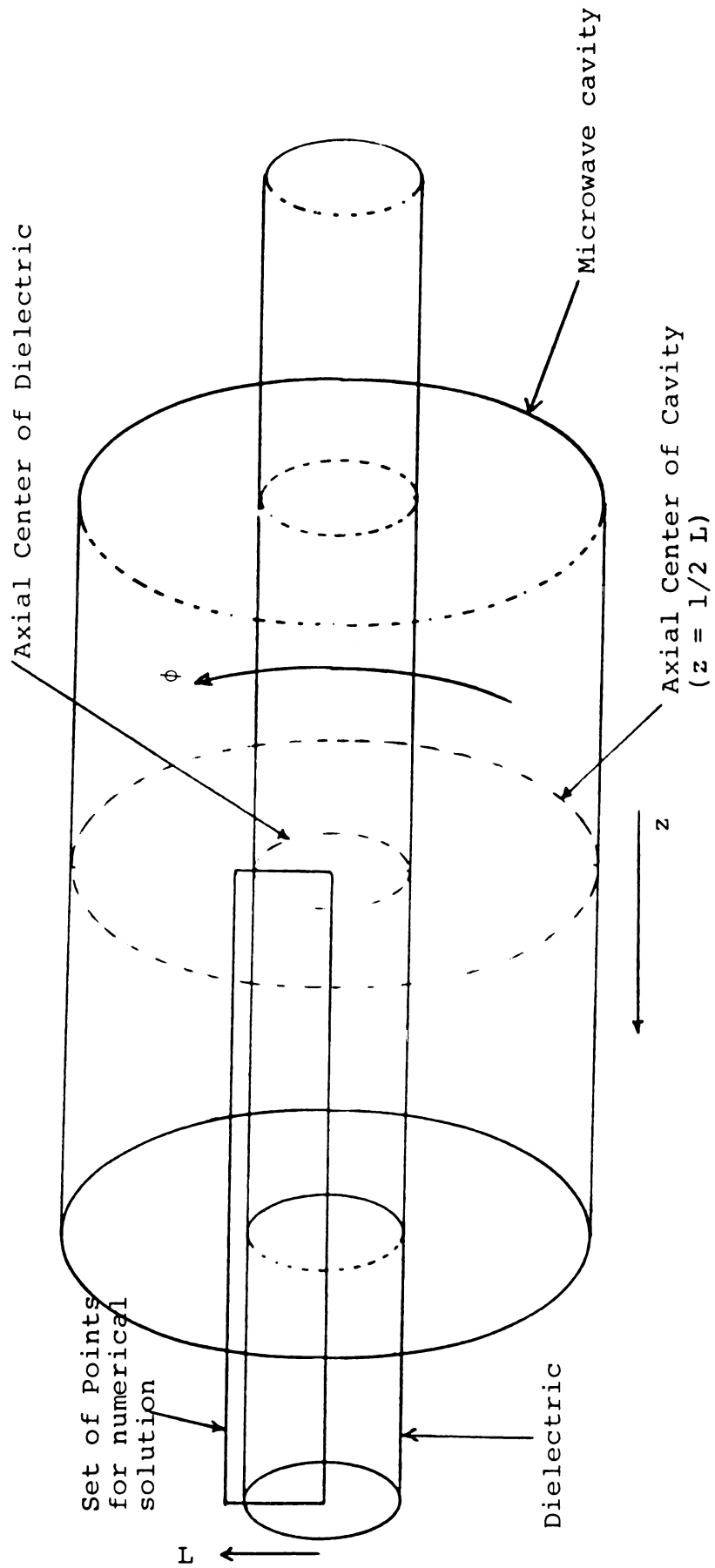


Figure 11. Schematic of Numerical Solution method. Electric field in Cavity is symmetric about $z = l/2 L$ and $r = 0$, and is independent of ϕ .

A convective heat transfer coefficient of 2.00 BTU/hr ft² °F was arbitrarily chosen to estimate heat transfer from the rod to the air.

Results are given in Table 10 for four different power levels and include (1) percent absorbed at $t = 5$ min and (2) number of minutes the rod takes to reach steady state. Additionally, Figures 12 - 15 show the evolution of temperature with time at varying positions in the rod at each power level at $t = 5$ min and at steady state.

It should be noted that after ten minutes in a 10 watt cavity, the nylon rod would have already exceeded its melting point of about 410° K. Power absorbed increases sharply once parts of the rod are heated above 323°K (T_g) because of the onset of the α -relaxation.

