MOLECULAR WEIGHT AND CONCENTRATION DEPENDENCE OF THE THERMAL CONDUCTIVITY OF POLYSTYRENE IN BENZENE

By

Lionel B. Epps, Jr.

Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute
in candidacy for the degree of

MASTER OF SCIENCE

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February 1968

Blacksburg, Virginia

TABLE OF CONTENTS

CHAPTER PAGE

APPENDICES

LIST OF TABLES

TABLE PAGE

LIST OF FIGURES

I. INTRODUCTION

The study of the thermal conductivity of liquids and solutions is important in that the results can be used to test theoretical models and thus help to elucidate the nature of molecular mechanisms involved in transport phenomena. Such studies also have significant technological applications in the design of thermal exchange processes.

Theories of liquid thermal conductivities can be categorized in the following general classes: extensions of the Kinetic Theory of gases, theories based on cell or free volume models of the liquid state, and rigorous Statistical Mechanical formulations. The limited success of these theories and the difficulties encountered in their use is discussed in the Literature Review. There are empirical relations for the conductivity of liquids and solutions, but they are, in general, of limited range and applicability.

The viscosity of polymer solutions has received a great deal of attention and the literature abounds with both phenomenological and molecular theories. In marked contrast, the diffusivities of polymer solutions have been studied very little and their thermal conductivities are virtually uninvestigated.

It was the object of this study to investigate the concentration and molecular weight dependence of the thermal conductivity of solutions of polystyrene in benzene at 25° C and atmospheric pressure. The concentrations ranged from 0.1 to 15.0 weight percent polystyrene and three molecular weights were studied: 21,000, 264,000, and 660,000 grams per mole (number average molecular weights). The conductivity measurements were made in a concentric cylinder apparatus with guard heaters to minimize end losses.

II. LITERATURE REVIEW

This section contains a brief review of the literature pertinent to this investigation. The first three sections (Theories of Thermal Conduction in Liquids, Experimental Methods for Determining Liquid Thermal Conductivities and Errors in Thermal Conductivity Determinations) treat liquid thermal conductivity and its measurement. The next three sections define the various types of molecular weight averages and discuss the two experimental techniques (intrinsic viscosity, and osmotic pressure) used to characterize the polymers of this investigation.

Theories of Thermal Conduction in Liquids

Predictive equations of the thermal conductivity of liquids fall into two categories: theoretical and empirical correlations. The empirical equations have, in general, met with greater success than the theoretical expressions. The limited success of the theoretical attempts is due, in part, to the lack of an adequate equation of state for liquids.

Conduction in liquids.- The mechanism of heat conduction in liquids is not clear. There are two possible modes by which excess energy can be transported down a temperature gradient: (a) by a vibrational mechanism and (b) by a "convective mechanism." Horrocks and McLaughlin (11) have made calculations which indicate that the "convective mechanism" (may be visualized as molecular "hopping") is the same as that operative in self-diffusion and is of negligible magnitude compared to the vibratory mode. Frenkel (10), on the other hand, in his "Kinetic Theory of Liquids," concluded that the convective mode is the only mechanism operative in liquids. The vibratory theory seems to conform to the data better; for example, in an isomeric series of o, m, and p - terphenyls, the structure dependence of the viscosity was found to be marked. In contrast, the thermal conductivity varied little with structures (14). The difference in the dependencies can be explained in terms of the mechanisms. To transport energy by thermal conduction, a molecule need only oscillate in its cell without breaking the intermolecular forces with its neighbors. For momentum transfer, continual disruption of the intermolecular forces between layers moving with different hydrodynamic velocities is essential for the process to occur and leads to sensitivity to structure. The vibratory mechanism also predicts the correct temperature dependencies for thermal conductivity (12).

Theoretical equations.- A full interpretation of the thermal conductivity can, in principle, be obtained from a statistical-mechanical treatment. The application of the theories to the calculation of the thermal conductivity is, as always, complicated because of a lack of knowledge of the force fields which operate in liquids. If a simple potential is chosen, usable but inaccurate equations are obtained. A more rigid approach leads to equations which are unwieldy and cannot be tested experimentally (37). The rigorous theories have, so far, appeared as complicated integro-differential equations, giving the thermal conductivity as a function of the disturbances of the radial distribution function (6). The results of Kirkwood are typical of these theories (18).

