

DEVELOPMENT OF AN APPARATUS TO  
MEASURE THE THERMAL CONDUCTIVITY  
OF POLYMER MELTS

by

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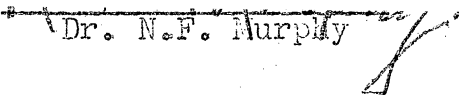
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## I. INTRODUCTION

Rapid technological development has resulted in an ever increasing demand for property data for a variety of working fluids, including polymeric fluids. Heat exchange plays an important part in the analysis of any process and the interpretation of research data. The knowledge of thermal conductivity is helpful in interpreting physical and chemical phenomena governing molecular transfer in liquids. As a result, during the past two decades, many investigations have been undertaken to further the understanding of the phenomena as well as the correct prediction of thermal conductivity of liquids.

Much information has been accumulated toward understanding thermal conductivity phenomena in simple liquids and liquid mixtures. Recent studies have broadened this information to include polymer solutions and homogeneous polymers at temperatures below their melting point. Very little investigation has been made, however, in determining the thermal conductivity of polymer melts, which is valuable in understanding and controlling polymer processing.

The purpose of this investigation was to select an appropriate method for measuring the thermal conductivity of polymer melts, design and construct a suitable apparatus, obtain thermal conductivity data for selected melts, and



attempt to relate the results to published results taken at temperatures below the melting points of the polymers.

## II. LITERATURE REVIEW

The following section contains a synopsis of published literature pertinent in the measurement of thermal conductivity of polymers. The most widely used methods for measuring thermal conductivity of materials are discussed along with limitations and advantages of the methods. This is followed by a brief discussion of previous results and postulated theories connected with thermal conductivity of polymeric materials.

### Experimental Methods for Determining Thermal Conductivity of Liquids

A system unaffected by a temperature gradient will be in thermal equilibrium and, thus, there will be no heat flux. However, if a system is perturbed from thermal equilibrium by a temperature gradient,  $\partial T / \partial x$ , the perturbation will be accompanied by a heat flux,  $Q$ , opposite to the gradient. This gives rise to the phenomenon of thermal conduction. The coefficient of thermal conductivity,  $\lambda$ , is then defined by Fourier's law

$$Q = - \lambda \frac{\partial T}{\partial x} \quad (1)$$

as the proportionality constant between the heat flux and

the temperature gradient. The law is assumed to be linear and McLaughlin<sup>(24)</sup> states that it is likely to hold for systems not far from thermal equilibrium, i.e., low thermal gradients.

To determine the thermal conductivity of fluids, conditions must be such that heat is transferred by conduction only.

Bulk motion or convection of the fluid must be absent or accurately accounted for. Under conditions of heat transfer by conduction only, with a small temperature difference,  $\lambda$  can be considered a constant<sup>(3,5)</sup>.

The energy equation, with the fundamental law of heat conduction (1), can be used to solve for the thermal conductivity of liquids. The general form of the differential equation for heat conduction without heat sources and sinks is given by

$$\frac{\partial T}{\partial \Theta} = \frac{\lambda}{c_p \rho} \cdot \nabla^2 T \quad (2)$$

where:

T = temperature

$\Theta$  = time

$\lambda$  = thermal conductivity

$c_p$  = heat capacity

$\rho$  = density

$\nabla^2$  = Laplacian operator.

Steady-state operation. For steady-state operation, the temperature at any point of a fluid system is independent of time and (2) reduces to the Laplace differential equation

$$\nabla^2 T = 0 \quad (3)$$

Solutions to this equation exist for the three coordinate systems in cases of one-dimensional heat conduction. Ziebland's<sup>(31)</sup> presentation of these solutions are;

1. Cartesian Coordinates - heat flow normal to the surfaces of two parallel, infinitely large plates

$$\lambda = \frac{Q L}{A (T_1 - T_2)} \quad (4)$$

where:

Q = normal heat flux

L = perpendicular distance between plates

A = surface area of plate

T<sub>1</sub> = upstream plate wall temperature

T<sub>2</sub> = downstream plate wall temperature.

2. Cylindrical Coordinates - heat flow radially between coaxial cylinders

$$\lambda = \frac{Q \ln r_2 / r_1}{2 \pi L (T_1 - T_2)} \quad (5)$$

where:

$r_2$  = outer cylinder radius

$r_1$  = inner cylinder radius

$L$  = inner cylinder length

$T_1$  = inner cylinder wall temperature

$T_2$  = outer cylinder wall temperature.

3. Spherical Coordinates - heat flow radially between concentric spheres

$$\lambda = \frac{Q (r_2 - r_1)}{4\pi r_1 r_2 (T_1 - T_2)} \quad (6)$$

where:

$r_2$  = outer sphere radius

$r_1$  = inner sphere radius

$T_1$  = inner sphere wall temperature

$T_2$  = outer sphere wall temperature.

An average value of  $\lambda$  can be obtained from these equations. Should the assumption of linear dependence between  $T$  and  $\lambda$  be inadmissible, the average thermal conductivity can be determined from<sup>(31)</sup>

$$\lambda = \frac{1}{(T_1 - T_2)} \int_{T_1}^{T_2} \lambda(T) dT \quad (7)$$

where:

$\lambda(T)$  = thermal conductivity at a particular temperature in the range  $T_1$  to  $T_2$ .

All three arrangements, flat plates<sup>(1,26)</sup>, concentric cylinders<sup>(29,31)</sup>, concentric spheres<sup>(6)</sup>, have been used with success.

Unsteady-state methods. All steady-state methods require careful experimentation to account for or eliminate heat losses, convective errors and geometric errors. In addition, should the apparatus have considerable mass, considerable time may be consumed in establishing steady-state. As a result, many investigators have attempted to design and use a transient-state device. In practice, these devices have been restricted to hot wire cells in which a change of temperature is observed in an electrically heated wire that is immersed axially in a fluid. The hot wire is contained in a cylindrical cell which is in thermal equilibrium. Suitable forms of this device have been used by Ball<sup>(2)</sup> and Falcao<sup>(12)</sup>.

Two basic means of measurement have been used in the unsteady-state, hot wire method for determining thermal conductivity. Both Ball<sup>(2)</sup> and Falcao<sup>(12)</sup> generated a time-dependent temperature field in a large volume of test fluid by continuously generating heat inside a solid body. The temperature gradient through the test specimen was measured continuously as a function of time. A different approach,

as discussed by Ziebland<sup>(31)</sup>, consists of generating heat for a short period of time in a large solid body. Heating is discontinued after the temperature of this body is raised a few degrees above the temperature of the heat receiving body, which is assumed to be constant. The temperature gradient between these two bodies is then measured as a function of time, giving the gradient over the test specimen.

#### Comparison of steady-state versus transient methods.

As previously mentioned, unsteady-state methods give faster experimental results than steady-state methods. Ziebland<sup>(31)</sup> points out that their chief disadvantage is that they are less accurate than steady-state methods. This is probably one of the main reasons why most of the experimental information accumulated on thermal conductivity of liquids has been obtained with steady-state methods.

#### Uncertainties in Thermal Conductivity Measurements

Without proper precautions in design and operation of apparatus, heat losses can lead to considerable error in results. Sugiyami<sup>(28)</sup>, for example, working with the guarded hot plate method, found that he could not obtain accurate temperature measurements due to heat losses. However, by careful placement of guard heaters on the apparatus, the heat flux can be made unidirectional. Two sources of error, radiation and convection, are invariably associated with all thermal conductivity measurements in fluids, but not necessarily in solids. Elimination

of these sources of error is extremely difficult. However, measures can be taken to reduce these and an experimental determination of their magnitude can be made. One additional error, geometric eccentricities, is present in the coaxial cylinder and concentric sphere methods. This type of error could also be present in the guarded hot plate method should the plates not be parallel. Proper design can reduce this error or allow the determination of its magnitude. These three sources of error are discussed below.

Radiation. Since this means of heat transfer depends on the molecular properties of the test fluid and the confining solid surfaces, it will always be present to some degree in thermal conductivity measurements. Measurement of thermal conductivity depends upon two surfaces being at different temperatures. Thus, radiation will occur between these surfaces. Eckert<sup>(8)</sup> is one of the investigators into this problem. His analysis of the problem in the simplest case is given below.

For a non-black body, the rate of radiant heat or energy emission is

$$Q_r = A e \sigma T_1^4 \quad (8)$$

where:

$Q_r$  = rate of heat emission

$A$  = surface area



$e$  = emissivity coefficient of the body

$\sigma$  = Stephan-Boltzmann constant

$T_1$  = absolute temperature of the body.

The rate of absorption of this energy by a receiving body or the surroundings is

$$Q_2 = A \alpha \sigma T_2^4 \quad (9)$$

where:

$Q_2$  = rate of energy absorption

$\alpha$  = absorptivity of the body

$T_2$  = absolute temperature of the body.

The net rate of heat exchange between the two bodies is then

$$Q_{r2} = A \sigma (e T_1^4 - \alpha T_2^4) \quad (10)$$

where:

$Q_{r2}$  = net rate of heat exchange

For most materials,  $\alpha$  and  $e$  are  $< 1$  and are approximately equal. By making  $\alpha = e = 1$ , the maximum radiant heat transfer would be obtained. For a small temperature difference between emitting and absorbing bodies,  $(T_1^4 - T_2^4)$  may be approximated

by  $4 T_m^3 \Delta T$ . Rearranging equation 10 yields

$$Q_{r2} = 4 A \sigma T_m^3 \Delta T \quad (11)$$

where:

$$T_m = \frac{T_1 + T_2}{2}$$
$$\Delta T = T_1 - T_2 \text{ if } T_1 > T_2.$$

Equation 5, that for radial heat conduction between coaxial cylinders, can be rearranged to read

$$Q = \frac{\lambda 2\pi L (T_1 - T_2)}{\ln r_2/r_1} \quad (12)$$

The ratio of heat transfer by radiation to heat transfer by conduction is then given by

$$Q_{r2}/Q = \frac{4 \sigma T_m^3 \ln r_2/r_1}{k} \quad (13)$$

where the area in equation 11 is given by the surface area of the inner cylinder in equation 12. Using equation 13, a measure of the significance of heat transfer by radiation can be obtained.

The above discussion concerning radiation effects upon heat conduction is valid only with a transparent, "non-participating" fluid. The effective emissivity of this type of fluid is 1.0, which means that it transmits all and absorbs

none of the radiant energy which it receives. Some materials, however, are semi-absorbent. Radiation calculations with a semi-absorbent material are more complex than with a transparent material. The emissivity and absorptivity depend on thickness of the sample, spectral wavelength and temperature<sup>(32)</sup>. It has also been shown<sup>(32)</sup>, that an upper limit of radiation effects can be found by assuming an emissivity of 1.0 if the actual emissivity cannot be determined.

Convection. Convective heat exchange is a hydrodynamic phenomenon and is caused by the bulk movement of portions of the fluid in or around the conductivity cell through excessive density gradients. In thermal conductivity measurements, only free convection, which results from gravity forces acting on a heated fluid of variable density, need be considered.

Hsu<sup>(17)</sup> has studied the problem of convective transfer of heat from a flat wall while Kraussold<sup>(20)</sup> studied the problem of convective heat transfer through liquids between coaxial cylinders. In their results, they showed that dynamic similarity considerations applied to the motion and energy equations yield two independent, dimensionless groupings of pertinent variables. These are the Grashof number

$$N_{Gr} = \frac{g B \rho^2 \Delta T d^3}{\nu^2} \quad (14)$$

and the Prandtl number

$$N_{Pr} = \frac{\nu C_p}{k} \quad (15)$$

where:

$N_{Gr}$  = Grashof number

$g$  = local gravitational acceleration

$B$  = bulk coefficient of volume expansion  
(evaluated at some reference temperature)

$\rho$  = fluid density

$\Delta T$  = temperature gradient(driving force)

$d$  = characteristic linear dimension

$\mathcal{U}$  = coefficient of viscosity

$N_{Pr}$  = Prandtl number

$C_p$  = constant pressure heat capacity

$k$  = thermal conductivity.

Kraussold<sup>(20)</sup> also pointed out that the Grashof number can be thought of as a relative measure of buoyancy to viscous forces, while the Prandtl number is a measure of the ratio of momentum to energy diffusivity. The ratio of apparent conductivity to the true molecular conductivity was found to be a function of the product of the Grashof and Prandtl numbers, commonly called the Rayleigh number

$$N_{Ra} = N_{Gr} N_{Pr} \quad (16)$$

where:

$N_{Ra}$  = Rayleigh number.

It was stated<sup>(20)</sup> that for coaxial cylinders, a value of

$$N_{Ra} < 1000$$

insures that convection is either negligibly small or comp-

pletely absent. Determinations made under these conditions yield true molecular conductivity. Tsederberg<sup>(29)</sup> feels that a more conservative estimate, such as

$$N_{Ra} < 700$$

insures determination of true molecular conductivity. Crosser<sup>(7)</sup> found that for the guarded hot plate method, true molecular conductivity could be obtained when

$$N_{Ra} < 1700.$$

These criterion can give an estimate of convection effects only if there are no additional effects, such as eccentricity or multidimensional heat flow. No author whose work was reviewed in this investigation has proved that his system is free of convective effects or that his system was one of pure conduction. It was suggested<sup>(11)</sup> that to demonstrate that pure conduction exists, the heat flux should be plotted as a function of the temperature difference. For pure conduction, a straight line which passes through the origin should result.

Eccentricity. When using the coaxial cylinder or concentric sphere methods, the axis, or center, of the inner body should coincide with that of the outer body. Should the axes not coincide, Ziebland<sup>(31)</sup> reports that experimentally determined values of  $\lambda$  or  $k$  will be high when using the

coaxial cylinder method. Should eccentricity be present, the equation for the coaxial cylinder method

$$\lambda = \frac{Q \ln r_2/r_1}{2 \pi L (T_1 - T_2)}$$

would be incorrect. In this case, Ziebland presents a modified equation

$$\lambda = \frac{Q \ln \frac{\sqrt{r_1^2 [(r_2/r_1)+1]^2 - b^2} + \sqrt{r_1^2 [(r_2/r_1)-1]^2 - b^2}}{\sqrt{r_1^2 [(r_2/r_1)+1]^2 - b^2} - \sqrt{r_1^2 [(r_2/r_1)-1]^2 - b^2}}}{2 \pi L (T_1 - T_2)} \quad (17)$$

where:

b = misalignment factor (normal distance between the two axes).

This correction applies to translation of the cylindrical axes only. No proposal is given for deviation of one or both axes from the vertical.

Comparison of steady-state methods in terms of experimental uncertainties. Ziebland<sup>(31)</sup> presents a critique of the most widely used methods of thermal conductivity measurements. In any method, some small portion of the total heat generated will not flow along the prescribed path. The precision to which this heat loss can be controlled or calculated is one means for choice of methods. Another factor which must be considered is range of operating conditions.

In evaluating the three steady-state methods as to expected error, the guarded hot plate method has smallest eccentricity error but heat losses are much greater than for the other two methods<sup>(7)</sup>. Concentric sphere and coaxial cylinder methods are comparable in terms of heat losses but geometric eccentricities in the concentric sphere method are greater.

In summary, Ziebland proposes that the coaxial cylinder method offers advantages of versatility to operating conditions and nature of fluids tested. He further states that this method is superior to the hot wire, unsteady-state method, because of higher precision.

Theory of Thermal Conductivity  
of Polymers

There exist two basic categories into which known theories of thermal conductivity of condensed matter can be divided. One category<sup>(13)</sup> consists of theories of quantized lattice vibrations, whereby the resistance to thermal energy transport is analyzed in terms of photon scattering. Alternatively, there are the liquid-state theories, as proposed by Horrocks and McLaughlin<sup>(16)</sup>. These analyses are based on a model of liquid structure in which each molecule vibrates about a mean equilibrium position, colliding and exchanging energy with nearest neighbor molecules.



Hanson and Ho<sup>(13)</sup> point out that although these theories are well suited to simple low molecular weight compounds, they are inadequate for larger molecules. In the case of polymer molecules, the existing theories do not include features which consider the effect of molecular weight and molecular orientation.

Proposed theory of thermal conductivity for linear amorphous high polymers. Hanson and Ho<sup>(13)</sup> have proposed a theory of thermal conductivity for linear polymers. It considers the fact that a segment of an amorphous linear polymer mass has two kinds of nearest neighbors. It has two neighbors on the same molecule to which it is chemically bonded. In addition, this segment is surrounded by other segments on other molecules. It is bonded to these segments only by secondary forces. Each segment interacts or collides with its nearest neighbors but the frequency with which it collides with chemically bonded neighbors differs from that with secondary bonded neighbors.

It is assumed that the energy transferred in each interaction is proportional to the energy difference between the interacting segments.

For a reasonably small energy flux range, the energy transferred can be linearly related to temperatures. Assuming a linear temperature gradient, these fluxes can be a simple function of temperature gradient and position.

With these assumptions, the thermal conductivity of the polymer can be found by

$$\lambda = (C_s \sqrt{V_1} P_1 / 2 (V^{2/3}) N) \sum_{i=1}^N Q_i' \quad (18)$$

where:

- $C_s$  = heat capacity per segment
- $\sqrt{V_1}$  = frequency of interaction between neighboring segments on the same molecule
- $P_1$  = proportionality factor
- $V$  = volume occupied by a segment
- $N$  = number of segments
- $Q_i'$  = energy flux through segment  $i$ .

Difficulties lie first in the fact that all molecules in a polymer are not equivalent, so it is required to average over many molecules. Secondly,  $\sqrt{V_1} P_1$  is not known and Hanson and Ho<sup>(13)</sup> present no method for calculating them.

Thermal conductivity of polymers below melting point.

Many studies have been made of thermal conductivity of thin film, solid state, polymer structures as a function of temperature. Anderson<sup>(1)</sup> and Kline<sup>(18)</sup> report that the thermal conductivity of an amorphous substance below the glass transition temperature should remain the same or increase as the temperature increases. In his study, made over a temperature range of 25°C to 85°C, Anderson reports the following results for ten amorphous polymers:

25°C:  $\lambda = 0.12$  to  $0.18$  kcal/m hr °C

85°C:  $\lambda = 0.14$  to  $0.21$  kcal/m hr °C.

In most cases,  $\lambda$  increased linearly with increased temperature. It was proposed<sup>(13,30)</sup> that the increase was due to increased segmental mobility in the polymer chains. Another factor which could offset or reverse this trend is the chain-to-chain density reduction which occurs with increasing temperature.