Table 10. Selected Results of Numerical Calculation
of Temperature

Power Level ω	% Power Absorbed (t = 5 min)	Steady State, min
1.5×10^{-3}	49.4	13
1	51.7	77
3	56.8	117
10	90.2	97

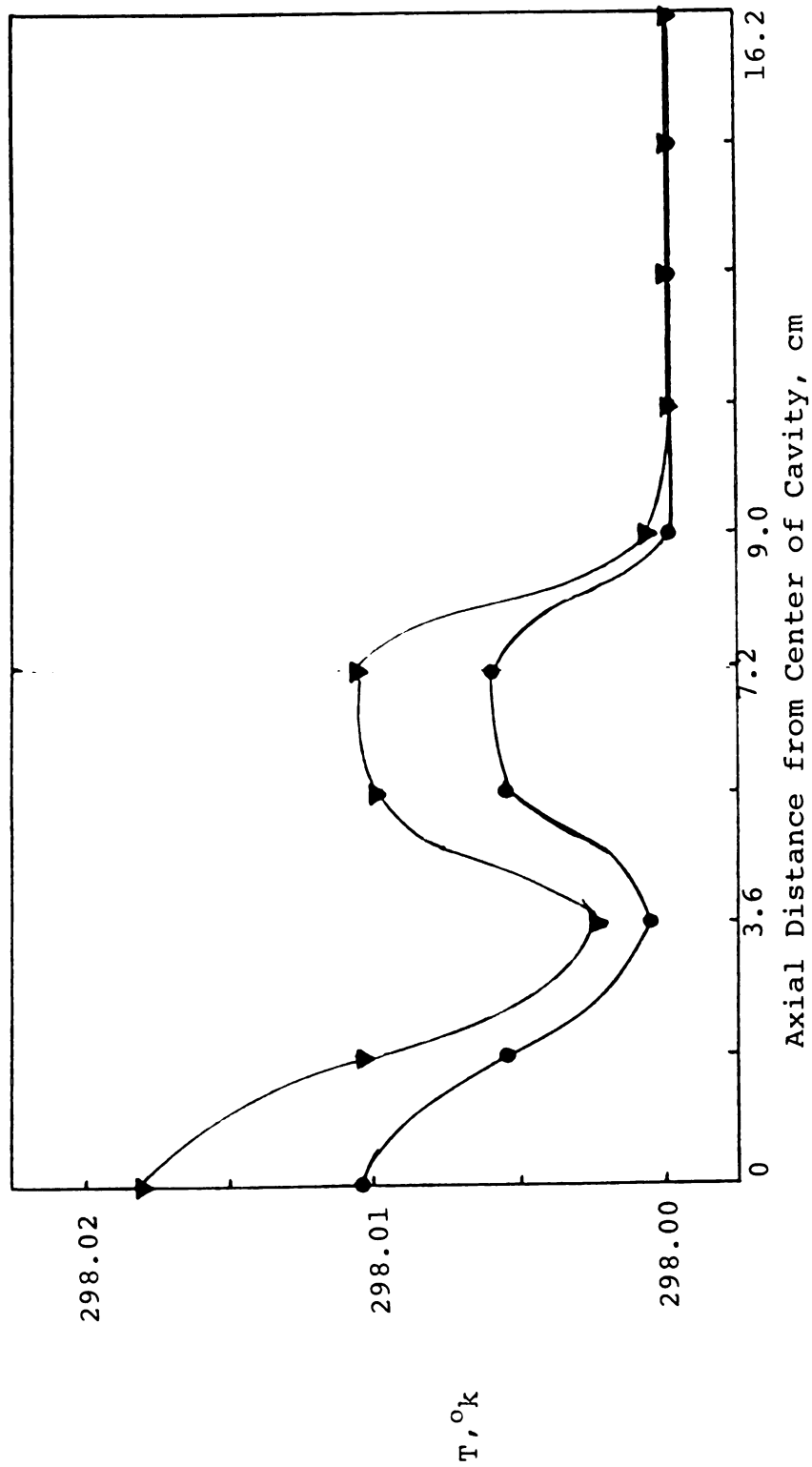


Figure 12. Temperature Distribution in Nylon Rod. points denote $t = 5$ min, points denote steady state solution. Points to the left of the dashed vertical line are inside the cavity. Power level is 0.0015 watts. This nomenclature applies to Figures 13-15, except for changing power level. ($r = 0$)