Theories of thermal conductivity based on the Free Volume theory of the liquid state yield somewhat more tractable results (see Horrocks and McLaughlin (11)). The thermal conductivities predicted by this theory show the best agreement with experimental data (23). An excellent review of the theories of thermal conductivity in liquids has been recently published by McLaughlin (18).

Empirical equations.- As mentioned in the opening paragraph of this section, empirical equations have been more successful in predicting the thermal conductivities of liquids than the best theoretical equations yet proposed. These empirical equations have been critically reviewed and their predictions compared with experimentally observed thermal conductivities (19).

Bridgeman's equation (35), while it has some theoretical basis, is considered here as being basically empirical. Bridgeman's empiricism lies in his somewhat arbitrary assumption that thermal energy is transmitted within the liquid at the velocity of sound and the fact that a numerical constant has to be adjusted to give good agreement with experimental data. Bridgeman's equation is of the form:

$$K = \frac{cRU_s}{d^2} \qquad (1)$$

where: c = numerical constant

R = universal gas constant

U_s = velocity of sound in the liquid

d = intermolecular spacing

K = thermal conductivity

Assuming (on the average) a cubical arrangement of the molecules, d can be calculated from

$$d = \left(\frac{\rho}{M}\right)^{1/3} \tag{2}$$

where: ρ = density

M = molecular weight

Bridgeman predicted a value of two for the numerical constant, but a slightly adjusted value gives predictions in better agreement with experimental data.

The first equation to relate the thermal conductivity to other properties of the liquid was that of Weber (35)

$$K = 3.59 \times 10^{-3}\ C_p\ \rho\left(\frac{\rho}{M}\right)^{1/3} \tag{3}$$

where: C_p = heat capacity at constant pressure

Other properties which have been used successfully in correlations of the thermal conductivity for certain classes of liquids include the heat of vaporization (23), viscosity and ASTM viscosity-temperature slope (19), molecular weight (19) (23), chain length of hydrocarbons (19), and functional group contributions (23) (19). These correlations and others have been reviewed by Tsederberg (36) who also gives recommendations as to their applicability.

Tsederberg (36) recommends the following empirical equation for binary liquid solutions

$$K = K_2 g_2 + K_1 (1 - g_2) - 0.72 (K_2 - K_1) g_1 (1 - g_2) \tag{4}$$

where: g_1 and g_2 = weight fraction of components 1 and 2

K_1 and K_2 = thermal conductivity of components 1 and 2

Experimental Methods for Determining Liquid Thermal Conductivities

If conditions for the measurements are such that convection is absent, the energy equation reduces to:

$$\rho\, C_p \frac{\partial T}{\partial t} = K \nabla^2 T \qquad (5)$$

where: ρ = fluid density

C_p = heat capacity

T = temperature

t = time

∇^2 = Laplacian operator

If further, the determination is made at steady-state, the equation becomes

$$0 = K \nabla^2 T \qquad (6)$$

Experimental methods for determining liquid thermal conductivities have been classified according to whether they are steady or nonsteady state and also by the geometry of the apparatus. The following classification was proposed by Sakiadis and Coates (28).

I. STEADY STATE METHODS

1. Thin Film Methods
    - a. Parallel plates
    - b. Concentric cylinders
    - c. Concentric spheres
    - d. Hot wire methods

2. Thick Film Methods
    a. Parallel plates

II. UNSTEADY STATE METHODS
  1. Thin Film Methods
    a. Hot wire
  2. Thick Film Methods
    a. Parallel plates

A detailed description or comparison of these methods will not be attempted here. Some brief comments are given below and the reader is referred to specific literature references for detailed accounts.