In the temperature range studied, the thermal conductivity of crystalline polymers was higher than for amorphous polymers. However, a decrease in thermal conductivity with increasing temperature was indicated for crystalline polymers. Hanson and Ho<sup>(13)</sup> proposed that this decrease with increase in temperature was due to breakup of the crystalline portions of the polymer. Since the present study is concerned with polymer melts which would be amorphous in structure, no further discussion of crystalline polymer thermal conductivity will be made.

Other investigators<sup>(9,14,19,27)</sup> have found a discontinuity in the thermal conductivity of polymers at the glass transition temperature. Hattori<sup>(14)</sup> proposed that this discontinuity could be attributed to the increase of inner mobility of polymer molecules from micro-Brownian motion. Through this micro-Brownian motion, the thermal conductivity is lowered, thus offsetting the weak increase with temperature.

Through experimental results, various authors have postulated effects of structure on the thermal conductivity of polymer films. Hattori<sup>(15)</sup> reports that, for like structures, the higher the density, the higher the thermal conductivity. His results were obtained with low pressure and high pressure polyethylene.

Increasing the size of any substituent connected to a hydrocarbon chain, or backbone, introduces increasing disorder and decreasing thermal conductivity. Polyethylene, which contains only a hydrogen as a substituent, has a higher thermal conductivity than either polyvinyl chloride or polystyrene. This was verified by Hattori<sup>(14)</sup>, whose results at approximately 50°C were:

polyethylene:  $\lambda = 8.0 \times 10^{-4}$  cal/cm sec °C

polyvinyl chl.:  $\lambda = 3.5 \times 10^{-4}$  cal/cm sec °C

polystyrene:  $\lambda = 2.7 \times 10^{-4}$  cal/cm sec °C.

He further determined that conductivity along the main polymer chain is higher than that between chains, thus higher molecular weight means higher thermal conductivity. Using two samples of polyvinyl chloride, he found that a sample whose molecular weight was 1300 had a value of

$$\lambda = 3.5 \times 10^{-4} \text{ cal/cm sec } ^\circ\text{C}$$

whereas one with a molecular weight of 1000 had a value of

$$\lambda = 3.1 \times 10^{-4} \text{ cal/cm sec } ^\circ\text{C.}$$

These values were determined at 50°C. The trends as a function of temperature for these two samples were alike.

Ueberreiter<sup>(30)</sup> reported the same results using polystyrene. He postulated that, in a substance with shorter chains, a larger number of energy transactions must take place between molecules and the thermal conductivity must be lower.

These results were obtained for polymers below their melting points. There is a lack of experimental data for thermal conductivity of polymer melts. Lohe<sup>(22)</sup> investigated the effect of temperature on the thermal conductivity of polystyrene and Nylon 6 above the glass transition temperature. His results showed a slight decrease in thermal conductivity of polystyrene with increasing temperature. He found the thermal conductivity of a Nylon 6 melt to be independent of temperature. In connection with these results, Eiremann and Hellwege<sup>(10)</sup> point out that good thermal contact at the surface of the sample is decisive to accurate results.

None of the articles reviewed contained information as to the differentiation between entangled and oriented polymer chains. Therefore, the published results cannot be categorized according to this property.

### III. EXPERIMENTAL

The following section contains the purpose of this investigation, the plan of experimentation, and the results obtained.

#### Purpose of Investigation

The purpose of this investigation was to develop an apparatus to measure the thermal conductivity of polymer melts. Following design and construction, the apparatus was to be used to measure the thermal conductivity of selected polymer melts as a function of temperature and attempt to relate the results to those for similar polymers at temperatures below their melting point.

#### Plan of Experimentation

The plan of experimentation for this project consists of selection of experimental method, design and fabrication of apparatus, collection of data and evaluation of experimental results.

Selection of experimental method. The various known methods for measuring thermal conductivity of liquids were studied and the steady-state, absolute, concentric or coaxial cylinder method was chosen. The choice was made with consideration of the following:

1. Steady-state methods yield more accurate and reproducible results than unsteady-state methods.
2. The flat plate steady-state method was eliminated because of heat losses from end effects. A large portion of these can be eliminated by use of guard heaters. However, guard heaters can be used more effectively in the coaxial cylinder method.
3. The steady-state, concentric sphere method requires no guard heaters. However, construction is more difficult as eccentricities are harder to eliminate or predict.

Description of apparatus. A brief description of the apparatus used to measure the thermal conductivity of polymer melts is given here. A more detailed description of the apparatus is given in Appendix A, page 64 .

The apparatus used to measure the thermal conductivity of polymer melts is shown schematically in Figure 1 , page 25. The equipment consisted of an externally heated melt cylinder, a concentric cylinder thermal conductivity cell, temperature and heat input measuring equipment(not shown in Figure 1 ), necessary piping, and a vacuum pump.

The cylindrical portion of the melt cylinder was constructed from ferrous pipe while the piston was made from aluminum. The seal between the piston and cylinder was made with O-rings which were positioned on the piston as shown in Figure 2 , page 26 . Heat input to the melt cylinder

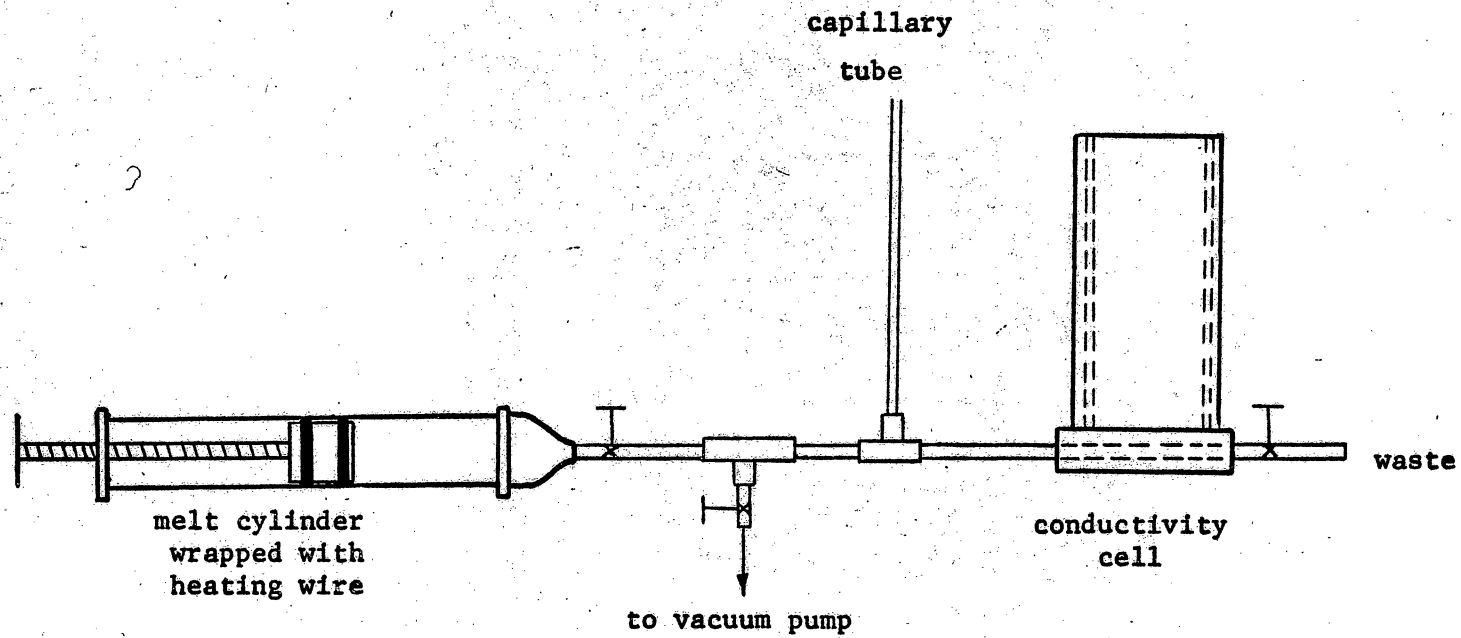


Figure 1 Schematic View of Melt Cylinder and Measuring Cylinder Indicating Melt Transport Medium



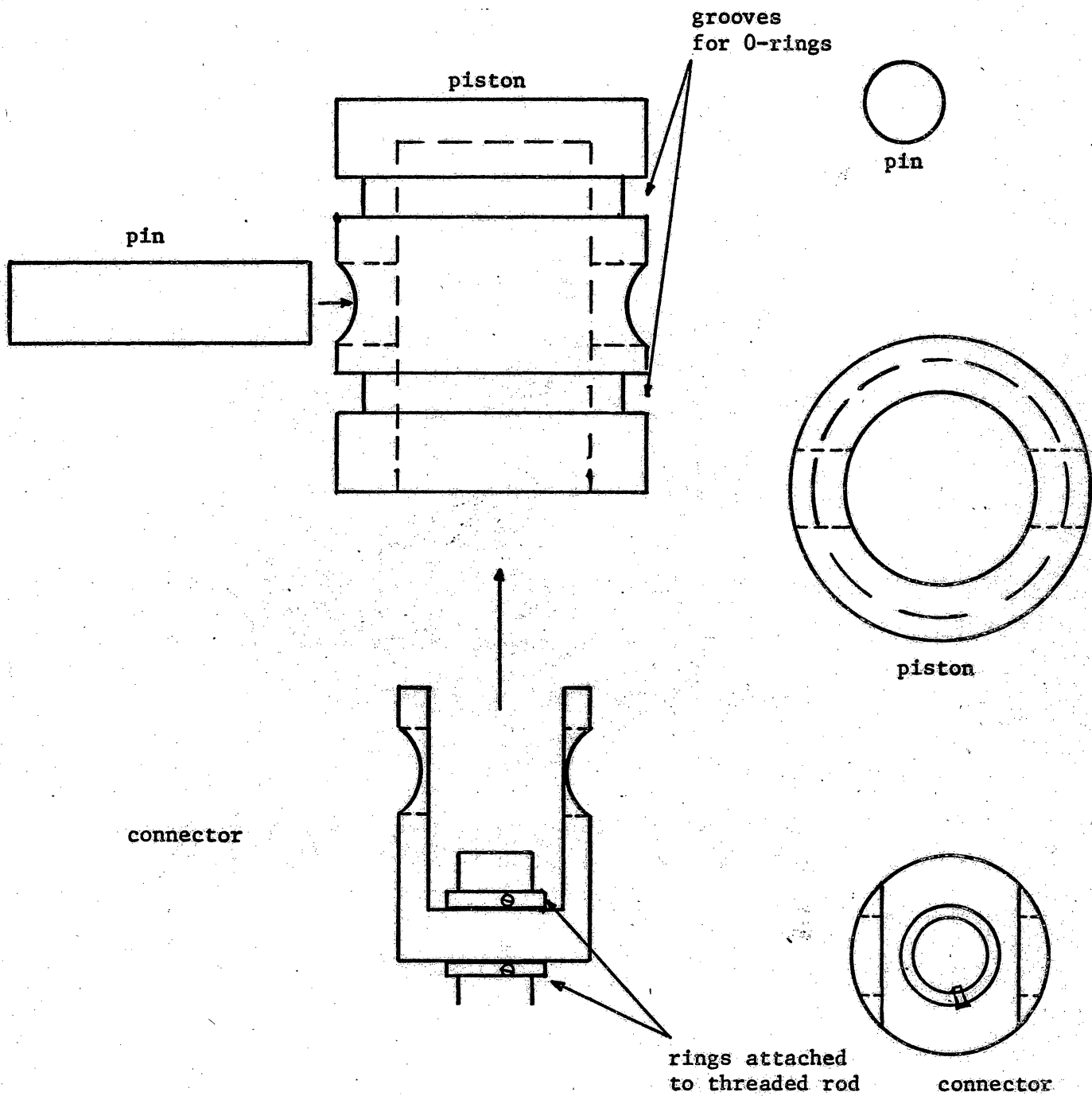


Figure 2 Piston For Melt Cylinder

was provided by resistance wire which was coiled around the melt cylinder. The heat input was controlled by a variac voltage regulator. As shown in Figure 1, movement of the piston was provided by a threaded rod which was connected to the piston. The threads, through which the rod was threaded, were located on a flange at one end of the melt cylinder.

The thermal conductivity cell consisted of three concentric cylinders with insulation as the outermost cylinder. The innermost cylinder was made from Type 316 stainless steel and consisted of three portions which were stacked vertically. Cylindrical cartridge heaters were centered axially in each of these portions, and served as the source of heat for the conductivity cell and guard heaters. The critical, or measuring portion, of the innermost cylinder was the middle portion. The upper and lower portions served as guard cylinders whose purpose was to prevent axial heat loss.

Concentric with the inner cylinder was an outer cylinder made from Type 316 stainless steel pipe. The annular gap between these two cylinders (0.075 inches) contained the polymer melt during experimentation. The outermost cylinder, insulation, was wrapped tightly around the stainless steel pipe to provide radial insulation and reduce the radial temperature gradient. This insulation was made from a magnesia-asbestos mixture, glass wool and asbestos tape.

Temperature measurements were made with calibrated, differential, iron-constantan thermocouples. A total of

seventeen thermocouples were used. These were used for thermal gradient determination, axial heat loss minimization, and melt cylinder wall temperature determination, if needed. Thermocouple positions in the conductivity cell are indicated in Figure 3 , page 29 .

The temperature measurement portion of the apparatus is shown in Figure 4 , page 30 . A multiple position switch comprised a portion of this equipment. Using this switch, a common cold junction could be used for all thermocouples. Further description of the temperature measuring equipment, including calibration procedures, are given in Appendix E, page 93 .

Heat input to the measuring cylinder was read directly from a wattmeter which comprised a portion of the electrical system as shown in Figure 5 , page 31. Input alternating current and voltage to the guard heaters was measured and used as a rough means of minimizing axial heat loss. The input power to each heater was controlled by variac voltage controllers as shown in Figure 5.

Experimental procedure. Only a brief description of the experimental procedure is given here. A more detailed description of the experimental procedure is given in Appendix B, page 78 .

The basic approach to obtaining thermal conductivity information was to determine a radial temperature gradient through the concentric stainless steel cylinders, and thus,