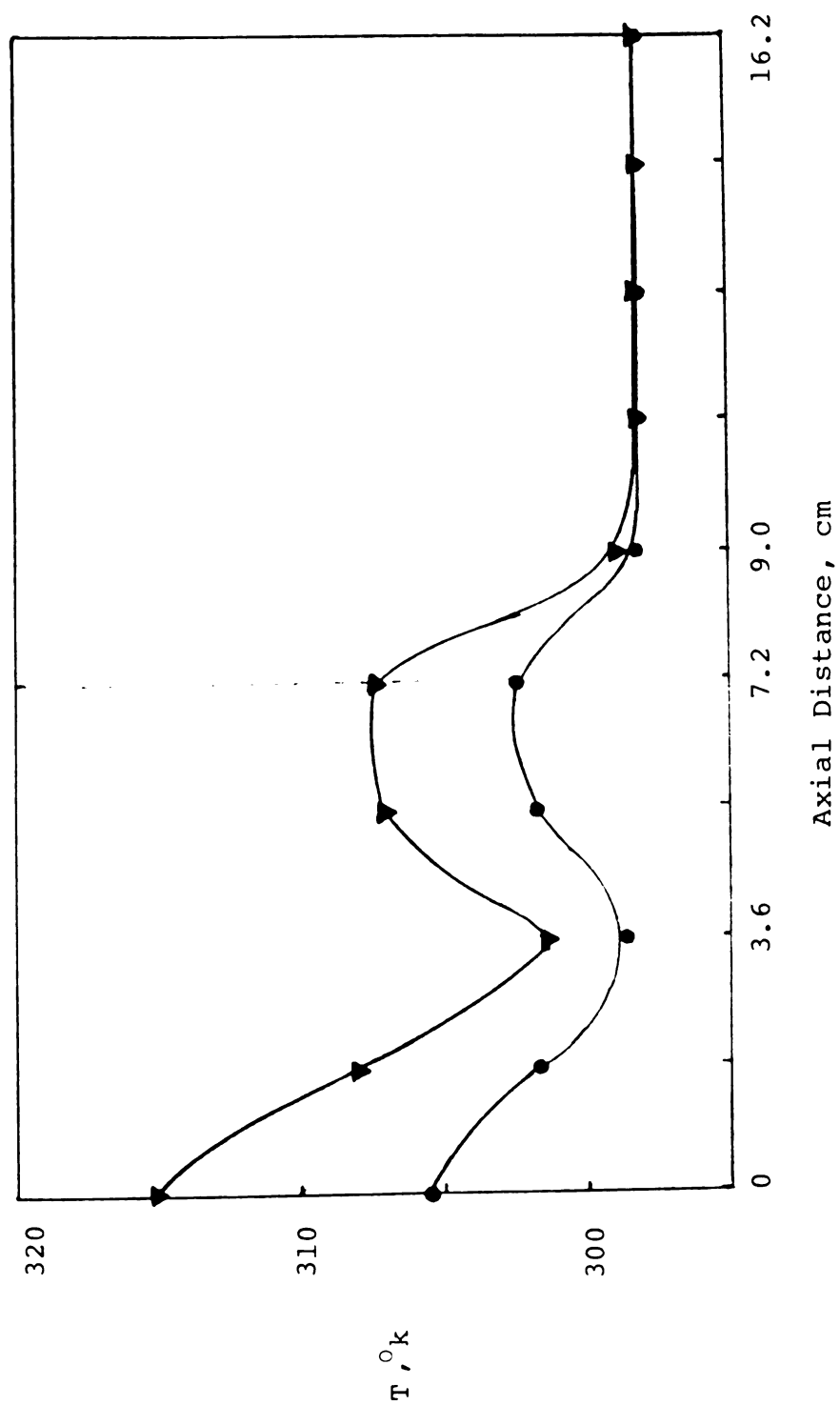


Figure 13. Temperature Distribution in Nylon Rod ($P_I = 1.0$ watts).