Of the steady-state methods, the concentric sphere eliminates end effects and most nearly conforms to unidimensional heat conduction. Construction and centering problems are, however, more formidable than for any other method. For a recent account of the development of a concentric sphere apparatus, see Couper (2).

The concentric cylinder apparatus is less difficult to construct than the spherical apparatus, but because of the geometry, end effects become appreciable and must be compensated. This is usually done with guard heaters at both ends of the apparatus. The apparatus of Tsederberg (34) is typical. An interesting variation of the concentric cylinder design involving hemispherical ends has been designed by Leidenfrost (17).

The parallel plate apparatus presents the least difficulty in construction and is simple to employ. In this geometry, guard rings around the liquid specimen must be used to avoid edge losses. Apparatus with both two (Sakiadis and Coates (29) and three (Orr (29)), parallel plates have been used.

Excellent reviews of the techniques which have been employed in measuring the thermal conductivity of liquids have been published (28), (29), (34), (15), and (31).

Errors in Thermal Conductivity Determinations

Radiation.- Because of the temperature gradient in an experimental apparatus, some heat is transferred by radiation. The precise evaluation of this loss is a complex problem (see Bird et al. (5)), but it is possible to estimate its limiting magnitude (18).

The radiant energy q_r' emitted from the surface of a nonblack body of emissivity e, at a temperature T_2 into a surrounding enclosure is given by

$$q_r' = A\, e\, \sigma T_2^4 \qquad (7)$$

where σ $(5.67 \times 10^{-12}$ joule sec^{-1} cm^{-2} $^{o}K^{-4})$ is the Stefan-Boltzman constant and A is the effective emitting area. The rate of energy absorption by the surface of absorptivity, a, from the surroundings at a temperature T_1 is given by

$$q_r'' = Aa\, \sigma\, T_1^4 \qquad (8)$$

assuming that the energy reaching the surface is black-body radiation corresponding to temperature T_1. The net rate of loss is, therefore,

$$q_r = A\, \sigma \left(e\, T_2^4 - a\, T_1^4\right) \qquad (9)$$

For real materials a and e are < 1 and approximately equal. Thus, by making the assumption $a = e = 1$, the maximum loss is obtained. For the small temperature difference employed in thermal conductivity measurements, $(T_2^4 - T_1^4)$ may be approximated as $T_m^3 \Delta T$. Thus, quation (9) can be written

$$q_r = 4A \sigma T_m^3 \Delta T \tag{10}$$

where: $T_m = \dfrac{T_1 + T_2}{2}$

The heat transfer by conduction in a concentric cylinder apparatus is given by

$$q = \frac{K 2\pi L (T_2 - T_1)}{ln\left(\frac{r2}{r1}\right)} \tag{11}$$

where: L = the length of the cylinders

r_2 and r_1 = the radii of the outer and inner cylinders, respectively.

It follows that the ratio of the heat loss due to radiation to that due to conduction is

$$\frac{q_r}{q} = \frac{4 \sigma T_m^3}{K} ln\left(\frac{r2}{r1}\right)$$

Convection.- If a temperature gradient is applied to a fluid initially at rest, the resulting density gradient produces a bouyancy force which, although opposed by viscous forces in the state of mechanical equilibrium, eventually causes instability. This instability manifests itself in bulk convective flow, free convection.

From thermodynamics, the change in density due to temperature at constant pressure is

$$d\rho = \beta dT \quad \text{where} \quad \beta = -\frac{1}{\rho}\frac{\partial \rho}{\partial T} \tag{12}$$