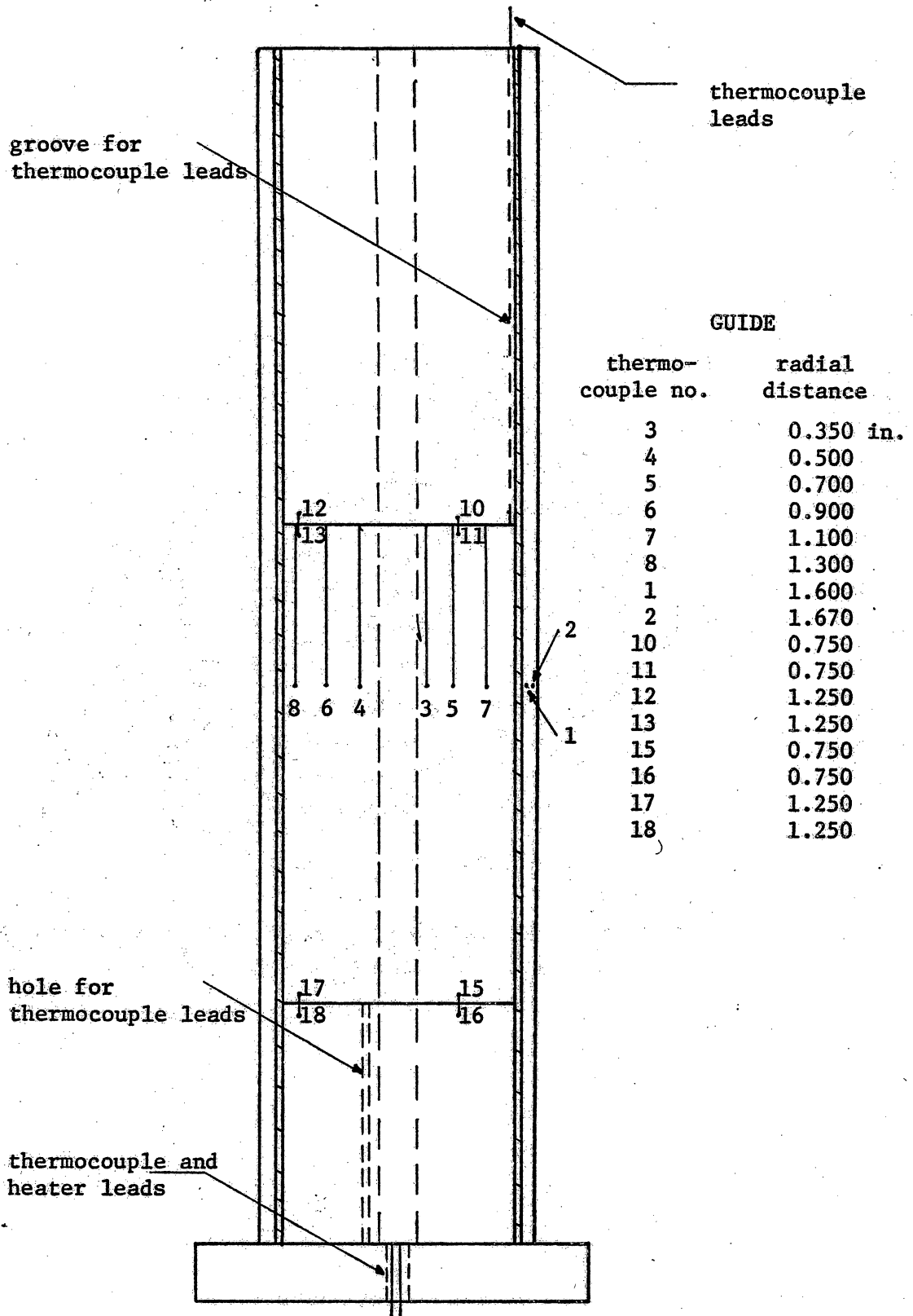


Figure 3 Schematic View of Measuring Cylinder Indicating Thermocouple Placements

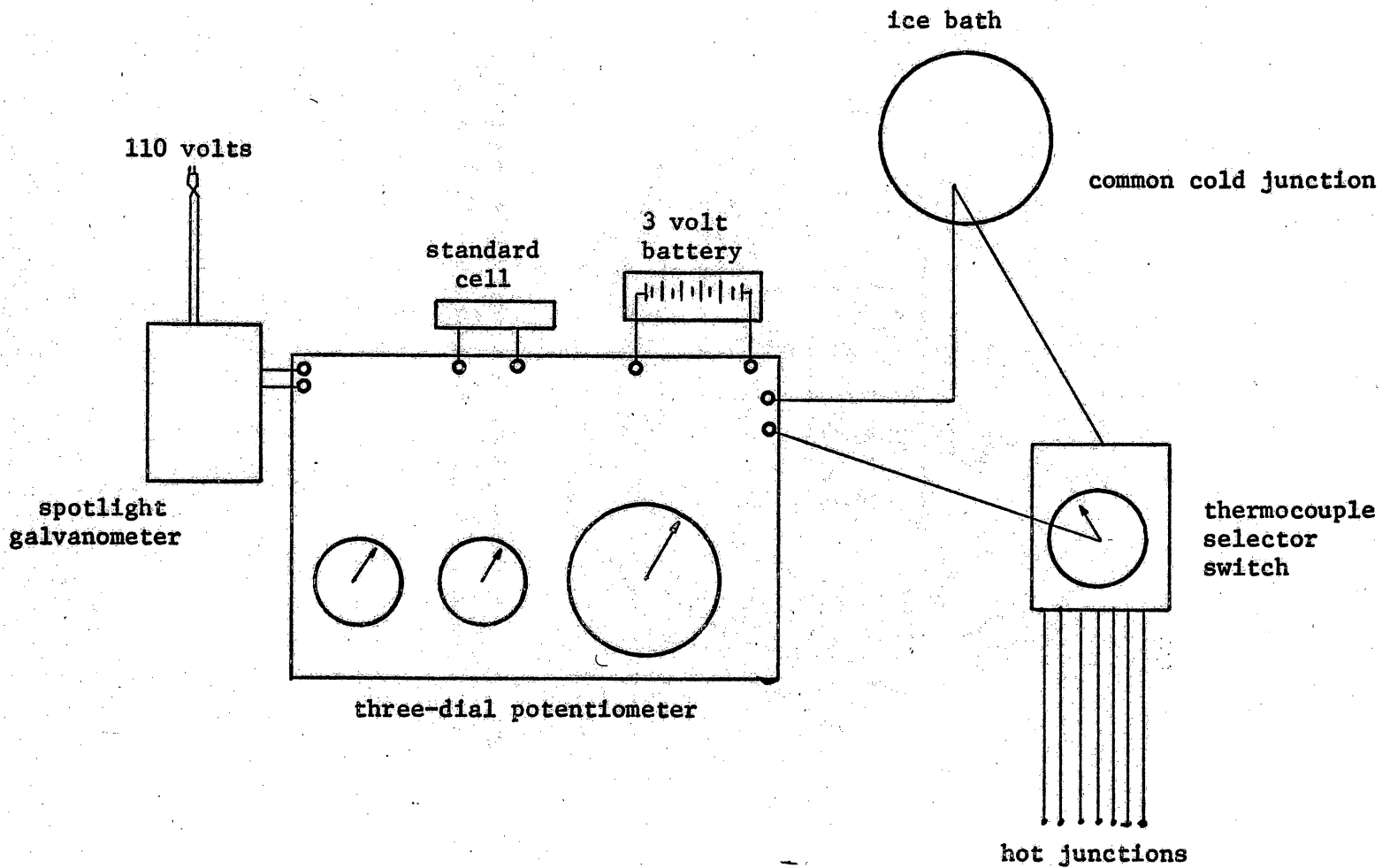


Figure 4 Potentiometer Circuit

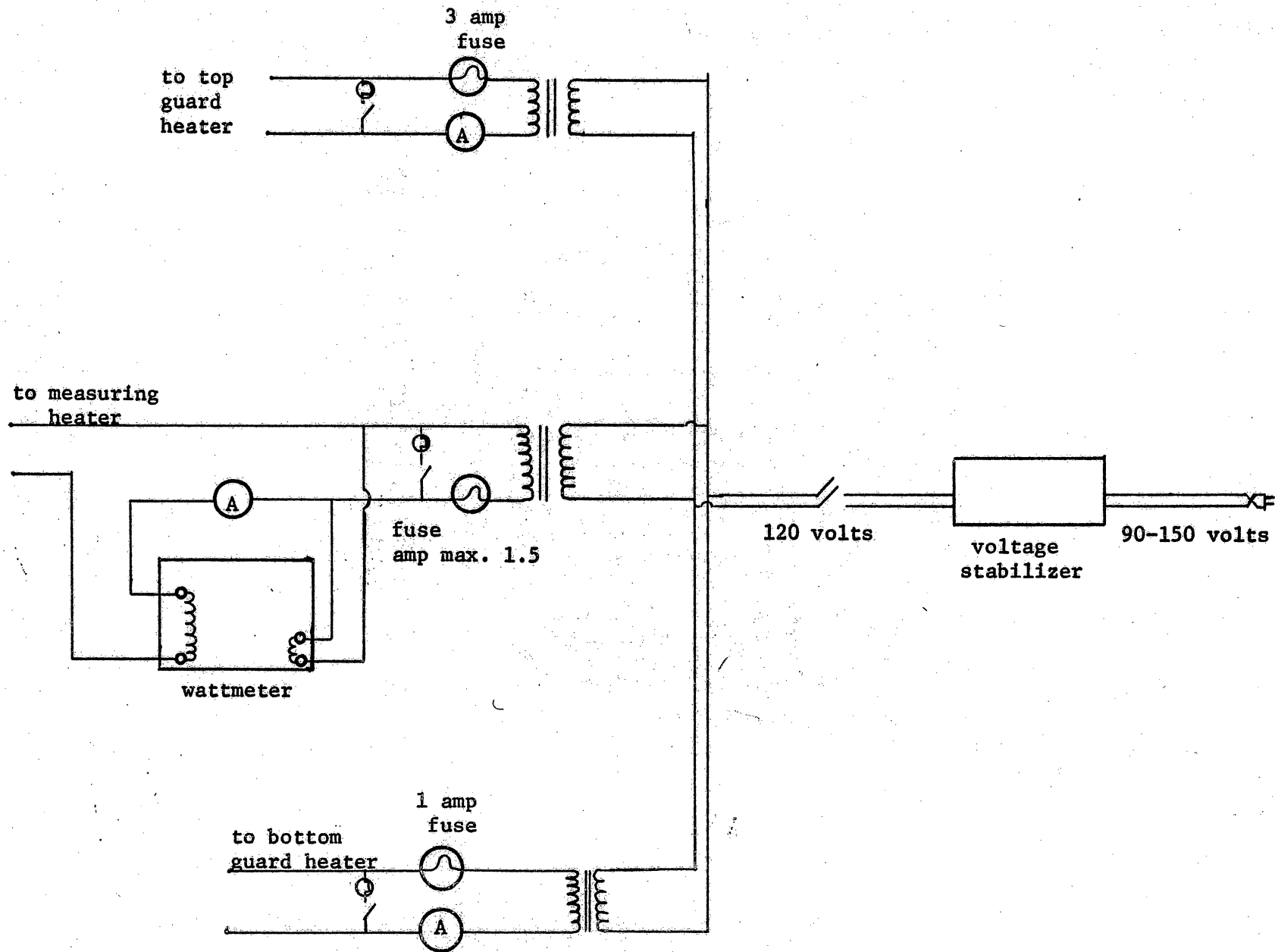


Figure 5 Alternating Current Circuit Used To Regulate Power To Measuring Cylinder Heaters

the temperature gradient through the medium in the gap between them. Then, knowing the heat input, the thermal conductivity could be determined. To obtain the thermal gradient, temperatures along a radial line from the vertical axis of the coaxial cylinders were measured.

For each test material, thermal conductivity information was to be obtained at four or five temperature levels. The temperature level inside the measuring apparatus could be raised or lowered by increasing or decreasing cartridge heater wattage. The initial objective was to determine thermal conductivity of melts within a 50 degree Centigrade range just above the melt temperature. This objective was not followed through exactly during experimentation.

### Results

Using the radial temperature profile data and a least squares<sup>(4)</sup> method of fitting a straight line to a series of points, the thermal gradient through the inner stainless steel cylinder was obtained. The temperature on the outer wall of this cylinder was obtained by extrapolation of the thermal gradient to the outer wall. The least squares method was not required to determine the temperature profile through the outer stainless steel cylinder. The temperature at only two radial points was measured in this cylinder and the temperature profile was simply a line through these two

points. The temperature on the inner wall of this outer cylinder was obtained from extrapolation of the temperature profile.

With these wall temperatures known, the temperature drop across the annular gap separating the two cylinders could be determined. With this information, the heat input, cylinder geometry information and equation 5, the thermal conductivity of the test material could be calculated. Information as to thermal conductivity dependence upon temperature was to be gathered. For this purpose, the test material temperature was taken as the arithmetic mean of the inside wall temperature and the outside wall temperature.

Experimentally determined thermal conductivity values are presented in the units of BTU/ft. hr. °F. These are the units most commonly encountered. However, the thermal conductivities of materials found in references for this investigation are given in the units cal./cm. sec. °C. The conversion between these is

$$241.9 \text{ BTU/ft.hr.}^{\circ}\text{F} = 1 \text{ cal./cm.sec.}^{\circ}\text{C.}$$

This conversion can be used to standardize units such that experimental values may be related quantitatively with reference values.

Preliminary testing. The apparatus was first checked for accuracy using glycerine as a test fluid. The thermal conductivity of glycerine(100 percent) was given as a constant at 0.164 BTU/ft.hr.°F. from room temperature to approximately



130°C<sup>(23)</sup>. The results obtained from these tests are given in Table I, page 35. As shown in Table I, the temperatures considered were within the temperature range over which the thermal conductivity of glycerine is considered to be constant. The Rayleigh number for glycerine in this temperature range is about 30, which is well below the limit for convection to be significant.

Thermal conductivity of vinyl melts. The thermal conductivity of four vinyl melts was determined at different melt temperatures. The four melts tested were Dupont Alathon (low density polyethylene), Phillips Marlex 6002 (high density polyethylene), Dow Styron (polystyrene) and Enjay Escon (polypropylene). The results from these tests are presented in Tables II and III, pages 36 and 37, respectively. The thermal conductivity of each of these vinyl melts is plotted as a function of average melt temperature in Figure 6, page 38. A straight line as determined by a least squares technique was fit to the data points for each polymer melt tested.

Thermal conductivity of nylon melts. The thermal conductivity of Dow-Badische (Nylon 6) and Dupont Zytel (Nylon 6-10) were determined at different melt temperatures. The results from these tests are presented in Table IV, page 39. The thermal conductivity of these nylon melts is plotted as a function of average melt temperature in Figure 7, page 40. As with the vinyl melts, the straight lines through the data points was determined by a least squares technique.

TABLE I

Results from Preliminary Thermal Conductivity Experiments  
with Glycerine as Test Fluid  
 ( $\ln r_2/r_1 = 0.0497$ ,  $L = 6$  in.)

Test No.	$T_i$ °C	$T_o$ °C	$\Delta T$ °C	$T_{av}$ <sup>a</sup> °C	Q watts	$Q_r$ watts	$Q_c$ watts	k BTU/ft hr° F
1	83.81	82.40	1.41	83	9.0	0.10	8.90	0.1892
2	103.50	100.80	2.70	102	13.0	0.24	12.76	0.1418
3	127.58	124.80	2.78	126	17.0	0.31	16.69	0.1801

<sup>a</sup> to nearest °C

TABLE II

Results from Thermal Conductivity Experiments with  
Low Density Polyethylene and High Density Polyethylene

( $\ln r_2/r_1 = 0.0497$ ,  $L = 6$  in.)

Material	Test No.	$T_i$ °C	$T_o$ °C	$\Delta T$ °C	$T_{av}$ <sup>a</sup> °C	Q watts	$Q_r$ watts	$Q_c$ watts	k BTU/ ft hr° F
Dupont Alathon (low dens.) P.E.	1	185.03	179.10	5.93	182	24.8	1.13	23.67	0.1197
	2	238.83	232.80	6.03	235	33.8	1.77	32.03	0.1594
	3	270.74	263.30	7.44	267	40.5	2.80	37.70	0.1520
	4	309.06	302.00	7.06	306	47.0	3.51	43.49	0.1848
Phillips Marlex (high dens.) P.E.	1	167.19	162.10	5.09	165	23.0	0.81	22.19	0.1308
	2	186.74	180.70	6.04	184	26.0	1.16	24.84	0.1235
	3	201.92	196.60	5.32	200	28.5	1.11	27.39	0.1544
	4	220.13	214.80	5.33	218	31.0	1.37	29.63	0.1669
	5	238.29	232.90	5.39	236	33.0	1.60	31.40	0.1748

<sup>a</sup> to nearest °C

TABLE III

Results from Thermal Conductivity Experiments with  
Polystyrene and Polypropylene  
 (ln r<sub>2</sub>/r<sub>1</sub> = 0.0497, L = 6 in.)

Material	Test No.	T <sub>i</sub> °C	T <sub>o</sub> °C	ΔT °C	T <sub>av</sub> <sup>a</sup> °C	Q watts	Q <sub>r</sub> watts	Q <sub>c</sub> watts	k BTU/ ft hr°F
Dow Styron Poly- styrene	1	197.86	191.90	5.96	194	20.0	1.14	18.86	0.0949
	2	224.84	217.10	7.74	221	27.5	2.04	25.46	0.0986
	3	256.12	246.60	9.52	252	34.8	3.16	31.64	0.0997
	4	288.84	278.60	10.24	284	41.0	4.30	36.70	0.1075
Enjay Escon Polypr- opylene	1	161.28	158.00	3.28	160	13.5	0.51	12.99	0.1188
	2	197.24	193.00	4.24	195	18.0	0.82	17.18	0.1216
	3	219.86	214.00	5.86	217	25.0	1.50	23.50	0.1203
	4	246.11	239.00	7.11	243	31.0	2.23	28.77	0.1214

<sup>a</sup> to nearest °C

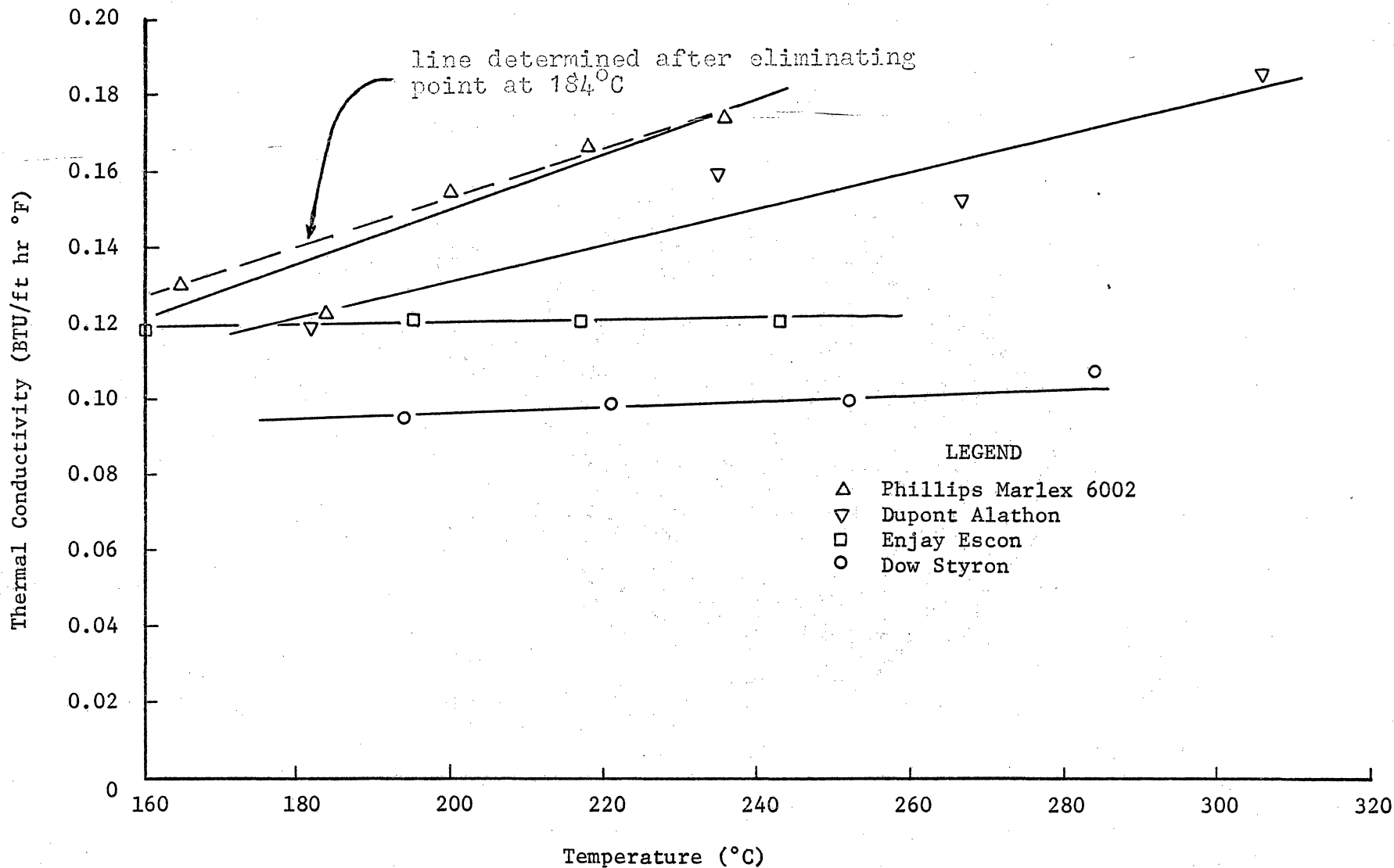


Figure 6 Thermal Conductivity of Vinyl Melts Tested as Function of Melt Temperature

TABLE IV

Results from Thermal Conductivity Experiments with  
Nylon 6 and Nylon 6-10  
 (ln r2/r1 = 0.0497, L = 6 in.)