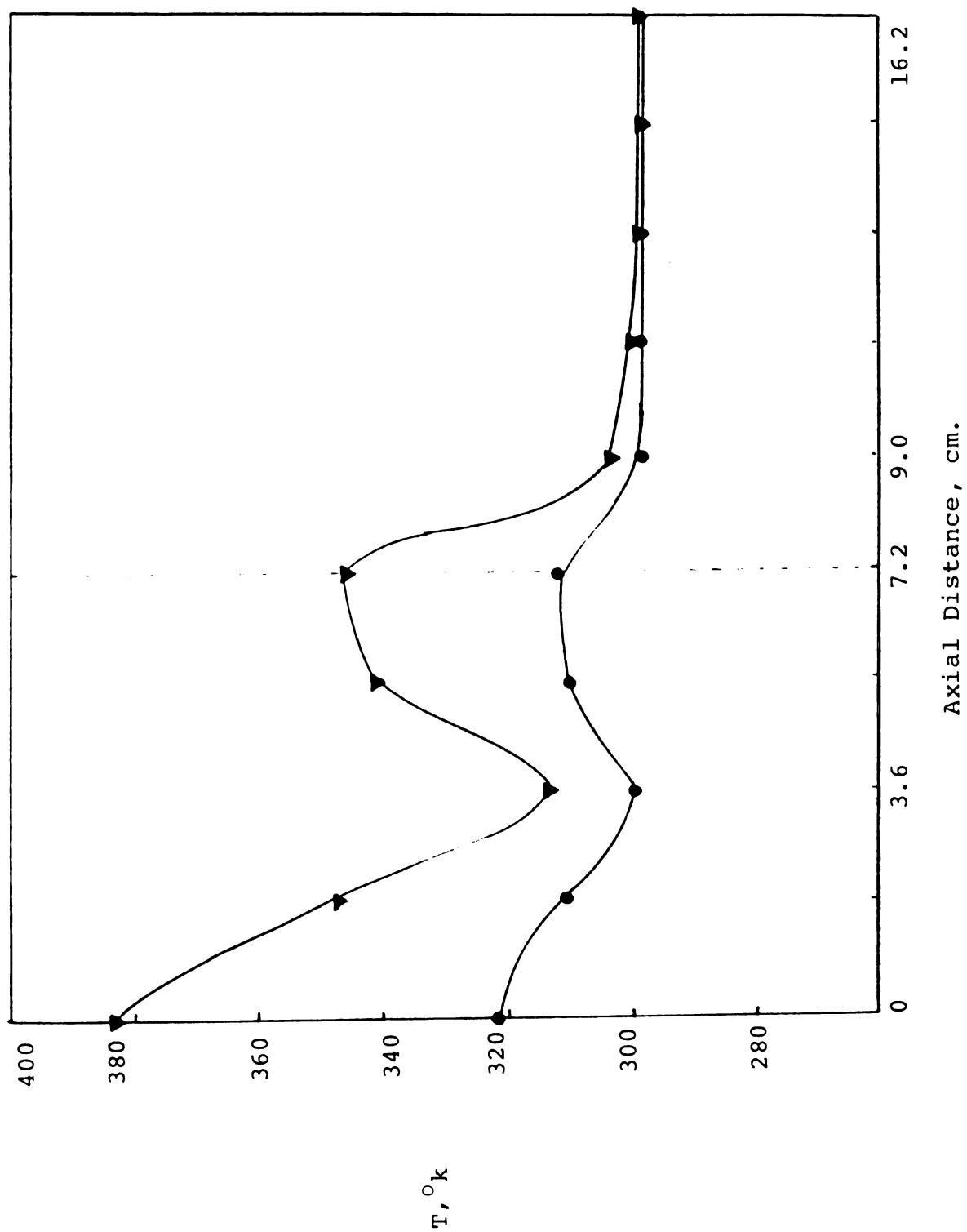


Figure 14. Temperature Distribution in Nylon Rod ($P_I = 3.0$ watts).

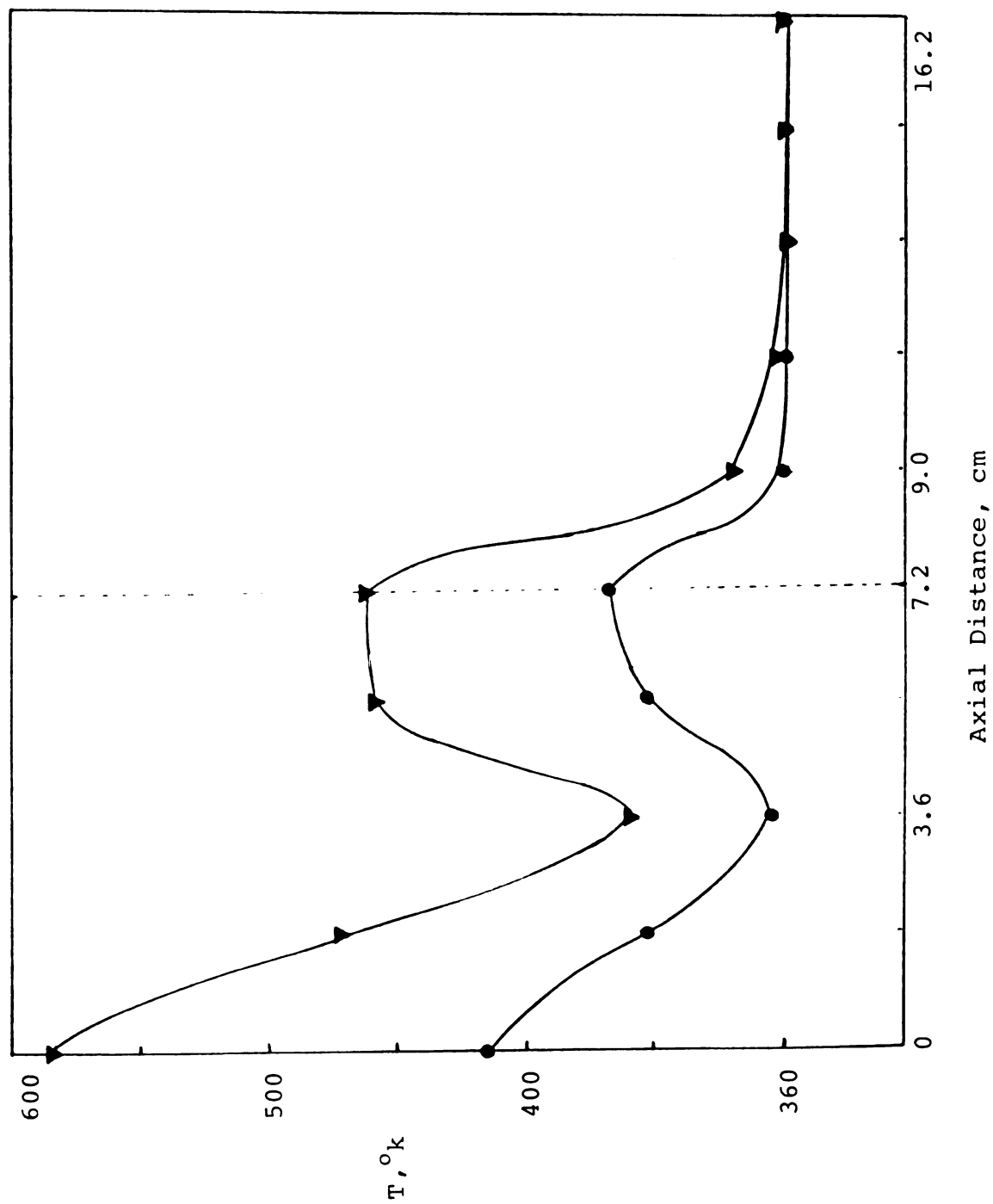


Figure 15. Temperature Distribution in Nylon Rod ($P_I = 10.0$ watts).