Consider a fluid contained between two parallel plates (a good approximation for concentric cylinders with small annular gaps) at $y = b$ and $y = -b$, with the temperature to be constant at T_1 at $-b$ and T_2 at b. The equation of motion for an incompressible fluid of constant viscosity is

$$\rho \frac{D\vec{v}}{Dt} = -\nabla p + \mu \nabla^2 \vec{v} + \rho \vec{g} \tag{13}$$

where: $\vec{v}$ = velocity vector

$\vec{g}$ = gravitational acceleration

t = time

p = pressure

Assuming the temperature gradient is linear, the energy equation at steady-state reduces to

$$\frac{d^2T}{dy^2} = 0 \tag{14}$$

This assumes that the viscous dissipation term is small compared to the convective transport of thermal energy which is a good approximation for nonviscous liquids. These differential equations have been solved, using the stated boundary conditions (see Bird (4)) to give the velocity distribution in terms of the dimensionless variable $n = y/b$

$$v_z = \bar{\rho}\,\bar{\beta}\, g b^2\, \Delta T \,\frac{(n^3 - n)}{12\mu} \tag{15}$$

where: $\bar{\rho}$ = density evaluated at mean fluid temperature

$\bar{\beta}$ = thermal expansivity evaluated at mean fluid temperature

v_z = component of the velocity in the z-direction

Equation (14) may be rewritten in terms of a dimensionless velocity

$$\xi = \frac{b\ v_z\ \bar{\rho}}{\mu}$$

$$\xi = \frac{1}{12}\Big(N_{Gr}\ (n^3 - n)\Big) \qquad (16)$$

where N_{Gr} is a dimensionless group known as the Grashof number,

$$N_{Gr} = \frac{\bar{\rho}^2\ \bar{\beta}\ gb^3\ \Delta T}{\mu^2} \qquad (17)$$

When the equations of state, motion, continuity, and energy are applied to specific convection problems, two independent dimensionless groups are seen to arise. They are the Grashof number and the Prandtl number N_{Pr}. The Prandtl number is a measure of the ratio of the molecular diffusivity of momentum to the molecular diffusivity of energy.

$$N_{Pr} = \frac{\mu Cp}{K} \qquad (18)$$

The product of N_{Pr} and N_{Gr} is defined as the Rayleigh number N_{Ra},

$$N_{Ra} = N_{Pr}\ N_{Gr} \qquad (19)$$

The onset of convection has been found experimentally to occur at a critical value of N_{Ra}.

Kraussold (34) studied the conditions at which convective heat transfer arose in various liquids in concentric cylinders. His results indicate that convection is negligible for $N_{Ra} < 1000$. Because of the errors in the quantities entering the Rayleigh number, Tsederberg (34) has recommended that N_{Ra} not exceed 700.

It is important to note that the use of this criterion assumes that there are no "end effects"; that is, that the temperature field contains no distortions or irregularities at the ends of the apparatus (14). Such distortions of the symmetry of the steady-state temperature field can induce convection. It is desirable to have some independent experimental check for the onset of convection.

"Ellington has contended that no previous author has offered definite proof that the system used was one of pure conduction." (30). While most investigators have considered the problem of convection in the design of equipment and operating conditions, they fail to demonstrate experimentally that the equipment is free of convection. To demonstrate for each apparatus that pure conduction exists, Ellington proposed that the heat flux be plotted as a function of the temperature difference. Then, for pure conduction, a straight line should result which passes through the origin.

Eccentricity.- In the concentric cylinder method, the axis of the external cylinder should coincide with the axis of the internal cylinder. If the axes do not coincide and an eccentricity δ exists between them, the correct equation for K will be (34)

$$K = \frac{Q\ ln}{2L\pi\ \Delta T} \left\{ \frac{\sqrt{\Sigma_{12}^{2} - \delta^{2}} + \sqrt{\Delta_{12}^{2} - \delta^{2}}}{\sqrt{\Sigma_{12}^{2} - \delta^{2}} - \sqrt{\Delta_{12}^{2} - \delta^{2}}} \right\} \qquad (20)$$

where: $\Sigma_{12} = r_1 + r_2$

$\Delta_{12} = r_1 - r_2$

This correction applies only to translation of the cylindrical axes. No correction has been proposed for the deviation of one or both axes from the vertical. The effect of an eccentricity of this sort is best estimated by testing the apparatus with a fluid of known thermal conductivity.

Polymer Molecular Weight Averages

In any finite sample of polymer, there exists a distribution of molecular weights. This is a natural consequence of the nature of polymerization processes in general. Because of this distribution, any experimental determination of molecular weight can give only an average value. The average depends on the nature of the averaging process and this, in turn, depends on the property which is being experimentally measured. The magnitude of the average will increase with increasing sensitivity of the measured effect to the weight of a molecule.