Material	Test No.	T <sub>i</sub> °C	T <sub>o</sub> °C	ΔT °C	T <sub>av</sub> <sup>a</sup> °C	Q watts	Q <sub>r</sub> watts	Q <sub>c</sub> watts	k BTU/ ft hr°F
Dow- Badische Nylon 6	1	222.07	214.10	7.97	218	21.0	2.04	18.96	0.0713
	2	235.25	226.30	8.95	231	23.0	2.55	20.45	0.0685
	3	248.92	240.20	8.72	245	25.5	2.77	22.73	0.0782
	4	262.36	253.50	8.86	258	29.0	3.11	25.89	0.0865
	5	282.80	272.40	10.40	278	32.0	4.23	27.77	0.0801
Dupont Zytel Nylon 6-10	1	196.97	189.30	7.67	193	16.0	1.45	14.55	0.0596
	2	215.29	207.50	7.79	211	19.0	1.89	17.11	0.0659
	3	226.91	218.40	8.51	223	21.5	2.27	19.23	0.0678
	4	241.53	232.50	9.03	237	24.5	2.71	21.79	0.0724
	5	255.94	244.90	11.04	251	28.0	3.68	24.32	0.0661

<sup>a</sup> to nearest °C

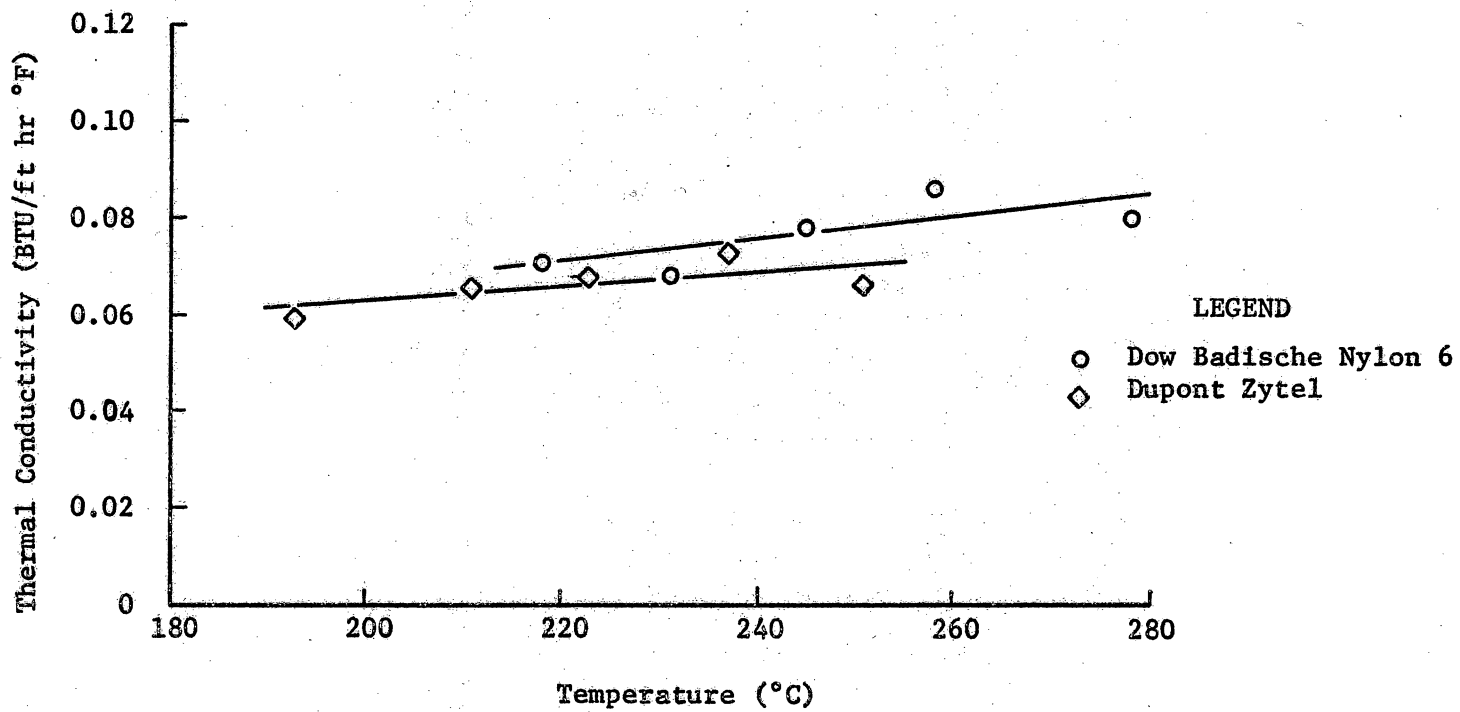


Figure 7 Thermal Conductivity of Nylon Melts Tested as Function of Melt Temperature

#### IV. DISCUSSION

This section contains discussions of the literature, procedures, analysis of errors, results, recommendations for further study, and limitations in the results obtained in this investigation.

##### Discussion of Literature

This section contains a discussion of the literature reviewed in this investigation. Experimental methods of measuring liquid thermal conductivities and uncertainties encountered in their use is discussed. This is followed by a discussion on the theories of thermal conductivity of polymers.

Experimental methods of determining liquid thermal conductivity. The basic equation for heat flux, Fourier's law, is used consistently in the theoretical development of steady-state means for measuring liquid thermal conductivity. Bird<sup>(3)</sup> and Ziebland<sup>(31)</sup>, for example, give identical development from Fourier's law to the final working equation with which the thermal conductivity is evaluated. In these developments, it was assumed that a linear dependence between temperature and thermal conductivity exists. Ziebland<sup>(31)</sup> presents a method and equation to use should this linearity assumption fail, but it is impractical in application. To use his method, a fluid temperature profile



with intermediate points as well as end points must be determined. If the temperature gradient across the fluid were so large that linearity of the gradient could not be assumed, steps should be taken to reduce the length over which the gradient is measured.

Literature pertaining to unsteady-state methods of measuring liquid thermal conductivity is not as complete as that for steady-state methods. Investigators who have worked with unsteady-state methods<sup>(2,12)</sup> mention that the accuracy of time measurement is a large factor in the determination of the accuracy of their results.

Uncertainties in thermal conductivity measurements.

The listing of factors contributing to error in liquid thermal conductivity measurements, given in the literature, is quite complete. All investigators who used the hot plate or coaxial cylinder, steady-state methods, employed guard heaters to eliminate or at least greatly reduce multidimensional heat flux, which is the one factor contributing to error whose magnitude or significance cannot be determined.

The theoretical development for radiation losses was simple for cases in which the fluid was transparent ( $e = 1$ ). One investigator<sup>(11)</sup> who made radiation loss calculations, assumed this to be true in his calculations. As mentioned in the Literature Review, the radiation heat transfer calculations are more complex as the fluid becomes opaque.

Only one reference of value<sup>(32)</sup> was located concerning semi-transparency of the fluid. No semi-transparency data for materials used in this investigation could be located in the literature.

A method for determining whether or not convective effects in liquid thermal conductivity measurements are significant has been clearly presented. Upper limit values of the Rayleigh number for convection-free heat transfer have been determined for the coaxial cylinder, steady-state method<sup>(20)</sup>; however, information pertaining to the consequence should this upper limit be exceeded, was not available. Kraussold<sup>(20)</sup> mentioned that corrective steps in terms of temperature gradient or cell geometry could be made to reduce the magnitude of the Rayleigh number to the "convection-free region" of operation.

The means for determination of eccentricity errors, as presented by Ziebland, although simple in theory, is difficult in application. The misalignment factor is difficult to measure. Most investigators have taken special care in designing their apparatus, to remove any random eccentricity of axes. Epps<sup>(11)</sup> made a determination of eccentricity error in his apparatus using what he felt to be a maximum value for the misalignment error. It was further stated that, with proper design such that the apparatus would be assembled the same way for each test, eccentricity errors would be systematic errors rather than random errors.

Theory of thermal conductivity of polymers. Hanson and Ho<sup>(13)</sup> presented a theoretical proposal for the thermal conductivity of linear polymers, but evaluation of the parameters involved in their proposal is difficult and no other investigator whose work was reviewed has attempted to use it. However, most authors have attempted to explain the trends in results in terms of molecular structure. The thermal conductivities of solid polymers were often presented as a function of temperature. Unfortunately, in terms of this investigation, almost all the literature pertains to the thermal conductivity of polymers below their melting point. Hanson and Ho<sup>(13)</sup> and Lohe<sup>(22)</sup> do present some information on the thermal conductivity of polymer melts but it is limited. However, the results and discussions reviewed are complete enough to relate to the results of this investigation.

#### Discussion of Procedures

This section contains a discussion of experimental procedures used in this investigation.

Thermocouple calibration. As described in Appendix E, all thermocouples were calibrated over the operating temperature range. The hot thermocouple junction was inside a thin glass tube during all thermocouple calibration measurements and, thus, did not actually come into contact with

the boiling water or melting metal. The fact that the experimentally determined emf's were all lower than the average emf, as given by Leeds and Northrup<sup>(21)</sup>, at each calibration data point, could have been a result of calibration procedures. The difference between experimental and standard values was approximately 1-2 degrees Centigrade and was rather consistent from thermocouple to thermocouple. Since the deviation was rather consistent, and it was the thermal gradient rather than absolute temperatures which was of importance, no error was caused by the thermocouple emf deviations.

Polymer melting process. The melt cylinder was filled with pellets of solid polymer before the melt cylinder was heated. Although the melt cylinder wall temperature could be measured and visual observation of the melting process could be made, it was difficult to recognize the point at which all the polymer had melted. Continued heating after melting could lead to degradation of the melt which would affect experimental results. The polymer was metered to the measuring apparatus as soon after the melting process was completed as was possible. No polymer degradation was noticeable in any polymer which was removed from the measuring apparatus, although some indication of polymer degradation was noticeable from melt cylinder waste. It appears that polymer melt degradation was not a problem.

Removal of air pockets. As was mentioned in the Experimental section, a vacuum pump was used to draw air from the melt system prior to pumping the melt to the measuring apparatus. The pump was used for approximately five minutes but no mechanical means was used to verify the fact that all air had been removed from the system. However, observation of the polymer melt during disassembling and cleaning of the apparatus revealed no entrapment of air bubbles. Thus all air appears to have been removed and the polymer melt contact with the metal walls was considered perfect. Any volume change in polymer melt which could cause imperfect contact with the metal walls, was compensated for by forcing polymer melt continuously, if possible, into the measuring apparatus.

Temperature measurement. Six differential thermocouples were used to determine the radial thermal gradient in the inner cylinder. However, only two thermocouples were used for this purpose in the outer cylinder. The emf's and corresponding temperatures of these outer cylinder thermocouples were periodically monitored to establish the level of steady-state. It was noticed during experimentation that the use of inner cylinder thermocouples for this purpose would lead to inaccuracies; the steady-state thermal gradient through the inner cylinder was established prior to that in the outer cylinder.

### Discussion of Errors

The following section contains a discussion of the errors involved in experimentation and uncertainties in the results of this investigation.

Radiation losses. Since operating temperatures were in the region 160-300 degrees Centigrade, radiation heat transfer was significant. Correct emissivity and absorptivity values for the materials involved were vital to the calculation of correct radiation heat transfer. McAdams<sup>(23)</sup> presented data on the emissivity of Type 316 stainless steel. For a smooth emitting surface, after repeated heating and cooling, the emissivity was 0.26-0.31. For calculations in this investigation,  $e = 0.30$  was used. No information was located on the transparency of polymers or polymer melts. The polymer melts appeared to be nearly, if not totally, transparent. For calculation purposes, total transparency was assumed and thus a maximum in radiation loss was calculated. The heat transferred by radiation, as calculated, was subtracted from the heat input indicated by the wattmeter and the difference was used as the heat transferred by conduction in thermal conductivity calculations. The calculated heat transfer by radiation is listed for each test in Tables I, II, III and IV. The percentage of heat transferred by radiation ranged from about 1 percent to about 13 percent. A sample radiation heat transfer calculation is given in Appendix F, page 98.

Convection. The magnitude of the calculated Rayleigh number was used as an indication of significance of convection. The properties of the materials used to calculate the Rayleigh number were located in the Modern Plastics Encyclopedia<sup>(25)</sup>. From the nature of the polymer melts, it appeared that convective heat transfer would not be a problem. The calculated Rayleigh number verified this as its magnitude was 0.012, compared to a conservative estimate of 700<sup>(29)</sup> necessary for convection to be of significance. The Rayleigh number calculation is given in Appendix F.

Eccentricity. Ziebland's<sup>(31)</sup> equation for heat conduction, through coaxial cylinders whose axes do not coincide, was used to determine eccentricity error. Actually, steps were taken in designing the apparatus such that eccentricity would be eliminated or be considered a systematic error. A measure of the effect of eccentricity was made assuming that the axes were misaligned by 0.005 inch. This assumed error in alignment causes about a 4 percent error in the calculated thermal conductivity, for the test used in the calculation. This calculation is presented in Appendix F.

Heat losses. Upper and lower guard heaters were employed to minimize heat losses due to multidimensional heat flow. Axial thermocouple measurements were used to regulate the heat input to these guard heaters. With this arrangement, the axial heat transfer was minimized such that the resulting error would be much smaller than other experimental errors.

Temperature measurement. The thermocouples used for radial temperature profile measurements in the inner cylinder were fitted into axially drilled holes. The diameter of these holes was 1/16 inch, which was larger than the diameter of the thermocouple beads. Thus an air space existed between the metal wall and the thermocouple. However, since there could be no convective currents in the thermocouple holes, no thermal gradient in these air spaces due to convection was possible.

Only two thermocouples were used to determine the thermal gradient in the outer cylinder. These were placed in holes drilled radially through the outer cylinder. The leads from these thermocouple beads were arranged radially, i.e., parallel to the thermal gradient. Once outside the stainless steel outer cylinder, the leads were arranged axially, i.e., perpendicular to the thermal gradient, along the outside wall of the outer cylinder. The distance over which the leads were arranged radially was approximately 0.10 inch. The thermal gradient across this distance was approximately 0.5 degrees Centigrade. Since the magnitude of this temperature drop is small and the thermocouples were insulated, it appears that errors resulting from thermal gradients along thermocouple wires, while not eliminated, were minimized as much as possible.

Differential error analysis. The equation for calculating thermal conductivity of a material, using the concentric cylinder method, is:



$$k = \frac{Q \ln r_2/r_1}{2 \pi L (T_1 - T_2)} \quad (1)$$

where:

- k = thermal conductivity
- Q = heat input
- r<sub>1</sub> = inner wall radius
- r<sub>2</sub> = outer wall radius
- T<sub>1</sub> = inner cylinder wall temperature
- T<sub>2</sub> = outer cylinder wall temperature

Differentiation of equation 1 and division of the result by k gives the fractional error, dk/k:

$$\frac{dk}{k} = \frac{dQ}{Q} + \frac{d(r_2/r_1) r_1}{\ln(r_2/r_1) r_2} + \frac{dL}{L} + \frac{d(\Delta T)}{\Delta T} \quad (2)$$

The terms involving r<sub>1</sub> and r<sub>2</sub> in this equation must be further reduced to:

$$d(r_2/r_1) = \frac{d(r_2)}{r_1} + r_2 \frac{d(r_1)}{r_1^2} \quad (3)$$

and thus:

$$\frac{d(r_2/r_1) r_1}{\ln(r_2/r_1) r_2} = \frac{\frac{d(r_2)}{r_2} + \frac{d(r_1)}{r_1}}{\ln r_2/r_1} \quad (4)$$

Substitution of equation 4 into equation 2 gives the differential equation:

$$\frac{dk}{k} = \frac{dQ}{Q} + \frac{\frac{d(r2)}{r2} + \frac{d(r1)}{r1}}{\ln r2/r1} + \frac{dL}{L} + \frac{d(\Delta T)}{\Delta T}. \quad (5)$$

It can be seen that all signs in equation 5 have been made positive, to give absolute values, although they had possibly been negative according to correct differentiation. Substitution of measured values of r1, r2 and L into equation 5 gives:

$$\frac{dk}{k} = \frac{dQ}{Q} + 0.01321 + 0.00167 + \frac{d(\Delta T)}{\Delta T}. \quad (6)$$

Substitution of the errors in heat input and temperature measurement, where  $d(\Delta T) = 2 dT$ , gives:

$$\frac{dk}{k} = 0.01488 + \frac{0.1}{Q} + \frac{2(0.05)}{\Delta T}. \quad (7)$$

With typical heat input and temperature drop values, an estimate of the average experimental error is:

$$\frac{dk}{k} = 0.01488 + 0.004 + 0.0125$$

$$\frac{dk}{k} = 0.0314 = 3.14 \text{ percent.}$$

The contributions to experimental error due to the degree of accuracy of measurements used in the gathering of data are the only ones considered in these calculations.

### Discussion of Results

The following section contains a discussion of the results obtained during this investigation.

Preliminary testing. The results from the three preliminary tests using glycerine, given in Table I, show a greater spread than those for any of the melts tested. Within the temperature range over which the tests were made, the published<sup>(23)</sup> thermal conductivity of glycerine is constant at 0.164 BTU/ft.hr.<sup>°F</sup>. The experimental results vary by as much as 15 percent from this value. However, the experimental results bracket the published value and apparently no gross error is involved, although the difference is greater than the estimated experimental error for the procedure used. The average value for thermal conductivity of glycerine was 0.170 BTU/ft.hr.<sup>°F</sup>, which is only about 4 percent greater than the published value. Since the average is quite close to the published value, and since the polymer data appears to be more precise, no correction factor was calculated and applied.

### Thermal conductivities of the tested polymer melts.

As indicated in Figure 6, Phillips Marlex 6002 melt had the highest thermal conductivity of those melts tested, ranging

from 0.130 BTU/ft.hr.<sup>°F</sup> at 160°C to 0.175 BTU/ft.hr.<sup>°F</sup> at 235°C. Dupont Alathon melt had the second highest thermal conductivity, ranging from 0.120 BTU/ft.hr.<sup>°F</sup> at 180°C to 0.185 BTU/ft.hr.<sup>°F</sup> at 305°C. It can be seen from Figure 6 that the temperature ranges over which melt thermal conductivity was determined, is not consistent from melt to melt. The thermal conductivities of Enjay Escon and Dow Styron melts were less affected by temperature. The thermal conductivity of Enjay Escon melt was constant at 0.120 BTU/ft.hr.<sup>°F</sup> in the temperature range 160-240°C. Dow Styron melt exhibited a slight thermal conductivity increase with temperature, ranging from 0.095 BTU/ft.hr.<sup>°F</sup> at 195°C to 0.107 BTU/ft.hr.<sup>°F</sup> at 285°C.