VII. Results and Discussion

Coupling efficiencies for various materials are presented in Table 11 and 12 along with values of their complex permittivities at room temperature. The results for nylon 66 and teflon are of course not directly comparable due to the larger diameters of those dielectrics (1.2 cm) as opposed to those of the liquids (0.45 cm). The most notable results are the coupling efficiencies for the solid systems. Coupling efficiencies for teflon range from 4% to 19%, which is higher than one would expect for such a lossless material ($\epsilon'' = 0.0002$).^[3] It is the large electric fields at the center of the resonant cavity in the TM_{012} mode which enable this high coupling to be accomplished.

Using the measured values of power absorbed per unit volume along with the literature values of ϵ'' in the equation.

$$P/V = \frac{1}{2} \omega \epsilon'' E^2$$

The values of E^2 at the cavity center for each material examined could be estimated. The fact that there is an obvious connection between these two parameters was the basis for a correlation developed and discussed in the previous section. Again, power absorbed depends on both the electric field in the dielectric and the

complex permittivities ϵ'' . A large value of one of the other leads to a high coupling efficiency.

Since ethylene glycol and propylene glycol have similar properties, a comparison of the experimental results for these two materials is in order. Both systems exhibit Debye relaxations and operate at approximately resonant conditions ($\omega \approx 1/\tau$), and both have similar values of ϵ' so that the ratio of their coupling efficiencies would be expected to correspond to the ratio of their complex permittivities. The difference in the ratios is well within experimental error.

Table 11

Material	Percent Power Absorbed	Power Absorbed, ω	Volume, cm^3	Power/ Volume ω/cm^3	ϵ''
Ethylene Glycol	90.0	1.350×10^{-3}	2.282	5.916×10^{-4}	14.6
Propylene Glycol	77.7	1.165×10^{-3}	2.282	5.105×10^{-4}	10.9
Polypropylene Glycol	23.7	3.554×10^{-4}	2.282	1.557×10^{-4}	.385
Nylon 66	51.1	7.664×10^{-4}	18.178	4.232×10^{-5}	0.0399
Teflon	18.6	2.783×10^{-4}	18.178	1.537×10^{-5}	0.0002

Table 12. Coupling Efficiencies at Varying Power Levels

Material	$1.5 \times 10^{-3} \omega$	1ω	3ω	$10 - 12 \omega$
Ethylene glycol	0.891	0.914	0.891	0.849
Propylene glycol	0.805	0.832	0.842	0.832 (12 ω)
Polypropylene glycol	0.247	0.247	-	0.247 (10 ω)
Nylon 66	0.533	0.533	0.600	0.833 (10 ω)
Teflon	0.040	—	—	0.040 (10 - 12 ω)

— Denotes measurement not taken

Looking at the values of the cavity Q for ethylene and propylene glycol at differing incident power levels, it can be seen that these species have resonant absorption peaks at or near the frequency of our apparatus ($\omega = 1.539 \times 10^{10}$ rad/sec). By interpreting increasing power level as increasing temperature one can see how absorption first increases then decreases with increasing temperature indicating the nearness of a resonant peak. Values of $\omega\tau$ for each system were estimated at various temperatures for each liquid using the ACT model and the calculated activator energies at 3940 kcal/mol for ethylene glycol and 4100 kcal/mol for propylene glycol. The results of this calculation are shown below. ($\omega = 1.539 \times 10^{10}$ rad sec⁻¹).

Table 13. Values of ω_T

$T, ^\circ K$	Et (OH) ₂	1, 2-Pr (OH) ₂
298	1.92	2.52
310	1.43	1.85
325	1.01	1.30
340	0.74	0.94
360	0.51	0.63

These values indicate that increasing temperature slightly can affect resonance sharply. The Q values for polypropylene glycol do not change as much with changing power levels. The resonance peak occurs at a much lower frequency so that the magnitude of change in $\omega\tau$ with temperature is slight at these frequencies.