In the determination of molecular weights from measurements of the thermodynamic properties of dilute polymer solutions, each module, regardless of size, makes the same contribution to the measured effect. Such determinations are, therefore, said to yield the number average molecular weight $\bar{M}_n$. If

$$\int_{M_1}^{M_2} N(M)dM$$

is the fraction of molecules with molecular weights in the range $M_1 \leq M \leq M_2$ where M is the molecular weight of a given molecule (treated here as a continuous, rather than discrete variable for large distributions (20)); then

$$\overline{M}_n = \frac{\int_0^\infty M\ N(M)dM}{\int_0^\infty N(M)dM} \tag{21}$$

The mathematical operations indicated in Equation (21) are equivalent to summing the fraction of molecules with molecular weight M over all values of M and dividing the result by the sum of the fractions $\left(\int_0^\infty N(M)dM\right)$. Since the sum of the fractions is by definition unity, Equation (21) may be written

$$\overline{M}_n = \frac{\int_0^\infty M\ N(M)dM}{1} \tag{22}$$

Techniques which might yield $\overline{M}_n$ include: boiling point elevation, freezing point depression, vapor pressure lowering, and osmometry.

The scattering of light by the solute molecules in solution is a phenomenon useful for polymer molecular weight determinations. The intensity of the light scattered by the solute is proportional to the square of the particle mass (3). The effect obtained with a polydisperse solute (i.e., a solute with a distribution of molecular weights) depends on its weight average molecular weight $\overline{M}_w$ defined by

$$\overline{M}_w = \int_0^\infty M\ W(M)dM \tag{23}$$

where $W(M)$ is defined such that

$$\int_{M_1}^{M_2} W(M)dM$$

is the weight fraction of material with molecular weights in the range $M_1 \leq M \leq M_2$. $W(M)$ is related to $N(M)$ by

$$W(M)dM = \frac{M\ N(M)dM}{\int_0^\infty M\ N(M)dM} \tag{24}$$

thus, $\bar{M}_w$ can be expressed as

$$\bar{M}_w = \frac{\int_0^\infty M^2\ N(M)dM}{\int_0^\infty M\ N(M)dM} \tag{25}$$

It can be seen from Equation (25) that $\bar{M}_w$ weights the larger molecules more heavily than $\bar{M}_n$, and for polydisperse systems $\bar{M}_w$ is always greater than $\bar{M}_n$. The ratio $\bar{M}_w/\bar{M}_n$ and $(\bar{M}_n/\bar{M}_n) - 1$ are both used as measures of the polydispersity of the system (20).

The molecular weight of linear polymers has been empirically correlated with the intrinsic viscosity $[\eta]$ of polymer solutions. Both $[\eta]$ and the nature of the correlation are discussed in the next section. The general form of the correlations is (32)

$$[\eta] = K'\ {M_v}^{\nu} \tag{26}$$

where: M_v = viscosity average molecular weight

K', ν = empirical constants

K' and ν are functions of the solvent and depend on such factors as the method and temperature of polymerization among others.

Figure 1 depicts the distribution of molecular weights in a typical polymer and shows the relative positions of the various averages.