As seen in Figure 7, the thermal conductivities of the two nylon melts tested were similar. The thermal conductivity of the Dow-Badische Nylon 6 melt ranged from 0.070 BTU/ft.hr.<sup>°F</sup> at 220°C to 0.080 BTU/ft.hr.<sup>°F</sup> at 280°C. The thermal conductivity of Dupont Zytel(Nylon 6-10) melt ranged from 0.060 BTU/ft.hr.<sup>°F</sup> at 195°C to 0.067 BTU/ft.hr.<sup>°F</sup> at 250°C.

Effect of temperature on thermal conductivity. As seen in Figures 6 and 7, all the melts except Enjay Escon, whose thermal conductivity is temperature independent, show an increase in thermal conductivity with increased temperature. With respect to the amount of data collected, the increase in the others is linear with temperature. The thermal conductivities of the two polyethylenes are affected greatest

by temperature. The lines determined by linear regression for these two melts are similar in slope(7 to 5 ratio). If one data point for Phillips Harlex 6002 melt, which appears to be in error, is eliminated and the line redetermined, the slopes for the two polyethylenes are more nearly equal(6 to 5 ratio). The dotted line indicates the re-determined line.

As with polymers below their melting point, the increase in thermal conductivity with temperature is caused by increased segmental mobility in the polymer chains. The results indicate that this effect is stronger than a possible thermal conductivity reduction with increased temperature caused by decreased chain-to-chain density. The segmental mobility increase is most pronounced in polyethylene, which had the greatest thermal conductivity increase with increased temperature.

Lohe's<sup>(22)</sup> results for thermal conductivity of polystyrene melts showed a slight decrease with temperature. The results in this investigation showed a slight increase with temperature. However, the thermal conductivity scale in Figure 6 is somewhat expanded. Should it be compressed, the effect of temperature on thermal conductivity would appear to be negligible. Lohe reported only trends, but no experimental values of thermal conductivity. Within the experimental errors involved, Lohe's results and those from this investigation could be quite similar. In addition, no

mention of the type of polystyrene used by Lohe was located. The thermal conductivities of two polystyrene melt samples, whose properties were not alike, could be different.

Hanson and Ho have presented a couple of thermal conductivity values for Phillips Marlex 6050 melt. At 150°C and 160°C, their value for the thermal conductivity is about  $6.2 \times 10^{-4}$  cal./cm.sec.°C and the thermal conductivity increases slightly with increasing temperature. This value, as given by Hanson and Ho, corresponds to a value of 0.149 BTU/ft.hr.°F. This is higher than an experimentally determined value of 0.131 BTU/ft.hr.°F at 165°C determined for Phillips Marlex 6002. The difference between these two values is 13 percent without consideration of experimental error. In addition, the difference could lie in the fact that these are different grades of polyethylene.

Effect of structure on thermal conductivity. The relative magnitudes of the thermal conductivities of the polymer melts tested show that increasing the size of substituents connected to a hydrocarbon chain lowers thermal conductivity. Hattori<sup>(14)</sup> found this to be true for solid polymers and results from this investigation indicate the same is true for polymer melts. The thermal conductivity of polyethylene melt, with a hydrogen as substituent, was higher than the thermal conductivity of the more complex polypropylene, which in turn was higher than that for the even more complex polystyrene. The thermal conductivities

of the nylon melts tested were lower than those for any of the vinyl melts tested. This would seem to be in agreement with the other results in that a melt with a more complex structure has a lower thermal conductivity.

The results showed that high density polyethylene has a higher thermal conductivity than low density polyethylene, which Hattori<sup>(15)</sup> had found to be true also for these structures below the melting point. This agrees with the suggestion that lower chain-to-chain density results in lower thermal conductivity.

#### Recommendations

Further investigation in this area is strongly advised and the following recommendations are made:

1. Only one melt of any type was investigated. Different melts of the same type, but with different molecular weights, should be used to determine the effect of molecular weight on thermal conductivity. In addition, the effect of branching on the polymer chain, in terms of melt thermal conductivity, should be determined.

2. The apparatus was designed such that it could be used to determine the thermal conductivity of any viscous fluid. Thus, fluids such as polymer solutions should be used as test fluids.

3. An adhesive should be located which could withstand some amount of tension and not degrade thermally. An adhesive such as this should be used to seal the three portions of the inner stainless steel cylinder.

4. The temperature difference between tests should be reduced such that a more exact determination of temperature effect on thermal conductivity can be made. In addition, the number of tests made with any one material should be increased.

5. When investigating the thermal conductivity of polymer melts, data should be gathered at the melting point and in the transition zone between solid polymer and melt, such that a more exact comparison between melt thermal conductivity and solid thermal conductivity can be made.

6. A more precise means of determining the point at which melting in the melt cylinder has been completed needs to be used. This could eliminate unnecessary thermal degradation of the polymer melts.

7. The transparency of the test material should be determined. This information would increase the reliability or accuracy of radiation heat transfer calculations and thus heat transferred by conduction.

#### Limitations

The results obtained in this investigation are subject to the following limitations:



1. The data points were forced to fit a linear regression, due to the limited number of points. It was not meant to relate a fact that thermal conductivity was an exact linear function of temperature.

2. The results presented in the form of thermal conductivity as a function of melt temperature are valid only within the temperature range studied, which was from just above melt temperature to about 100-150°C above the melting point.

3. The average experimental measurement error for each test was estimated at slightly over 3 percent. Meaningful confidence limits cannot be calculated because of limited number of data points.

4. The results presented are valid only for the melts of materials with properties alike or similar to those used in this investigation.

## V. CONCLUSIONS

The following section contains conclusions drawn from this investigation. The steady-state, coaxial cylinder method was used to determine the thermal conductivity of polymer melts. Thermocouples were used to measure thermal gradients and heat input was provided by cartridge heaters. A temperature range of 50-100 degrees Centigrade above the melt temperature was studied for melts of several molding compounds.

The conclusions drawn upon this investigation are as follows:

1. The apparatus, as designed, is suitable for measuring thermal conductivity of polymer melts within an experimental measurement error of 3 percent.

2. The thermal conductivity of the polyethylene, polystyrene and nylon samples tested increased with increase in temperature, whereas the thermal conductivity of the polypropylene sample was temperature independent.

3. Melt thermal conductivity decreases as the size of substituent connected to the hydrocarbon chain increases.

4. The apparatus, when used with polymer melts, operates in the convection-free region of heat transfer.

5. The measured thermal conductivities ranged from 0.0596 BTU/ft.hr.<sup>°F</sup> for Nylon 6-10 at 193°C to 0.1848 BTU/ft.hr.<sup>°F</sup> for Dupont Alathon polyethylene at 306°C.

## VI. SUMMARY

The purpose of this investigation was to develop an apparatus to measure the thermal conductivity of polymer melts, and to use the apparatus to measure the thermal conductivity of selected melts as a function of melt temperature.

The steady-state, coaxial cylinder method with guard heaters was used and the annular gap was 0.075 inch. The polymer was melted in a cylindrical melt chamber, then metered to the thermal conductivity measuring apparatus. Cartridge heaters provided heat input and temperature measurements were made with calibrated, differential, iron-constantan thermocouples.

The thermal conductivity of five of the six melts tested increased with increased temperature. Complexity of molecular structure lowered melt thermal conductivity.

Radiation losses were accounted for and convection was determined to be absent. The results were shown to be within a 3 percent experimental measurement error. Meaningful confidence limits cannot be calculated because of the limited number of data points.

Thermal conductivity magnitudes ranged from 0.0596 BTU/ft.hr.<sup>°F</sup> for Nylon 6-10 at 193°C to 0.1848 BTU/ft.hr.<sup>°F</sup> for Dupont Alathon polyethylene at 306°C.

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APPENDIX A

Detailed Description  
of Apparatus

### Detailed Description of Apparatus

This section contains a detailed description of the apparatus used. Included are critical dimensions as well as features critical to successful use of the apparatus.

The melt cylinder is shown as part of the schematic drawing in Figure 1 , page 25. The cylinder was 30 inches long and was made from 2 inch, Schedule 40 pipe. The inner surface of this pipe was reamed to remove nonuniformities. On one end of this pipe was a 2 inch to  $\frac{1}{2}$  inch pipe reducer, while a flange with  $\frac{1}{2}$  inch threads cut through it was attached to the other end. A threaded aluminum rod, which was attached to the melt cylinder piston, was threaded through this flange. By manually turning this rod and thus moving the piston, pressure could be applied to the polymer melt. As pressure was applied to the piston, the polymer melt flowed from the melt cylinder to the measuring cylinder.

Twenty feet of heating wire with a resistance of 0.635 ohms per foot of length was coiled around the pipe cylinder. The cylinder was insulated with layers of asbestos tape. A powerstat was used to vary the voltage applied to the heating wire and thus to control heat to the melt cylinder.

The piston portion of the melt cylinder, as shown in Figure 2 , page 26, was constructed from aluminum, and was designed such that O-rings could be used to form the seal



between the piston and the cylinder wall. Teflon O-rings served to form this seal. The diameter of the piston was 2.035 inches while the inside diameter of the pipe was 2.048 inches.

The connector piece, as shown in Figure 2 was constructed from brass. It served to connect the threaded aluminum rod to the piston. It was designed such that the rod could be rotated while allowing the piston to move along the pipe without turning on its axis. Two brass rings on the connector piece formed the actual connection between the piston and rod. These rings were attached to the rod by screws. No permanent connection was made, however, between the main portion of the connector and the threaded rod. As indicated in Figure 2, the connector was positioned inside the piston, then the two were fastened together by an aluminum pin.

Only a schematic view is given of the apparatus connecting the melt cylinder with the measuring cylinder. This consisted of piping, a vacuum pump and a manometer and is shown in Figure 1. The entire piping equipment was covered with heating tapes to heat the pipe so the polymer would not solidify during transport. The vacuum pump was used to remove air pockets from the system prior to pumping the polymer melt through the apparatus. The manometer was used to indicate the level of the polymer melt in the measuring cylinder.

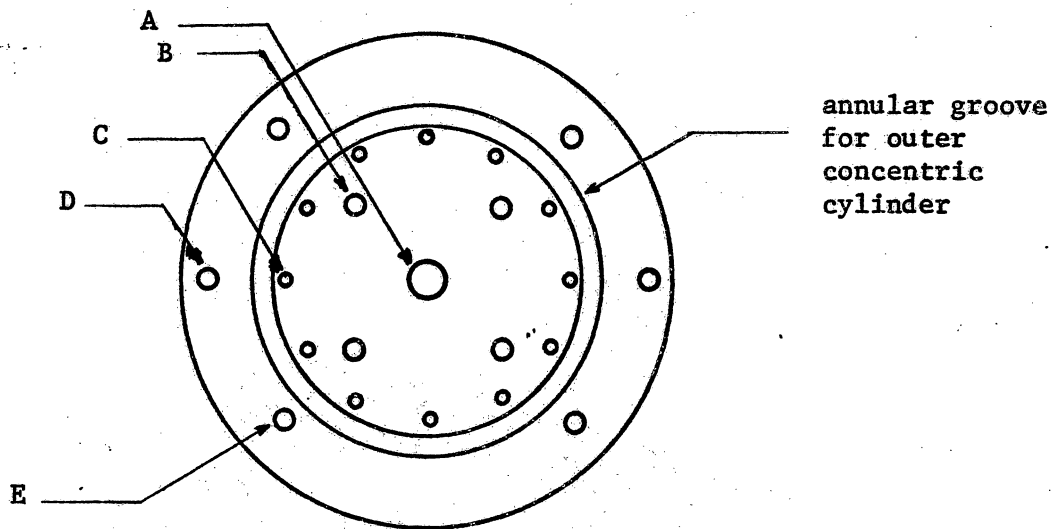
The two parts of the base plate, through which polymer melt entered the measuring cylinder, are shown in more detail

in Figures 8, page 68, and 9, page 69. The means by which the melt entered through channels cut in the base plate are indicated in Figure 9. Also shown is a means by which polymer melt could flow into and out of the base plate without flowing into the measuring apparatus.

A semi-circular groove was cut in each portion of the base plate as shown in Figures 8 and 9. When the two parts of the base plate were put together, an annular ring was formed. To prevent leakage between base plate portions, O-ring seals were positioned as indicated in Figure 9. As polymer melt entered the base plate, it flowed inside this annular ring and then into the annular gap between the inner and outer stainless steel cylinders.

A 3/8 inch deep groove was cut, in the top portion of the base plate, which served as foundation for the outer stainless steel cylinder. The inner and outer diameters of this groove, 1.55 inches and 1.75 inches, respectively, were the same as that of the outer cylinder. A pin on the outer stainless steel cylinder which fit into a hole in the base plate assured that the positioning of the outer stainless steel cylinder and the base plate were the same for every test. The outer cylinder was held in place by a threaded rod which was screwed into the base plate. Caulk( silicone rubber) was used to complete this seal.

Polymer melt entered the annular gap between the concentric cylinders through the 12, 3/32 inch diameter, holes



- A : 1 hole,  $D=3/8''$
- B : 4 holes,  $D=1/4''$
- C : 12 holes,  $D=3/32''$
- D : 2 holes,  $D=1/4''$
- E : 4 holes,  $D=1/8''$

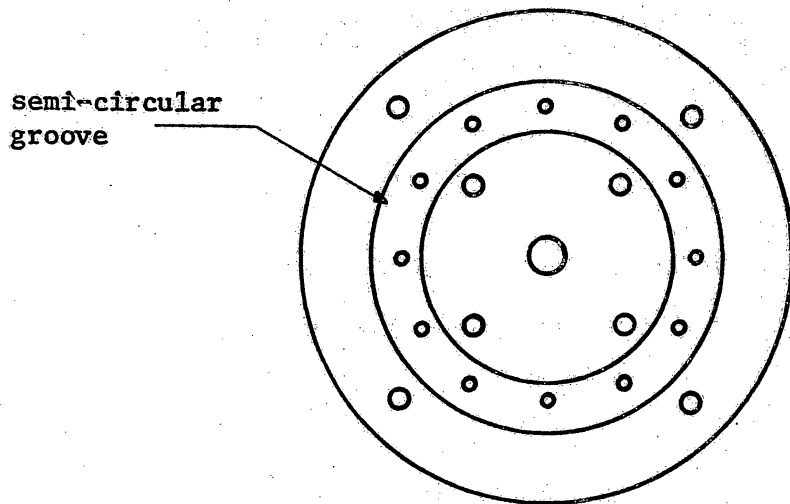
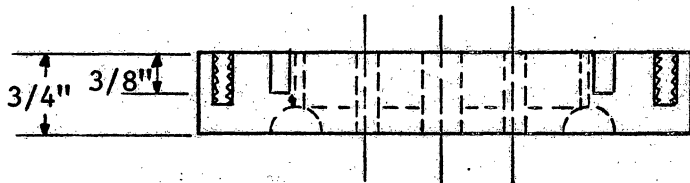


Figure 8 Top Portion Of Base Plate For Concentric Cylinder Apparatus

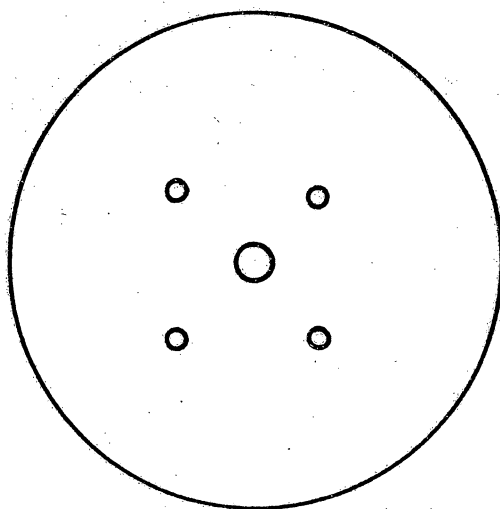
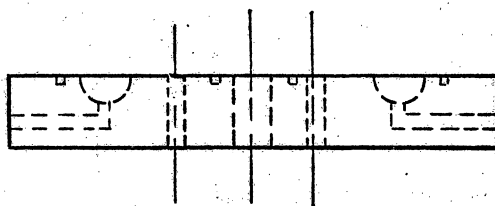
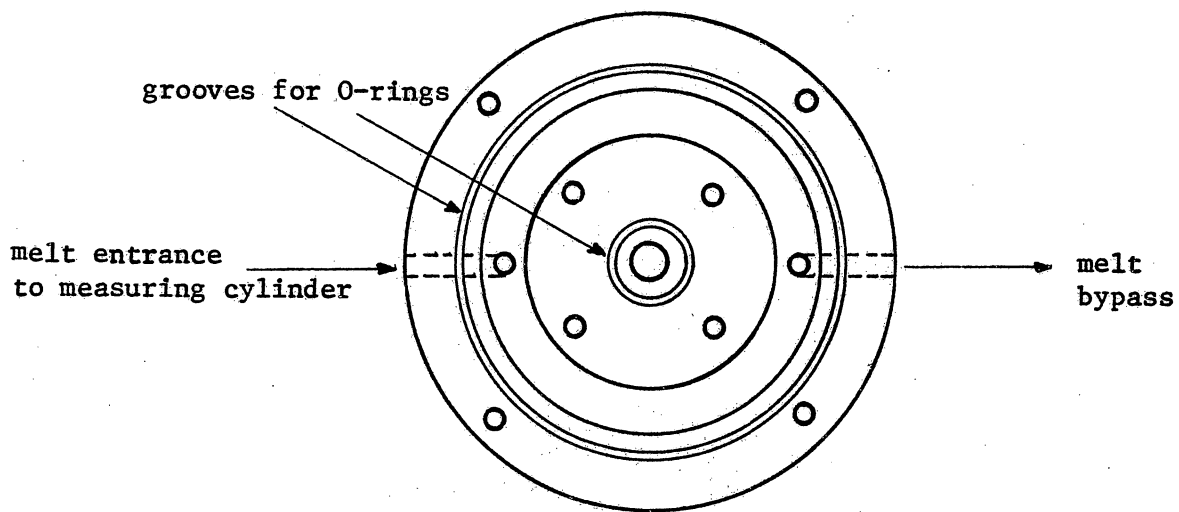


Figure 9 Bottom Portion of Base Plate For Concentric Cylinder Apparatus

in the top portion of the base plate. These are indicated in Figure 8.

The inner stainless steel cylinder was attached to the base plate by four Allen screws. As indicated in Figure 10, page 71, these slipped through the base plate and threaded into the inner concentric cylinder, fitting flush against the bottom surface of the base plate. Finally, the hole in the center of the base plate served as a conduit for thermocouple and heater lead wires from the measuring apparatus.