The temperature field for the nylon 66 dielectric at differing power levels was determined numerically using an explicit method solution. Power absorbed increased sharply as temperature increased. The experimentally determined coupling efficiency for Nylon 66 ranged from approximately 50% for minimal power levels to around 80% for the highest power level used. Theoretically determined percent power absorbed is plotted versus time and compared to the measured power levels in Figure 16. It can easily be seen that the calculated values conform to the experimentally determined values within experimental error. As it turns out, the Q measurements for the nylon rod at differing power levels were probably not taken at steady states, as was implied earlier. All measurements were taken within ten minutes or so after the field was turned off, while it is estimated that the rod takes about 90

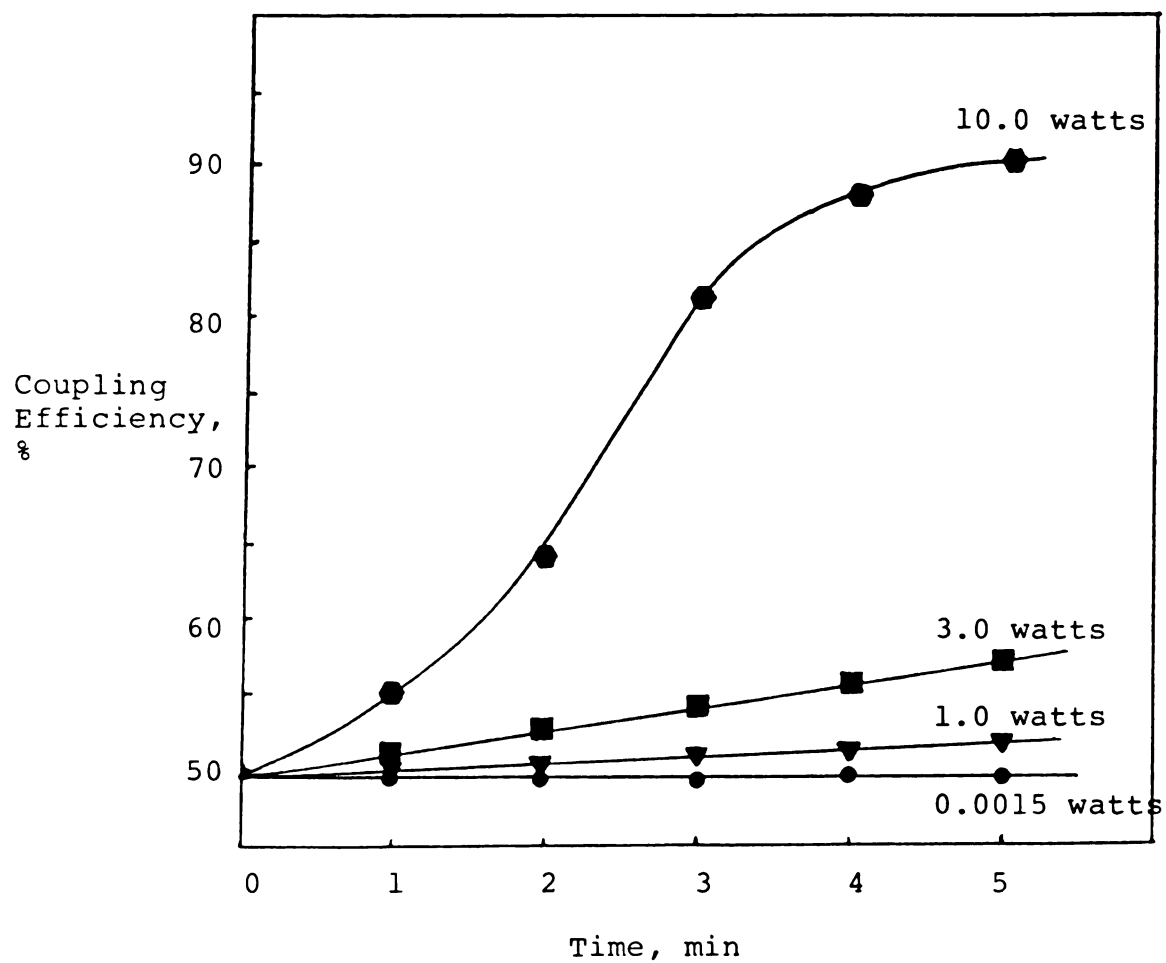


Figure 16. Dependence of Coupling Efficiency on time for varying incident power levels.

minutes to reach a steady state. These estimated steady state times were presented in a previous section. It should be commented that for the 10 watt measurement, it is fortunate that only ten minutes or so elapsed as the rod probably would have melted before too much longer.

VIII. Conclusions and Suggestions for Future Work

Several factors influence the absorption of microwave power by liquids and solids. The size of the dielectric, the temperature of the dielectric and its influence on ϵ' all affect the amount of power absorbed, along with the electric field strength. The temperature (and frequency dependency) of ϵ'' can be interpreted using the Arrhenius activation energy and activated complex theory. Coupling to materials of low ϵ'' is possible since the electric field at the cavity center in the TM_{012} mode is large.

Future investigations of these phenomena could include measurements of temperature outside the cavity at different axial and radial positions using thermocouples and inside the cavity using fluoroptic thermometry on the dielectric surface. The modeling already developed would be used to compare these measured temperatures to experiment. The modeling will be expanded not only to include a more detailed consideration of the electric fields in the cavity but also to determine the effect of more than one dielectric on the absorption. Also, a reaction term will be included to describe heat generation resulting from the curing of a thermosetting resin along with a material balance for the extent of curing of the resin. It is hoped that the modeling can be used to monitor

the extent of curing in order to be used to develop an automated, intelligent microwave processing system for the curing of thermosetting resins and composites.