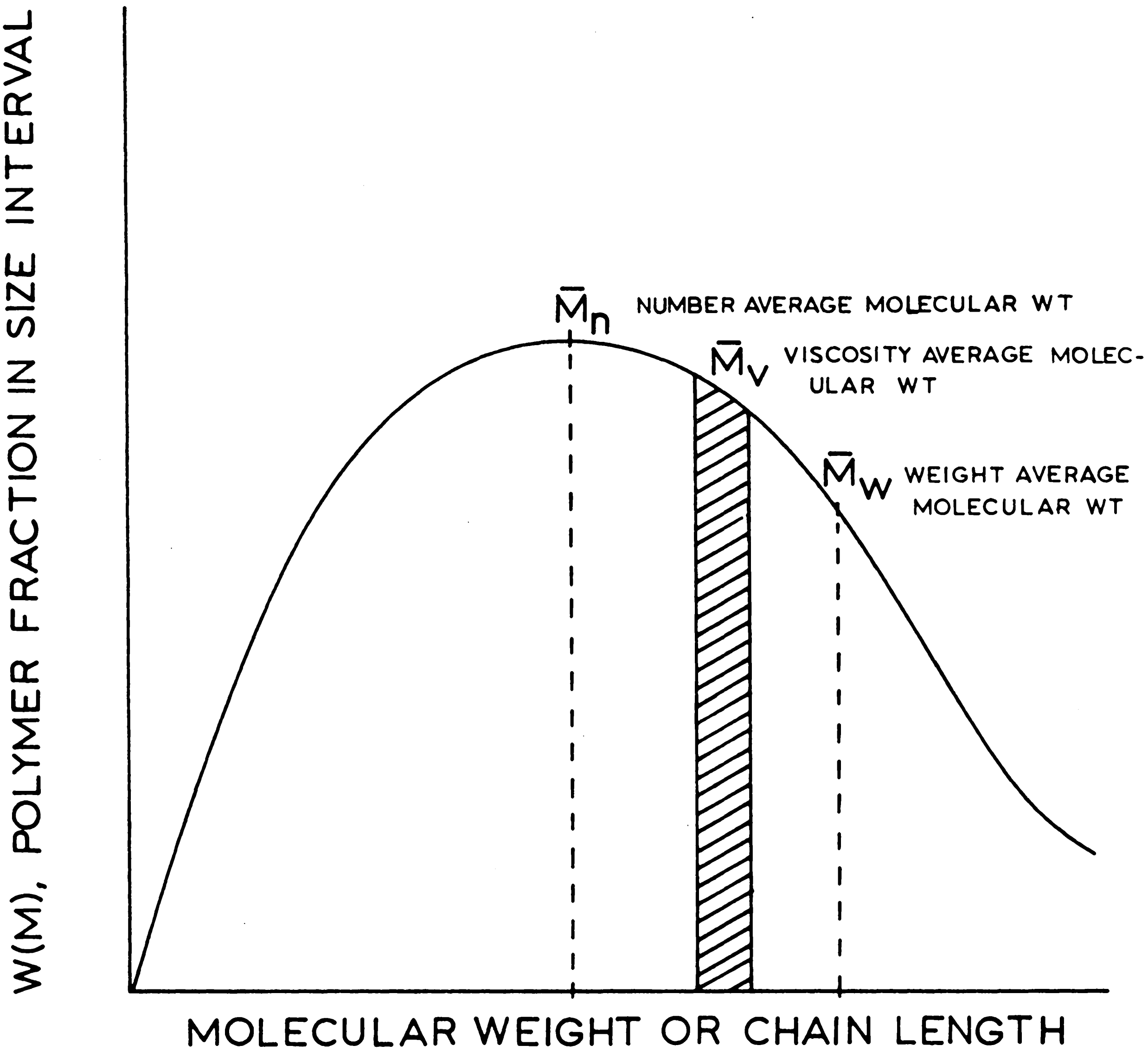

FIGURE 1.- MOLECULAR WEIGHT DISTRIBUTION IN TYPICAL POLYMER.

Other molecular weight averages have been defined, but these are not pertinent to this investigation. For detailed accounts of the experimental techniques of molecular weight determination see Allen (1).

Intrinsic Viscosity and its Relation to Molecular Weight

Before any discussion of the viscosity of polymer solutions is possible, it is necessary to define some terms. Some confusion exists in the literature because there are two sets of nomenclature in common use. These are given in Table I, page 19, along with the units that will be used herein. The "common" nomenclature will be used here because it is more prevalent in the literature. The reader should experience no difficulty in converting from one system to the other with this table.