The base plate and bottom portion of the inner cylinder were sealed together by cement. Three different cements were used at one time or another. These were aluminum cement, epoxy cement and Saureisen cement. All were successful to a certain degree with a limitation being thermal degradation of the epoxy cement, which occurs at approximately 260°C. The other two cements would not degrade at operating temperatures but would fail should tension be placed on the bond.

Cartridge heaters were located in the holes along the bottom portion axis and also along the axis of the center and upper portions of the inner cylinder assembly. Additional features of the bottom portion of the inner cylinder are shown in Figure 11.

The three portions of the inner cylinder were positioned and aligned by stainless steel pins and then sealed together. The bottom portion of this assembly was welded to the center

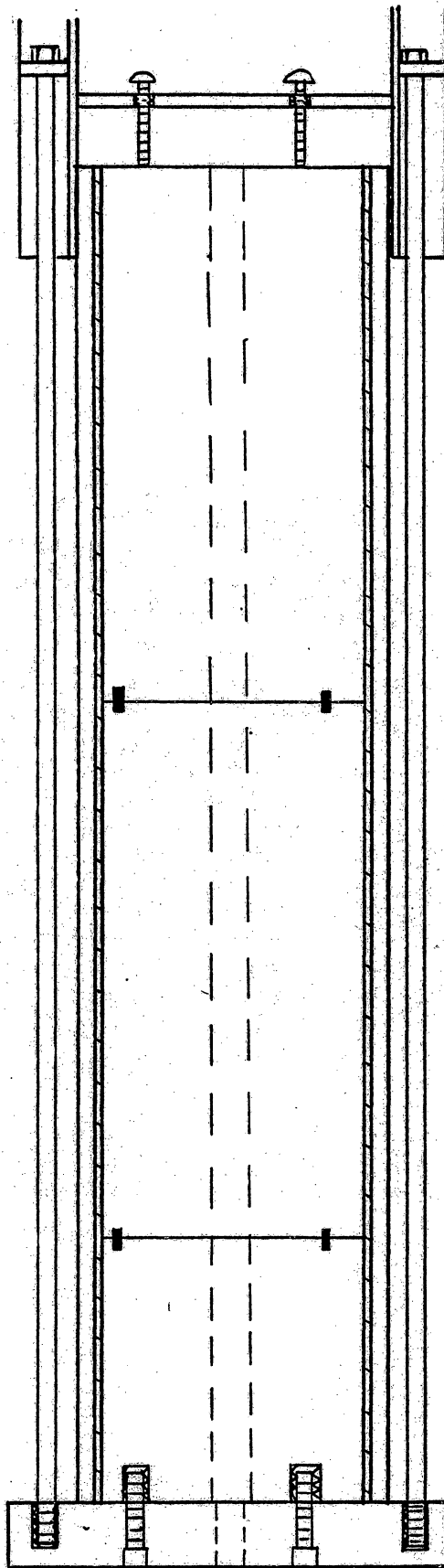
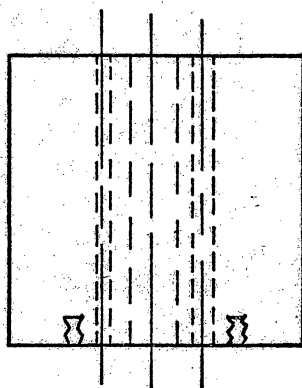
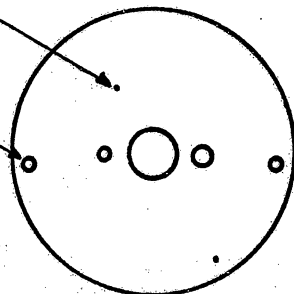


Figure 10 Schematic View of Measuring  
Cylinder Indicating Means  
of Aligning Apparatus

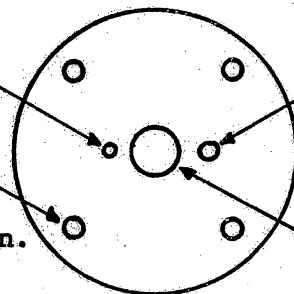
thermocouple  
holes, 1/32 in.  
diameter, 1/4 in.  
deep

pin holes for  
cylinder alignment



1/8 in. diameter  
hole for thermocouple  
leads

1/4 in. diameter  
holes drilled and  
tapped to depth = 1/2 in.



3/16 in. diameter  
hole for measuring  
heater leads

hole for lower  
guard heater  
diameter = 1/2 in.

Figure 11 Lower Portion of Inner Concentric Cylinder

portion. The seal or bond between the center portion and upper portion was made by epoxy cement or Saureisen cement. Limitations of use for both were mentioned earlier in this section. Additional details of the three portions of the inner cylinder assembly are given in Figures 11, page 72, 12, page 74 and 13, page 75.

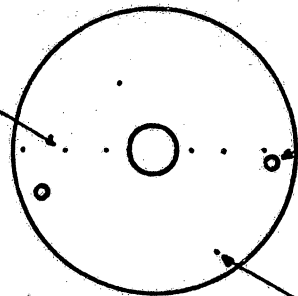
Features of the top portion of the measuring cylinder are shown in Figure 14, page 76. The positioning of a teflon ring with a metal ring backing used to form the upper seal for the annular gap is shown. Figure 14 also shows the vertical extension rods which were welded to the metal backing ring. These extension rods were the means through which the level of the teflon and metal rings and thus the level to which the polymer melt rose, were controlled. A crossbar connecting these extensions and held as shown in Figure 14 assured proper and consistent ring positioning.

Two machine screws were used to exert downward pressure on the inner cylinder and thus remove the possibility of tension being placed on a cement bond. These were threaded through a crossbar which was attached to the outer stainless steel cylinder.

The function of the alternating current circuit was to regulate the electric power to the cartridge heaters. Actual power control or regulation was made with the use of power-stats. Figure 5, page 31, shows the alternating current circuit.

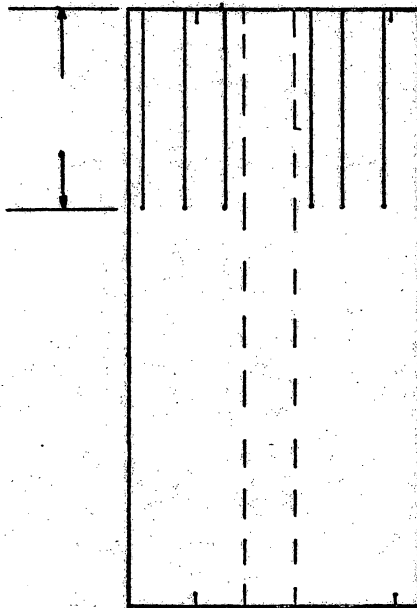


thermocouple  
holes, 1/32 in.  
diameter, 2 in. deep



pin holes for  
cylinder alignment

thermocouple holes,  
1/32 in. diameter,  
2 in. deep



hole for measuring  
heater diameter = 1/2"

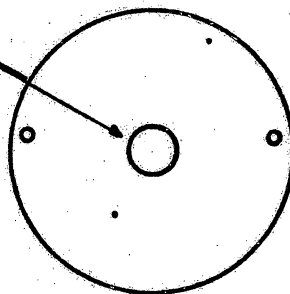


Figure 12 Center Portion of Inner Concentric Cylinder

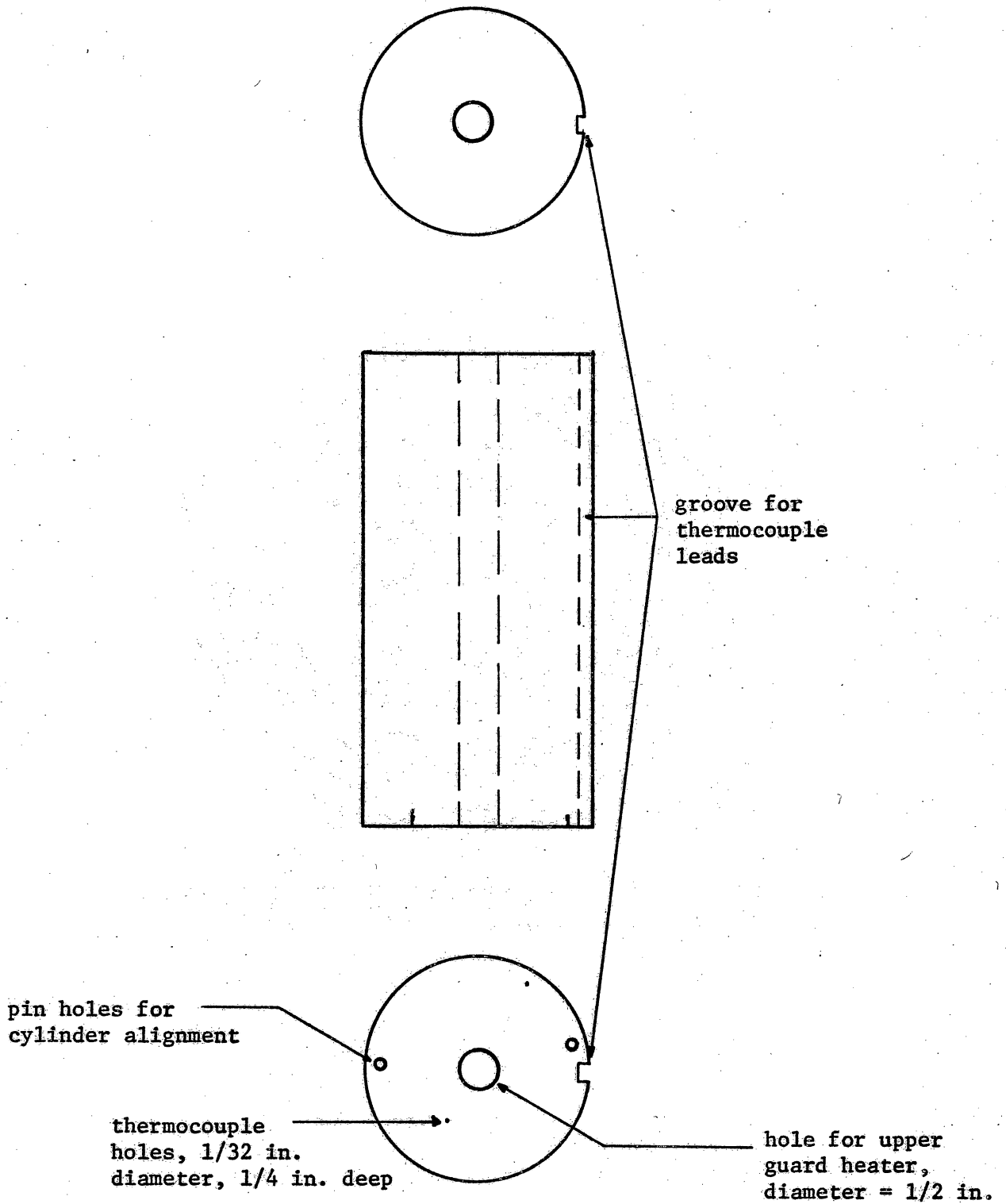


Figure 13 Upper Portion of Inner Concentric Cylinder

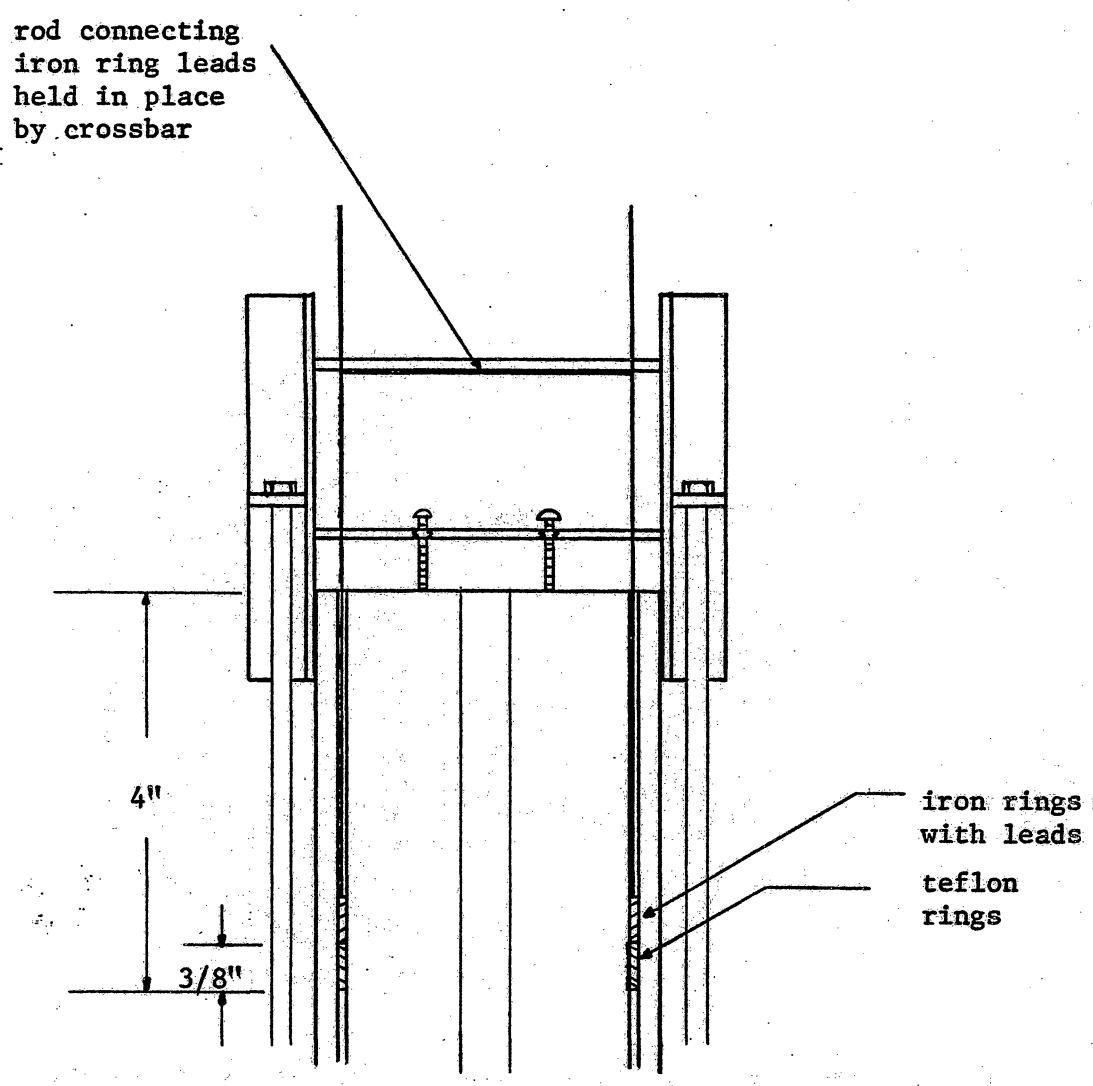


Figure 14 Upper Portion of Measuring Cylinder  
Indicating Placement of Annular Gap  
Seal Rings

The potentiometer circuit was used in conjunction with the thermocouples for temperature measurement. This circuit is shown in Figure 4 , page 30 .

APPENDIX B

Experimental Procedure

## Experimental Procedure

This section contains a description of the experimental procedure used. A brief discussion of equipment assembly is given first, followed by the procedure used when gathering data.

When assembling the measuring apparatus, the teflon and metal rings were positioned inside the stainless steel pipe(outer cylinder) at the proper position(see Figure 14, page 76), as the initial step. A thin layer of silicon rubber(caulk) was spread over the lower outside surface of the outer cylinder. This layer of caulk generally extended to about  $\frac{1}{4}$  inch from the bottom of the outer cylinder. The outer cylinder was then placed over the inner cylinder, fitted into position and bolted to the base plate. Finally, the crossbars were fastened in place and the machine screws as shown in Figure 14 were tightened against the inner cylinder.

Heating tapes were closely wound but not overlapped around the pipe connecting the melting cylinder with the measuring cylinder as well as the measuring cylinder base plate.

Prior to pumping the melt into the measuring cylinder or even melting the polymer, the potentiometer circuit was standardized and the electric circuit was checked for flaws.

The melt cylinder was then filled with pellets or granules of solid polymer, the form varying from polymer to polymer.

The melt cylinder was filled to approximately two-thirds of its cylindrical volume. Heat was then applied to the melt cylinder to melt the polymer. A check of melt cylinder wall temperature could be made, if necessary, with a differential iron-constantan thermocouple.

One part of the connecting piping was a pipe union. This was left unassembled during the melting of the polymer such that the inside of the melt cylinder could be seen and visual inspection of the melting process could be made.

Simultaneously with commencement of melting was the application of heat to the measuring cylinder heaters and to the heating tapes. This was mainly a time saving procedure as the melt could not be pumped past any part of the apparatus whose temperature was below the melting point of the polymer.

After the polymer had been melted and the temperature of all parts of the apparatus was above the melting point of the polymer, the pipe union was connected and a vacuum was drawn on the flow system. This was used in an attempt to remove air pockets from the system. These air pockets, if not removed, could cause imperfect contact between the polymer melt and the stainless steel cylinders.

The vacuum pump was then shut off and the polymer melt was metered from the melt cylinder to the measuring cylinder. As indicated in Figure 1, page 25, the level to which the polymer melt rose inside the measuring cylinder could be

determined from the manometer tube. This means of indication proved to be unnecessary. When the melt had risen to the level of the teflon ring, no more melt could be metered to the measuring cylinder. The resistance to turning the aluminum rod which pushed the melt cylinder piston was noticeably greater. In addition, the viscosity of the melts was such that a long settling out period was necessary before the melt levels in the manometer and measuring cylinder were the same. The level inside the manometer was higher than that inside the measuring cylinder until the melt levels had completely balanced themselves.

After filling the apparatus with melt to the designated level, preliminary temperature measurements were made to adjust the guard heaters and thus eliminate axial heat losses. Successive time-separated temperature measurements of the outer cylinder temperatures were used to determine steady-state conditions. The time separation between two measurements was about one-half hour. If the temperature was the same for two consecutive readings, steady-state conditions were assumed. The time required for reaching steady-state varied. To reach an initial steady-state after the input of heat was begun, four to six hours was necessary. Two to three hours was necessary to reach each additional steady-state.