APPENDIX A

Calculation of ΔH^* for H_2O

The following data was used to model the dielectric relaxation of H_2O at various temperatures and frequencies.

Table A1. ϵ' and ϵ'' for H_2O

Temperature °C	ϵ_0	ϵ_∞	ϵ''		
			$f = 3 \times 10^8 \text{ sec}^{-1}$	3×10^9	1×10^{10}
1.5	85.0	2.0	2.80	25.00	39.00
25	76.2	2.0	1.25	12.26	30.0
55	66.2	2.0	0.63	6.00	23.87
85	56	2.0	0.42	3.10	14.0

(Source - Ref. 3)

This data was used to find τ under various conditions using the Debye equation for ϵ'' with $\omega = 2 \pi f$.

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

Finding a τ for each temperature and frequency listed above, and averaging them, the following results for $\tau(^{\circ}C)$ were obtained along with the corresponding value of ΔH^* from the ACT expression.

Table A2. τ and $\Delta H^\ddagger$ at various temperatures

Temperature, $^\circ\text{C}$	$\tau \times 10^{12}$ sec	$\Delta H^\ddagger$ (kcal/mol)
1.5	15.05	2.43
25	8.34	2.34
55	5.32	2.34
85	3.73	2.37

These values of $\Delta H^\ddagger$ average out to 2.37 kcal/mol
(± 0.04 kcal/mol).

APPENDIX B

Finite Difference Equation for Laplace's Equation in Cylindrical Coordinates and FORTRAN Program for Temperature Field.

Laplace's equation for the temperature field in cylindrical coordinates without heat generation is: [29]

$$\nabla^2 T = \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} + \frac{\partial^2 T}{\partial z^2}$$

The finite difference form of this equation is:

$$\nabla^2 T = \frac{1}{r} \frac{(T_{i+i,j} - T_{i-1,j})}{2\Delta r} + \frac{(T_{i+1,j} + T_{i-1,j} - 2T_{i,j})}{(\Delta r)^2} + \frac{(T_{i,j+1} + T_{i,j-1} - 2T_{i,j})}{(\Delta z)^2}$$

If $\Delta r = \Delta z$, and $r = i\Delta r$, than

$$\nabla^2 T = \frac{1}{2i} (T_{i+1,j} - T_{i-1,j}) + \frac{(T_{i+1,j} + T_{i-1,j} + T_{i,j-1} + T_{i,j+1} - 4T_{i,j})}{(\Delta r)^2}$$

This equation will be used to evaluate how conduction affects the temperature field. This will be added to a term describing how power is absorbed and numerically integrated using a time increment of 5 seconds. Larger time step sizes were not effective as they resulted in oscillatory

solutions. Electric field (E_z) dependency was included by using a $(\cos^2 (\frac{2\pi z}{L}))$ term.

The program determines in turn:

- (1) Fraction power absorbed in reference volume.
- (2) Power absorbed in reference volume (PABS (I,J))
- (3) Conduction contribution (T COND (I,J))
- (4) Absorption contribution (T NEXT (I,J))
- (5) $\Delta T/\Delta t$ for each volume, and finally ΔT

Program reads as input data:

- (1) Frequency in megahertz. (2450 MHz)
- (2) Initial temperature (usually 25°C)
- (3) Incident power and ϵ'
- (4) Time step (5 sec) and heating time (60-120 min)

Program outputs at one minute intervals:

- (1) Percent power absorbed
- (2) Time in minutes
- (3) Temperature at intervals of 0.2 cm radially
1.8 cm axially

A copy of the program is included for reference.