Solutions of polymers are, in general, non-Newtonian fluids and their viscosities are, thus, functions of shear rate (see Appendix D, page 103). For the dilute solutions used in intrinsic viscosity determinations, however, the deviation from Newtonian behavior is not great and shear rate corrections are negligible. Intrinsic viscosity measurements are made in capillary viscometers. If the efflux time of the solvent is greater than 100 seconds, then the kinetic energy correction (see Appendix D, page 103) is negligible. Since all the viscosity measurements are made relative to the solvent, the efflux times may be compared directly and the viscometer need not be calibrated.

In order to calculate the intrinsic viscosity $[\eta]$ for a polymer solution, it would be necessary to calculate the flow of solvent around the dissolved molecule and obtain from the flow pattern the increase in

TABLE I.- NOMENCLATURE OF SOLUTION VISCOSITY

Common name (3)	Recommended name (11)	Symbol and defining equation (a)
Relative viscosity	Viscosity ratio	$\eta_r = \eta/\eta_o \approx t/t_o$
Specific viscosity		$\eta_{sp} = \eta_r - 1 = (\eta - \eta_o)/\eta_o$ $\approx (t - t_o)/t_o$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp}/C$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = (ln\ \eta_r/C)$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = (\eta_{sp}/C)_{C=o}$ $[\eta] = \left[(ln\ \eta_r)/C\right]_{C=o}$

(a) Where η = viscosity

t = efflux time

C = concentration

Subscript zero denotes solvent

Billmeyer, F. W.: Textbook of Polymer Science. John Wiley and Sons, Inc. New York, N. Y., 1962, p. 80.

the viscosity due to the presence of the disturbance. As in the case of thermal conductivity, the exact solution of the hydrodynamic equations is hampered by lack of an adequate model of the liquid state. For only one case has an exact calculation been made. The intrinsic viscosity for a suspension of spherical particles was derived by Einstein (33).

$$\eta_{sp} = 2.5\ \rho_2 \quad \text{and} \quad [\eta] = \frac{2.5}{\rho_2} \tag{27}$$

where: η_{sp} = specific viscosity

ρ_2 = solute density

There are some rather restrictive assumptions involved in obtaining the result (see Tompa (33)), but there is evidence that Stoke's law on which the derivation of Equations (27) are based is applicable far beyond the limitations of the assumptions. By assuming various simple models for polymer solutions and making some approximations, it is possible to relate the intrinsic viscosity to the parameters of the system.

A convenient model to assume for the polymer molecule is the "Pearl-Necklace Model" (33). It depicts the polymer as a statistical chain of beads joined by rigid lengths.

The most probable configuration for such a chain is a spherically shaped random coil with a segment density which is given approximately by the Gaussian distribution.

The flow of solvent through the molecule has been described by two extreme cases.

The free-draining coil concept assumes that the liquid is undisturbed by the presence of the polymer molecule except in the immediate neighborhood of each bead. This theory results in a relationship between $[\eta]$ and the molecular weight of the form (33)

$$[\eta] \approx M^{\nu} \tag{28}$$

where M is the molecular weight and ν is a constant > 1. Such a dependence for $[\eta]$ on M is contrary to all the experimental evidence, and the free-draining coil has been generally abandoned as a model for polymer solutions in viscous flow.

At the other extreme is the impermeable-coil model. This model assumes that the molecule is tightly coiled and that the liquid within the coil is completely immobilized. Thus, the flow outside the coil does not penetrate it, and the coil and enclosed liquid can be treated as a single hydrodynamic entity. Such spherical coils roughly fit the conditions of Equation (27), page 20, and the intrinsic viscosity can be expressed (33)

$$[\eta] = (2.5)\frac{4}{3}\pi R_e^3 \frac{N}{M} \tag{29}$$

where: N = Avogadro's number

R_e = hydrodynamic radius of spherical coil

This result is, however, not useful unless R_e can be related to dimensions of the molecular coil. If it is assumed that R_e is proportional to the root-mean-square end-to-end distance $(\overline{r^2})^{1/2}$ of the polymer chain, then it can be shown (Flory (9)) that R_e is also proportional to $M^{1/2}$. From Flory's relationship between M and R_e and Equation (29), it can be seen that the intrinsic viscosity is proportional to $M^{1/2}$. Flory's result is

$$[\eta] = \frac{\Phi(\overline{r^2})^{3/2}}{M} \tag{30}$$

As indicated above, this equation predicts a simple proportionality between $[\eta]$ and $M^{1/2}$, but this dependence has not been experimentally observed. Flory attributed this discrepancy to a volume effect which had not been considered.