It was proposed that thermal gradients, heat inputs and thus thermal conductivity should be determined for each test material at four or five different temperatures. The lowest



thermal steady-state and test temperature was the initial one reached. Ideally, this temperature should have been just above the melting point of the polymer. However, it was heat input and not steady-state temperature which could be closely controlled. Thus, the desired steady-state temperature could not always be exactly attained.

After attaining a condition of steady-state, all thermocouple readings were taken and recorded.

Next, the heat input from the cartridge heaters was increased. By balancing powerstat and ampere meter readings with that of the measuring heater circuit, a rough idea of the correct heat input to the guard heaters could be determined. For the top guard heater, a power input of 1.1 times the measuring heater wattage would roughly eliminate upward axial thermal gradients. A rough estimate of correct lower guard heater power input was 0.6 times the measuring heater wattage. Thermocouple readings determined final necessary heat input to the guard heaters.

As mentioned earlier, four or five tests with one polymer melt constituted a run. Cleaning the apparatus to remove the polymer was simplified by disassembling the apparatus before the melt could harden. This included separating the inner stainless steel cylinder from the outer one, cleaning the entrance and exit channels of the base plate, cleaning valves and removing all melt from the melt cylinder.

Generally, most of the solidified polymer had to be scraped or cut from the metal surfaces. If this procedure was not completely effective, solvents were used to remove the polymer. The solvents were not used exclusively because application was difficult and the nature of the solvents was such that they could be handled only with extreme care.

APPENDIX C

Materials

## Materials

The following section contains the materials used in this investigation.

Aluminum cement. Plastic aluminum, no. spa-1. Obtained from Woodhill Chemical Corporation, Cleveland, Ohio. Used as liquid seal between base plate and inner cylinder.

Asbestos tape. Asbestos strip no. JM-MX 4095. Obtained from Johns-Manville Products, Philadelphia, Pa. Used as insulating material for melt cylinder and measuring cylinder.

Caulk. Silicon rubber, white. Obtained from Dow Corning Corporation, Midland, Michigan. Used to complete seal between outer stainless steel cylinder and base plate of thermal conductivity cell.

Decalin. Also named decahydronaphthalene, lot no. 780148. Obtained from Fisher Scientific Company, Fair Lawn, N.J. Used as solvent for polyethylene.

Epoxy. Hysol Epoxy-Patch kit, production no. V0515. Obtained from Dexter Corporation, Olean, N.Y. Used to seal portions of inner stainless steel cylinder together.

Glass wool. Fine-waved-domestic, cat. no. 11-391. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as insulating material for measuring cylinder.

Glycerine. White, F.W. 92.097, cat. no. G-32, lot. no. 750592. Obtained from Fisher Scientific Co., Fair Lawn, N.J. Used as preliminary testing fluid in thermal conductivity cell.

High density polyethylene. Phillips Marlex 6002, lot no. 0152046. Obtained from Phillips Petroleum Co., Bartlesville, Okla. Used as test material with thermal conductivity cell.

Ice. Obtained from Chemical Engineering Dept. of Virginia Polytechnic Institute and State University. Used as reference medium for thermocouple measurements.

Lead. Granular, impurities 0.035%, lot.no. 530771. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used in calibration of thermocouples.

Low density polyethylene. Dupont Alathon I, lot no. 500613. Obtained from E.I. du Pont de Nemours & Co., Wilmington, Del. Used as test material with thermal conductivity cell.

Cresol-meta. Purified 95-98%, lot no. 753564. Obtained from Fisher Scientific Co., Fair Lawn, N.J. Used as solvent for Nylon 6-10 and Nylon 6.

Nylon 6. Dow Badische Caprolactan, cat. no. B-300, lot no. 2971. Obtained from Dow Badische Co., Freeport, Texas. Used as test material with thermal conductivity cell.

Nylon 6-10. Dupont Zytel, 0.13% water. Obtained from E.I. du Pont de Nemours & Co., Wilmington, Del. Used as test material with thermal conductivity cell.

O-rings.(2) Parker O-rings, teflon, size 2-327. Obtained from Louis H. Hein Co., Richmond, Va. Used to form seal between piston and melt cylinder wassl

O-rings. Parker O-rings, teflon, sizes 2-116 and 2-154. Obtained from Louis H. Hein Co., Richmond, Va. Used to form seals between two parts of measuring cylinder base plate.

Polypropylene. Escon grade 103, lot no. 566. Obtained from Enjay Chemical Co., Plainfield, N.J. Used as test material with thermal conductivity cell.

Polystyrene. Dow Styron, lot no. PT61009. Obtained from Dow Chemical Co., Midland, Mich. Used as test material with thermal conductivity cell.

Sauereisen cement. Low expansion, no. 29, binder and filler separate. Obtained from Sauereisen Cements Co., Pittsburgh, Pa. Used to form seal between portions of inner stainless steel cylinder.

Tin. Granulated, 20 mesh, impurities 0.03%, lot no. 8576. Obtained from Mallinckrodt Chemical Works, St. Louis, Mo. Used in calibration of thermocouples.

Xylene. Non-volatile matter 0.001%, lot no. 771849. Obtained from Fisher Scientific Co., Fair Lawn, N.J. Used as solvent for polystyrene.

APPENDIX D

Apparatus

### Apparatus

The following equipment was used in this study.

Ampere Meter. Alternating current, range 0.-1. amperes.  
Obtained from Weston Electric Instr. Corp., Newark, N.J.  
Used to indicate current to bottom guard heater.

Ampere Meter. Alternating current, range 0.-3. amperes.  
Obtained from Weston Electric Instr. Corp., Newark, N.J.  
Used to indicate current to top guard heater.

Cartridge Heater. Chromalox type C, cat. no. C-301, 75  
watts, 120 or 240 volts. Obtained from Edwin L. Wiegand Co.,  
Pittsburgh, Pa. Used as bottom guard heater.

Cartridge Heater. (2) Chromalox type C, cat. no. C-304,  
150 watts, 120 or 240 volts. Obtained from Edwin L. Wiegand  
Co., Pittsburgh, Pa. One used for measuring heater and the  
other for top guard heater.

Dewar Flask. Obtained from Chemical Engineering Dept. of  
Virginia Polytechnic Institute and State University. Used as  
container for ice bath.

Dry Cell. (2) Wizard, 1.5 volts, serial no. 7D7905.  
Obtained from Western Auto Supply Co., Blacksburg, Va.  
Used as portion of potentiometer circuit.

Electric Support Equipment. Various wires, fuses, fuse  
receptacles, lights, switches and connectors. Obtained from  
Chemical Engineering Dept. of Virginia Polytechnic Institute  
and State University. Used in indication of power input to  
cartridge heaters.



Galvanometer. Spotlight, series 3400, dc, serial no. 117034, sensitivity 0.001 microamp per millimeter. Obtained from Rubicon Division of Minneapolis-Honeywell Regulator Co., Philadelphia, Pa. Used in conjunction with potentiometer as null detector.

Heating Tape. 140 watts, 45 volts, 480°F maximum, det. 0.05-4. Obtained from Glas-Col Apparatus Co. Used to heat pipe which connected melt cylinder with measuring cylinder and to heat base plate.

Melt Cylinder. Designed and constructed at Virginia Polytechnic Institute and State University for this experiment. Detailed description is given elsewhere in the text.

Potentiometer. Range 0.-1.6 volts with three ranges, three dials, serial no. 52218. Obtained from Rubicon Division of Minneapolis-Honeywell Regulator Co., Philadelphia, Pa. Used in conjunction with thermocouples for temperature measurement.

Powerstat. Type 116, primary voltage 120 volts, output voltage 0-140 volts, max. amps 7.5. Obtained from Superior Electric Co., Bristol, Conn. Used to regulate heat input to melt cylinder.

Powerstat. Type 116, primary voltage 120 volts, output voltage 0-140 volts, max. amps 7.5. Obtained from Superior Electric Co., Bristol, Conn. Used to regulate heat input to heating tapes.

Powerstat. Type 116, primary voltage 120 volts, output voltage 0-140 volts, max. amps 7.5. Obtained from Superior

Electric Co., Bristol, Conn. Used to regulate heat input to measuring heater.

Powerstat. Type 116, primary voltage 120 volts, output voltage 0-140 volts, max. amps 7.5. Obtained from Superior Electric Co., Bristol, Conn. Used to regulate heat input to top guard heater.

Powerstat. Type 116, primary volatge 120 volts, output voltage 0-140 volts, max. amps 7.5. Obtained from Superior Electric Co., Bristol, Conn. Used to regulate heat input to bottom guard heater.

Sparger. ASTM 25-50  $\mu$ , por c. Obtained from Ace Glass Inc., Vineland, N.J. Used to saturate ice bath with air.

Standard Cell. Calibrated to 1.01804 volts, EPLAB student's cell. Obtained from Research Division of Randolph Hall, Virginia Polytechnic Institute and State University. Used to standardize potentiometer circuit.

Thermal Conductivity Cell. Designed and constructed at Virginia Polytechnic Institute and State University for this experiment. Detailed description is given elsewhere in the text.

Thermocouples. Made from 30 gauge iron and 30 gauge constantan wire, iron wire from spool no. 2035-27, constantan wire from spool no. 2042-22. Made by Leeds and Northrup Co., Philadelphia, Pa. Used for temperature measurement in thermal conductivity cell.

Thermocouple Selector Switch. Lewis Engineering Co., low emf, silver contact thermocouple selector switch, 20 position. Used to select thermocouples used with potentiometer.

Thermometer. Glass, 0-140 degrees F with one degree F subdivisions, no. 14-992B. Made by Fisher Scientific Co., Pittsburgh, Pa. Used as check for ice-water bath temperature.

Vacuum Pump. Obtained from Chemical Engineering Dept. of Virginia Polytechnic Institute and State University. Used to draw vacuum on thermal conductivity cell.

Voltage Stabilizer. Serial no. W6308, input 90-150 volts, 60 cycle, single phase, output 120 volts, 4.17 amps. Made by Raytheon Manufacturing Co., Waltham, Mass. Used to stabilize input voltage to electrical system.

Wattmeter. Alternating current, double range 0-75 watts and 0-150 watts, 1.5 amps max., serial no. 2944. Obtained from Weston Electric Instr. Corp., Newark, N.J. Used to measure input power to measuring heater.

APPENDIX E

Calibration of Thermocouples

### Calibration of Thermocouples

Differential thermocouples made from iron and constantan wire were used for temperature determination. Detailed description of the thermocouple materials is given in the Materials section.

A total of seventeen thermocouples were used during experimentation. As shown in Figure 4, page 30, use of a multiple position switch, which allowed a common cold junction to be used, was employed. In addition to showing the use of the multiple position switch, Figure 4 also indicates use of the potentiometer and galvanometer in temperature measurement.

Temperatures up to approximately 300°C were to be measured with the thermocouples. Thus, the thermocouples had to be calibrated at points in this temperature range or slightly higher to avoid extrapolation of thermocouple calibration curves.

During calibration procedures, the cold thermocouple junction was kept in an ice bath in a Dewar flask. The normal freezing point of water is defined as the freezing point of water saturated with air. To attain this, air was periodically bubbled into the ice bath. Mechanical agitation was applied to the ice bath during the bubbling of air into the bath but was discontinued prior to calibration measurements.

The initial calibration point was obtained with the hot thermocouple junction in the ice bath along side the cold

junction. This data was used to determine a null or zero point for the thermocouple potentials.

A second calibration point was obtained with the hot thermocouple junction inside a thin glass tube which was immersed in a flask of boiling water. This data yielded a calibration point at approximately  $100^{\circ}\text{C}$ , subject to local barometric conditions.

A third calibration point was obtained at the melting point of pure tin. This yielded a calibration point at  $232^{\circ}\text{C}$  which is the melting point of pure tin.

The final calibration point was obtained at the melting point of pure lead. This yielded a calibration point at  $327^{\circ}\text{C}$ , the melting point of pure lead.

Data obtained during thermocouple calibration tests is given in Table V, page 97. An average emf, as given by Leeds and Northrup<sup>(21)</sup> for iron-constantan thermocouples, was used in preparation of the calibration charts. At the temperature concerned (melting point of tin, etc.), the average value given was subtracted from the experimentally determined value. This difference was used as the ordinate of the calibration chart with temperature as the abscissa.

The procedure for using the calibration charts is

1. Read the indicated emf from the potentiometer.
2. Using Leeds and Northrup<sup>(21)</sup> manual, determine corresponding temperature.

3. With the calibration charts, determine the deviation from average value (ordinate) for the thermocouple concerned.
4. Correct potentiometer emf value by amount indicated from calibration curve.
5. Determine corrected temperature from Leed and Northrup manual.

TABLE V  
Preparative Data for Calibration Curves  
for Iron-Constantan Thermocouples

Thermocouple Number	EMF Potential (millivolts)			
	A	B	C	D
1	0.000	5.030	12.333	17.555
2	0.000	5.030	12.311	17.553
3	0.000	5.055	12.354	17.522
4	0.000	5.047	12.359	17.575
5	0.000	5.046	12.375	17.560
6	0.000	5.063	12.279	17.520
7	0.000	5.065	12.251	17.525
8	0.000	5.076	12.363	17.577
10	0.000	5.066	12.440	17.536
11	0.000	5.026	12.336	17.624
12	0.000	5.028	12.342	17.636
13	0.000	5.054	12.450	17.605
14	0.000	5.071	12.457	17.629
15	0.000	5.050	12.324	17.589
16	0.000	5.050	12.310	17.595
17	0.000	5.043	12.310	17.560
18	0.000	5.041	12.358	17.581

A - Data obtained with hot junction in ice bath

B - Data obtained with hot junction in boiling water  
at barometric pressure= 71.07 cm. Hg.

C - Data obtained at melting point of tin

D - Data obtained at melting point of lead



APPENDIX F

Sample Calculations

### Sample Calculations

The following section contains a sample of the calculations which were used in preparing the results of this investigation.

Thermal conductivity calculation. The experimental test used in these sample calculations is Test 1 with Enjay Escon as the test material. After the thermocouple potentials had been recorded, the temperature corresponding to each potential had to be determined. With, for example, thermocouple number 8, for which the recorded potential was 8.532 millivolts, the corresponding temperature as given by Leeds and Northrup<sup>(21)</sup> was 159.3°C. From the thermocouple calibration curve for thermocouple number 8, Figure 15, page 100, at this temperature, the experimentally determined potential was 0.120 millivolts lower than the standard or average. The other thermocouple calibration charts are in the laboratory notebook for this investigation. As described in Appendix E, Thermocouple Calibrations, the thermocouple potential correction must be added to the indicated potential, giving a corrected potential of

$$\begin{array}{r}
 8.532 \\
 + \quad 0.120 \\
 \hline
 8.652 \text{ millivolts}
 \end{array}$$

which corresponds to a temperature of 161.5°C in Leeds and Northrup<sup>(21)</sup>.

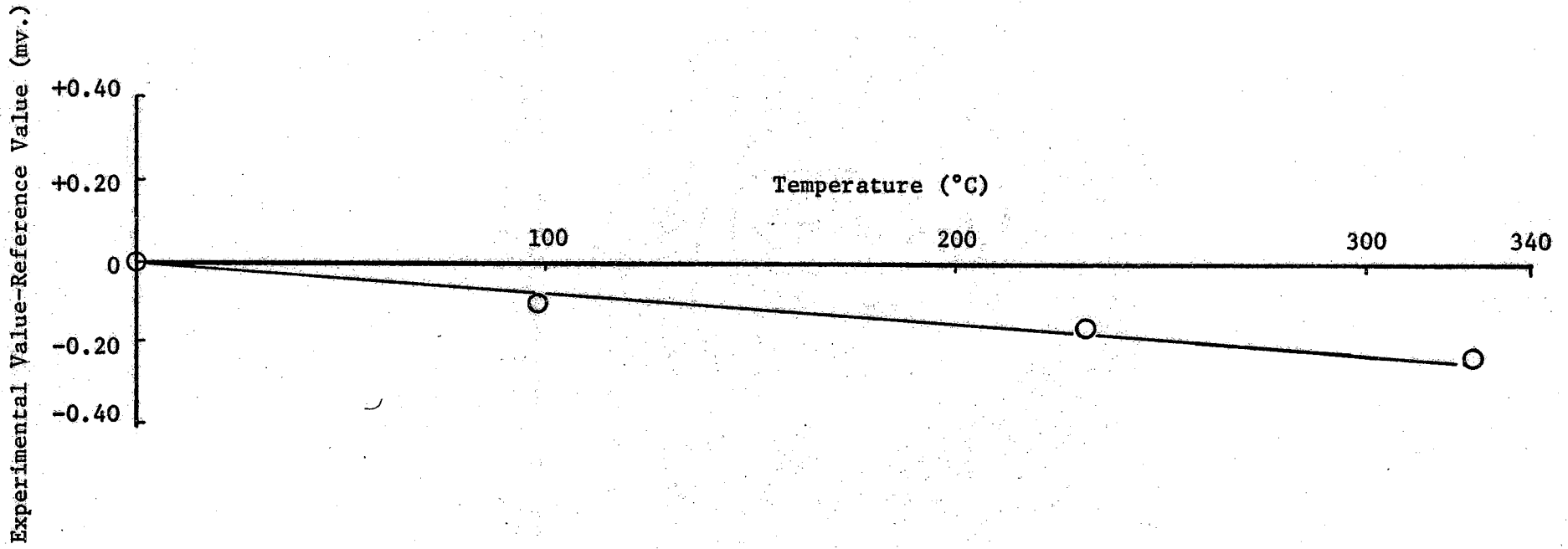


Figure 15 A Typical Thermocouple Calibration Curve  
Calibration Curve For Thermocouple No. 8

This procedure was followed for all thermocouples used in determining the thermal gradient through the stainless steel cylinders. A linear regression by a least squares technique<sup>(4)</sup> was used to determine the inner wall temperature. The thermal gradients and wall temperatures for the test used in this sample calculation are shown in Figure 16, page 102. For this test,

$$\begin{aligned} T_1 &= 161.28^\circ\text{C} \\ T_2 &= 158.00^\circ\text{C} \\ \text{and } \Delta T &= 3.28^\circ\text{C}. \end{aligned}$$

The inner and outer wall radii of the polymer melt annulus were 1.475 inch and 1.550 inch, respectively. Thus, in the thermal conductivity equation, the term:

$$\ln \frac{1.550}{1.475} = 0.0497$$

would appear.

The indicated heat input had to be modified by the amount of heat which was transferred through the polymer gap by radiation. The equation used to determine radiation heat transfer was:

$$Q_r = 4 e A \sigma T_m^3 \Delta T$$

where:

A = emitting surface area.