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```

PROGRAM TFIELD1 (INPUT,OUTPUT,TAPE1=INPUT,TAPE2=OUTPUT)
DIMENSION T(5,80),TNEXT(4,82),TCOND(4,82),PABS(4,82)
READ (1,11) NUNIT
FORMAT (11)
DO 100 I=1, NUNIT
  READ (1,1) FMHZ
  FORMAT (F10.5)
  READ (1,2) TIME10
  FORMAT (F10.4)
  READ (1,3) PI10
  FORMAT (F10.5)
  READ (1,4) TOTFR,TIME17
  FORMAT (F10.4,F10.5)
  J=1
  DO 101 J=1, 80
    T(I,J)=TIME10+.01
    CONTINUE
  CONTINUE
  DO 102 I=1, 4
    IT=1, NUNIT
    DO 103 J=1, 82
      TCOND(I,J)=0
      IF (J.EQ.41) THEN
        TA=((2.144E-30)/T(I,J))*(EXP(24.1./T(I,J)))
        TB=((3.11E-11)/T(I,J))*(EXP(7.1./T(I,J)))
        TC=((3.4E-25)/T(I,J))*(EXP(427./T(I,J)))
        IF (T(I,J).LE.300.) THEN
          TA=0.
        ELSE
          TA=3.011E*((W*T1)/(1.+W*W*T1*TA))**.504)-
+3.911E*((W*.0003)/(1.+W*W*.0003*TA))**.504)
        ENDIF
        TB=.11E4*((W*TB)/(1.+W*W*TB*TB))**.031)
        TC=.21E3*((W*TC)/(1.+W*W*TC*TC))
        EPS=EA+EB+EC
        XL=.2*(J-41)
        FRAC=.12E3+FMHZ*(1./EP)**4.957)*EPS
        IF (FRAC.GE.1.0) THEN
          FRAC=1.
        ELSE
          CONTINUE
        CONTINUE WITH NO STATEMENT L FFL -- IGNORED
        IF (I.EQ.1) THEN
          PABS(I,J)=1. *FRAC*(PI/4.171)*(COS(.434E3*XL))**.5)
        ELSE
          PABS(I,J)=0.
        ENDIF
        IF (J.EQ.80) THEN
          IF (I.EQ.1) THEN
            TCOND(I,J)=.317E5*ISTEP*(1.*T(I+1,J)+2.*T(I,J-1)-4.*T(I,J))
          ELSE
            IF (I.EQ.4) THEN
              TCOND(I,J)=1.0E-1*TOTFR*(.1201E+(T(I-1,J)-T(I,J))-1.1247E*(T(I,J)-
+T(I+1,J))+.1242E*(T(I,J-1)-T(I,J)))
            ELSE
              TCOND(I,J)=.317E5*ISTEP*((1.-.5/(I-1))*T(I-1,J)+(1.+0.5/(I-1))*T
+(I+1,J)+2.*T(I,J-1)-4.*T(I,J))
            ENDIF
          ENDIF
        ELSE
          IF (I.EQ.1) THEN
            TCOND(I,J)=.317E5*ISTEP*(2.*T(I+1,J)+T(I,J-1)+T(I,J+1)-4.*T(I,J))
          ELSE
            IF (I.EQ.4) THEN
              TCOND(I,J)=2.0E-1*ISTEP*(.1201E*(T(I-1,J)-T(I,J))-1.1247E*(T(I,J)-
+T(I+1,J))+.1242E*(T(I,J-1)+T(I,J+1)-2.*T(I,J)))
            ELSE
              TCOND(I,J)=.317E5*ISTEP*((1.-.5/(I-1))*T(I-1,J)+(1.+0.5/(I-1))*T
+(I+1,J)+T(I,J-1)+T(I,J+1)-4.*T(I,J))
            ENDIF
          ENDIF
        ENDIF
        TNEXT(I,J)=T(I,J)+.024*ISTEP*PABS(I,J)+TCOND(I,J)
      CONTINUE
    CONTINUE
  CONTINUE
  DO 104 I=1, 4
    T(I,J)=TNEXT(I,J)
  CONTINUE
  IF (I.EQ.4) THEN
    IF (I.EQ.1) THEN
      TCOND(I,J)=.317E5*ISTEP*(2.*T(I+1,J)+T(I,J-1)+T(I,J+1)-4.*T(I,J))
    ELSE
      IF (I.EQ.4) THEN
        TCOND(I,J)=2.0E-1*ISTEP*(.1201E*(T(I-1,J)-T(I,J))-1.1247E*(T(I,J)-
+T(I+1,J))+.1242E*(T(I,J-1)+T(I,J+1)-2.*T(I,J)))
      ELSE
        TCOND(I,J)=.317E5*ISTEP*((1.-.5/(I-1))*T(I-1,J)+(1.+0.5/(I-1))*T
+(I+1,J)+T(I,J-1)+T(I,J+1)-4.*T(I,J))
      ENDIF
    ENDIF
  ENDIF
  TNEXT(I,J)=T(I,J)+.024*ISTEP*PABS(I,J)+TCOND(I,J)

```

```

IF (ABS(TNEXT(I,J))-T(I,J)).LE..1E-5) THEN
  II=1
ELSE
  II=1
ENDIF
ICONV=ICONV+1
CONTINUE
CONTINUE
IF (ITIME.EQ.10) THEN
  ITIME=1
  WRITE (6,1) ITIME,ICONV
  FORMAT (" ",1X,"TIME=",".13," MIN"         ICONV=",".13)
  PAESTOT=1
  DO 4-1 I=1,4
    DO 5-1 J=2,82
      IF (I.EQ.4) V=.0811
      IF (I.EQ.3) V=.1015
      IF (I.EQ.2) V=.15127
      IF (I.EQ.1) V=.16283
      PAESTOT=PAES(I,J)*V+PAESTOT
    CONTINUE
  CONTINUE
  PCTABS=(PAESTOT/PI)*200.
  WRITE (6,1) PI,PCTABS
  FORMAT (" ",1X,"INCIDENT POWER ","F10.5," WATTS ","F8.2," PCT ABS")
  DO 3-1 IWRITE=10,82,9
    WRITE (6,1) (TNEXT(I,IWRITE),I=,4)
    FORMAT (" ",1X,4(5X,F10.4))
  CONTINUE
ELSE
  CONTINUE
CONTINUE
CONTINUE WITH NO STATEMENT LABEL -- ICKOPE
ENDIF
DO 4-1 I=1,4
DO 4-1 J=2,82
T(I,J)=TNEXT(I,J)
CONTINUE
CONTINUE
CONTINUE
CONTINUE
CONTINUE

```

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