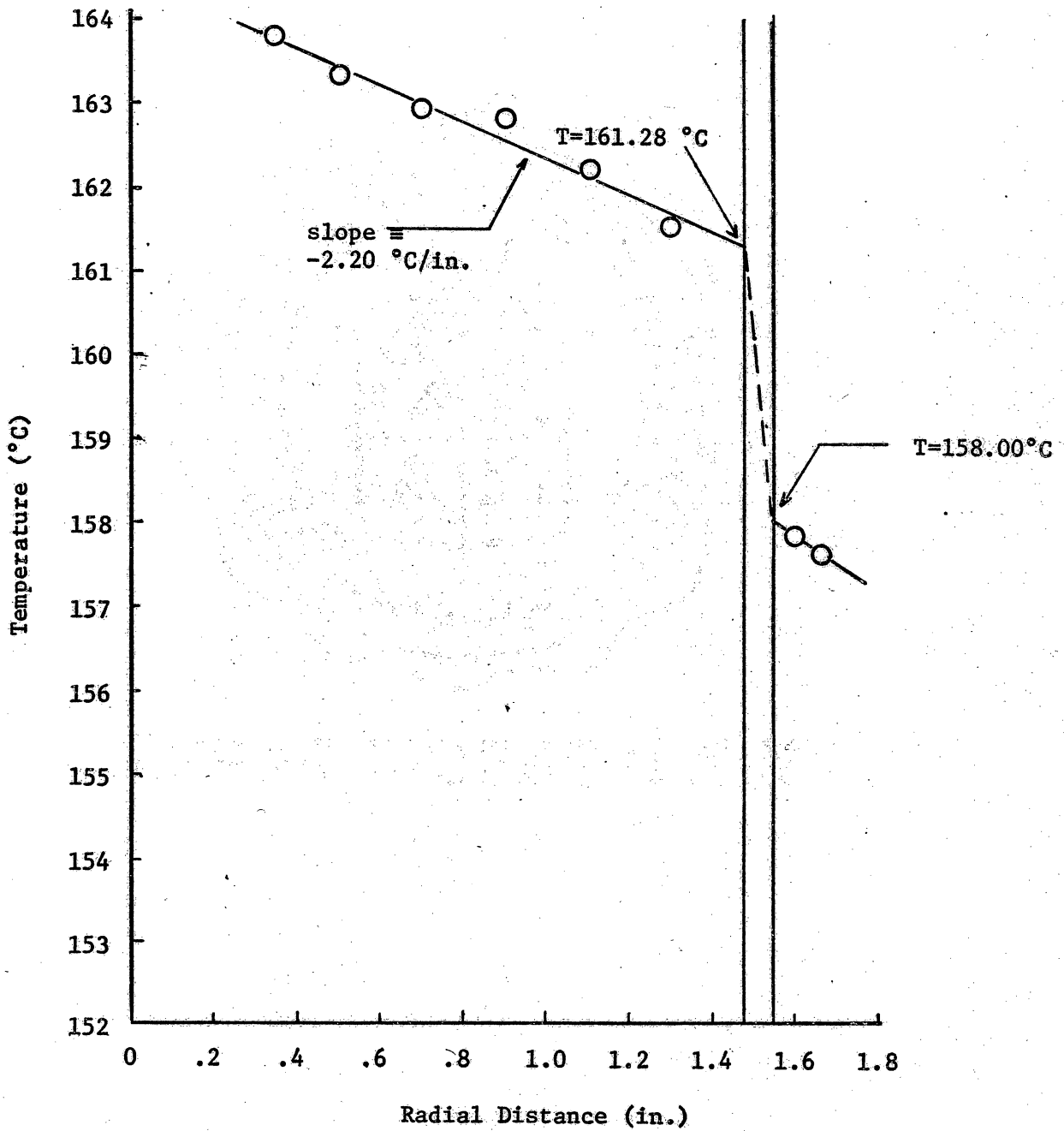


Figure 16 A Typical Radial Temperature Profile. Temperature Profile For Test 1 Using Enjay Escon Melt As Test Fluid

With the use of cylindrical geometry, the emitting surface area was:

$$\begin{aligned} A &= 2 \pi r L \\ &= 2 \pi (1.475 \text{ in.}) (6 \text{ in.}) \\ &= 55.8 \text{ in.}^2 \\ A &= 0.387 \text{ ft.}^2 \end{aligned}$$

An emissivity value for Type 316 stainless steel of  $e = 0.30$  was used<sup>(23)</sup>. The inner and outer wall temperatures were  $158.00^\circ\text{C}$  and  $161.28^\circ\text{C}$ , respectively. Thus, the mean or average melt temperature, to the nearest degree, was:

$$\begin{aligned} T_m &= 160^\circ\text{C} = 730^\circ\text{R} \\ \text{and } T_m^3 &= 3.70 \times 10^8 \text{ }^\circ\text{R}^3. \end{aligned}$$

With the Stephan-Boltzmann constant:

$$\sigma = 0.1713 \times 10^{-8} \text{ BTU/ft.}^2\text{hr.}(\text{ }^\circ\text{R}^4),$$

the radiation heat transfer for this particular test was:

$$Q_r = 1.74 \text{ BTU/hr.}$$

noting that  $\Delta T = 3.28^\circ\text{C} = 5.90^\circ\text{R}$ . Using the conversion,  $3.412 \text{ BTU/hr.} = 1 \text{ watt}$ ,

$$Q_r = 0.51 \text{ watts.}$$

Thus  $Q_c$ , heat transferred by conduction, is equal to the indicated input, 13.5 watts, minus that transferred by radiation; or:

$$Q_c = \frac{13.50 - 0.51}{12.99} \text{ watts.}$$

With the equation for thermal conductivity determination using the coaxial cylinder method:

$$k = \frac{Q \ln r_2/r_1}{2 \pi L (T_1 - T_2)},$$

and inserting proper values for the mentioned test and conversion factors:

$$k = \frac{(12.99 \text{ watts})(0.0497)}{(12 \pi \text{ in.})(3.28^\circ\text{C})} (3.412 \text{ BTU/hr.watt})(12 \text{ in./ft.}) \\ \times (1^\circ\text{C}/1.8^\circ\text{F}) = 0.1188 \text{ BTU/ft.hr.}^\circ\text{F.}$$

This was the experimentally determined thermal conductivity of Enjay Escon at the mean, or average, melt temperature of  $160^\circ\text{C}$ .

Convection calculation. A measure of the significance of convection was determined by the magnitude of the Rayleigh number, using typical values for the polymer melts tested. The terms used in the determination of the Rayleigh number were defined in the Literature Review. The values substituted for application in this instance were:

$$g = 970 \text{ cm./sec.}^2$$

$$d = 0.075 \text{ in.} = 0.19 \text{ cm.}$$

$$\Delta T = 10.0^\circ\text{C}$$

$$B = 10 \times 10^{-5}/^\circ\text{C}$$

$$\rho = 1 \text{ gm/cm.}^3$$

$$\nu = 1 \text{ lb}_f \text{ sec./in.}^2 = 480 \text{ gm./cm./sec.}$$

$$C_p = 0.45 \text{ cal./}^\circ\text{C gm.}$$

$$k = 0.12 \text{ BTU/ft.hr.}^\circ\text{F} = 0.0005 \text{ cal./cm.sec.}^\circ\text{C.}$$

Substituting these values, the resulting magnitude of the Grashof number is:

$$N_{Gr} = 2.91 \times 10^{-8}$$

The value of the Prandtl number is:

$$N_{Pr} = 4.32 \times 10^5$$

Thus, the value of the Rayleigh number is:

$$\begin{aligned} N_{Ra} &= (2.91 \times 10^{-8}) (4.32 \times 10^5) \\ &= 1.257 \times 10^{-2} \\ N_{Ra} &= 0.01257. \end{aligned}$$

For convection to be significant, the Rayleigh number must be greater than 700<sup>(29)</sup>.



Eccentricity calculation. Although the apparatus was assembled so that eccentricity of axes would be minimized, a calculation of the effect of eccentricity for this system is presented. The working equation is presented in the Literature Review. The values substituted were:

$$r_1 = 1.475 \text{ in.}, r_1^2 = 2.176 \text{ in.}^2$$

$$r_2/r_1 = 1.051$$

$$b = 0.005 \text{ in.}, b^3 = 25 \times 10^{-6}$$

$$\Delta T = 5.90^\circ\text{F}$$

$$Q = 12.99 \text{ watts} = 44.30 \text{ BTU/hr.}$$

Substituting these values,

$$k = 0.1141 \text{ BTU/ft.hr.}^\circ\text{F}$$

compared to the experimentally determined

$$k = 0.1188 \text{ BTU/ft.hr.}^\circ\text{F}$$

for this particular test. Thus, an eccentricity of 0.005 inch of 0.075 inch (polymer gap) gives an error about 4 percent.

APPENDIX G

Temperature Profile Data

Material	Thermocouple No.	Test					
		emf <sup>1</sup> mv.	T <sup>a</sup> °C	emf <sup>2</sup> mv.	T <sup>a</sup> °C	emf <sup>3</sup> mv.	T <sup>a</sup> °C
Glycerine	1	4.250	82.2	5.222	100.6	6.507	124.3
	2	4.257	82.3	5.228	100.7	6.524	124.6
	3	4.395	84.8	5.449	104.7	6.757	129.2
	4	4.414	84.9	5.453	104.6	6.713	128.4
	5	4.399	84.7	5.454	104.6	6.737	128.5
	6	4.384	84.8	5.412	104.2	6.707	128.5
	7	4.341	84.0	5.405	104.1	6.696	128.1
	8	4.353	83.9	5.412	103.5	6.693	127.7

Thermal Gradient  
(inner cylinder)  
°C/in.

-1.07

-1.18

-1.23

<sup>a</sup> corrected according to thermocouple calibration curves

Material	Thermo- couple No.	Test							
		emf mv.	<sup>1</sup> T <sup>a</sup> °C	emf mv.	<sup>2</sup> T <sup>a</sup> °C	emf mv.	<sup>3</sup> T <sup>a</sup> °C	emf mv.	<sup>4</sup> T <sup>a</sup> °C
Dupont Alathon	1	9.319	176.3	12.344	230.7	13.983	262.2	16.110	301.3
	2	9.416	178.0	12.390	232.0	14.014	262.8	16.132	301.7
	3	10.027	189.4	12.900	242.4	14.651	274.5	16.725	312.6
	4	9.980	188.0	12.883	241.2	14.623	273.5	16.736	312.1
	5	9.968	187.8	12.862	240.8	14.601	273.3	16.674	311.2
	6	9.890	187.1	12.790	240.6	14.512	272.6	16.579	310.5
	7	9.876	186.8	12.764	240.0	14.484	271.9	16.580	310.2
	8	9.871	185.4	12.782	239.3	14.463	271.3	16.609	309.8
Thermal Gradient (inner cylinder) °C/in.		-3.57		-2.83		-3.17		-3.31	

<sup>a</sup> corrected according to thermocouple calibration curves

Material	Thermo- couple No.	Test									
		1	2	3	4	5	6	7	8	9	10
		emf mv.	T <sup>a</sup> °C	emf mv.	T <sup>a</sup> °C	emf mv.	T <sup>a</sup> °C	emf mv.	T <sup>a</sup> °C	emf mv.	T <sup>a</sup> °C
Phillips Marlex 6002	1	8.534	161.9	9.546	180.5	10.352	196.3	11.392	214.6	12.382	232.6
	2	8.541	162.0	9.552	180.6	10.362	196.5	11.400	214.7	12.395	232.8
	3	8.914	168.9	10.032	189.5	10.863	204.8	11.822	222.6	12.871	241.7
	4	8.935	168.9	10.025	188.8	10.845	204.1	11.836	222.3	12.866	241.0
	5	8.907	168.5	9.997	188.4	10.824	203.7	11.824	222.1	12.855	241.0
	6	8.856	168.3	9.968	188.5	10.762	203.3	11.753	221.7	12.749	240.0
	7	8.843	167.9	9.922	187.5	10.755	203.1	11.736	221.2	12.732	239.5
	8	8.851	167.3	9.944	187.1	10.752	202.2	11.731	220.2	12.749	238.7
Thermal Gradient (inner cylinder) °C/in.		-1.67		-2.31		-2.42		-2.34		-3.04	

<sup>a</sup> corrected according to thermocouple calibration curves

Material	Thermo- couple No.	Test							
		emf mv.	1 T <sup>a</sup> °C	emf mv.	2 T <sup>a</sup> °C	emf mv.	3 T <sup>a</sup> °C	emf mv.	4 T <sup>a</sup> °C
Dow Styron	1	10.131	191.2	11.498	215.3	13.093	245.7	14.727	277.6
	2	10.149	191.6	11.517	215.6	13.112	246.2	14.755	278.1
	3	10.634	200.6	12.172	228.6	13.859	260.0	15.657	293.0
	4	10.638	200.2	12.165	227.9	13.836	259.0	15.628	291.8
	5	10.582	199.4	12.131	227.2	13.830	258.9	15.591	291.2
	6	10.541	199.2	12.055	227.0	13.742	258.4	15.536	291.3
	7	10.533	199.0	12.007	226.1	13.695	257.4	15.489	290.3
	8	10.537	198.1	12.021	225.3	13.717	256.5	15.504	289.2
Thermal Gradient (inner cylinder) °C/in.		-2.38		-3.27		-3.37		-3.44	

<sup>a</sup> corrected according to thermocouple calibration curves

Material	Thermo- couple No.	Test							
		emf mv.	1 T <sup>a</sup> °C	emf mv.	2 T <sup>a</sup> °C	emf mv.	3 T <sup>a</sup> °C	emf mv.	4 T <sup>a</sup> °C
Enjay Escon	1	8.201	157.6	10.197	192.4	11.332	213.3	12.687	238.3
	2	8.210	157.8	10.208	192.7	11.353	213.7	12.709	238.7
	3	8.628	163.8	10.612	200.2	11.817	222.5	13.325	250.2
	4	8.631	163.3	10.603	199.5	11.825	222.5	13.312	249.2
	5	8.609	162.9	10.581	199.3	11.807	221.8	13.274	248.6
	6	8.564	162.8	10.551	199.3	11.748	221.6	13.222	248.7
	7	8.542	162.2	10.485	198.1	11.724	221.0	13.152	247.3
	8	8.532	161.5	10.491	197.5	11.722	220.0	13.172	246.6

Thermal Gradient  
(inner cylinder)  
°C/in.

-2.20

-2.62

-2.57

-3.48

<sup>a</sup> corrected according to thermocouple  
calibration curves

Material	Thermocouple No.	1		2		Test 3		4		5	
		emf mv.	T <sup>a</sup> °C	emf mv.	T <sup>a</sup> °C	emf mv.	T <sup>a</sup> °C	emf mv.	T <sup>a</sup> °C	emf mv.	T <sup>a</sup> °C
Dow Badische Nylon 6	1	11.353	213.9	12.019	225.0	12.768	239.8	13.487	253.0	14.515	272.1
	2	11.358	214.0	12.032	225.2	12.781	240.0	13.501	253.3	14.527	272.3
	3	11.881	223.6	12.674	238.1	13.429	252.0	14.162	265.5	15.297	286.4
	4	11.914	223.7	12.703	238.1	13.470	252.2	14.154	264.8	15.304	285.9
	5	11.892	223.3	12.641	237.1	13.421	251.5	14.158	264.9	15.292	285.7
	6	11.808	222.7	12.642	237.1	13.304	250.3	14.054	264.1	15.211	285.3
	7	11.813	222.6	12.571	236.4	13.297	249.9	14.053	263.7	15.130	283.8
	8	11.851	222.4	12.607	235.5	13.340	249.6	14.027	262.5	15.166	283.2
Thermal Gradient (inner cylinder) °C/in.		-1.48		-2.69		-3.00		-2.84		-3.38	

<sup>a</sup> corrected according to thermocouple calibration curves



Material	Thermo- couple No.	Test									
		emf mv.	1 $T^a$ $^{\circ}\text{C}$	emf mv.	2 $T^a$ $^{\circ}\text{C}$	emf mv.	3 $T^a$ $^{\circ}\text{C}$	emf mv.	4 $T^a$ $^{\circ}\text{C}$	emf mv.	5 $T^a$ $^{\circ}\text{C}$
Dupont Zytel	1	10.007	189.1	10.984	207.1	11.586	218.1	12.566	232.1	13.019	244.5
	2	10.014	189.2	11.002	207.3	11.599	218.3	12.579	232.3	13.030	244.7
	3	10.572	199.5	11.581	218.0	12.274	230.6	13.055	245.1	13.859	260.0
	4	10.576	198.9	11.604	217.9	12.253	229.9	13.084	245.1	13.867	259.5
	5	10.538	198.5	11.554	217.0	12.226	229.4	13.022	244.0	13.847	259.2
	6	10.491	198.2	11.468	216.5	12.181	229.5	12.943	243.7	13.722	258.0
	7	10.492	198.2	11.483	216.4	12.116	228.1	12.914	242.8	13.697	257.4
	8	10.466	197.0	11.482	215.7	12.127	227.2	12.919	242.0	13.707	256.5
Thermal Gradient (inner cylinder) $^{\circ}\text{C}/\text{in.}$		-2.17		-2.45		-3.31		-3.38		-3.76	

<sup>a</sup> corrected according to thermocouple calibration curves

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DEVELOPMENT OF AN APPARATUS TO MEASURE THE  
THERMAL CONDUCTIVITY OF POLYMER MELTS

by

Thomas R. Fuller

ABSTRACT

The purpose of this investigation was to develop an apparatus to measure the thermal conductivity of polymer melts, and to use the apparatus to measure the thermal conductivity of selected melts as a function of melt temperature.

The steady-state, coaxial cylinder method with guard heaters was used and the annular gap was 0.075 inch. The polymer was melted in a cylindrical melt chamber, then metered to the thermal conductivity measuring apparatus. Cartridge heaters provided heat input and temperature measurements were made with calibrated, differential, iron-constantan thermocouples.

The thermal conductivity of polyethylene, polystyrene and nylon melts tested increased with increased temperature. The thermal conductivity of the polypropylene sample was temperature independent. Complexity of molecular structure lowered melt thermal conductivity.

Radiation losses were accounted for and convection was determined to be absent. The results were shown to be within a 3 percent experimental measurement error. Meaningful confidence limits cannot be calculated because of the limited number of data points.