The concept of the polymer molecule as a statistical chain fails to recognize the finite volume of a segment of the chain. The relation

$$(\overline{r^2})^{1/2} = \lambda\ z^{1/2} \tag{31}$$

where: λ = length of a segment

z = number of segments in a polymer chain

is a result of random flight calculation. These calculations consider those spatial requirements that affect the flexibility of the chain (rotations about single bonds, etc.) but do not attribute any volume to the chain segments and allow them to approach each other with arbitrary closeness. The consideration of a finite volume for the segments reduces the number of possible configurations from random flight considerations considerably. The volume occupied by one segment is obviously excluded to all other segments; this principle has been called the "excluded volume effect." This consideration tends, generally, to expand the molecular coil. In Flory's theory (33), all linear dimensions of the coil are uniformly expanded by an expansion factor α. Thus,

$$(\overline{r^2})^{1/2} = \alpha \, (\overline{r_o^2})^{1/2} \qquad (32)$$

where the subscript zero indicates the coil dimensions "unperturbed" by molecular interactions. Interactions occur within the excluded volume and tend to contract the coil due to intramolecular, nearest neighbor, attractions. Thus, α is the function of two effects: the expansion of the coil due to the excluded volume and its contraction due to intramolecular interactions.

Flory has defined a characteristic temperature, the theta temperature θ, which represents the lowest temperature for complete miscibility of a polymer of infinite molecular weight in a given solvent. At this temperature, there is no net interaction between polymer and solvent, and the solution is considered to be ideal. At this temperature, which varies from solvent to solvent, the chain dimensions will be unperturbed and α will equal 1.

Flory has also shown (25) that

$$\alpha^5 - \alpha^3 = C_T \sqrt{M} \qquad (33)$$

where C_T depends on properties of both the polymer and solvent as well as the temperature, but is independent of M. Thus,

$$\overline{r^2} \approx M^{(1+\epsilon)} \qquad (34)$$

where, with increasing C_T, ϵ increases from 0 to 0.20, it follows then that ϵ is related to ν

$$\nu = \frac{(1 + 3\epsilon)}{2} \qquad (35)$$

and increases from 0.50 to 0.80 which is in agreement with experiment (25).

The preceding section has been an attempt to acquaint the reader with the theoretical significance of the constants in the relation

$$[\eta] = K' \, M^{\nu} \qquad (36)$$

Throughout the development of Equation (36) it has been assumed that the polymer was monodisperse. Thus, the symbol M represents the actual polymer molecular weight as opposed to an average. To use this empirical relation, it is necessary to have two well-fractionated samples of polymer of known molecular weight. With the intrinsic viscosity and molecular weight data, the constants K' and ν can be determined from a log-log plot of $[\eta]$ against M.

When this method is applied to polymers with a distribution of molecular weights, Equation (36) must be modified as follows:

$$[\eta] = \lim_{c \to 0}\left(\frac{\eta_{sp}}{c}\right) = K' \frac{\sum_i M_i^{\nu} c_i}{\sum_i c_i} \qquad (37)$$

where: c_i = weight fraction of polymer with molecular weight M_i

$c = \sum_i c_i$

The intrinsic viscosity of the heterogeneous sample is interpreted in terms of Equation (36) by defining a viscosity average molecular weight $\bar{M}_v$. Thus,

$$[\eta] = K' M_v^{\nu} \tag{26}$$

and from Equation (37) on page 24

$$\bar{M}_v = \left(\frac{\sum_i M_i^{\nu} c_i}{\sum_i c_i} \right)^{1/\nu} \tag{38}$$

Osmotic Pressure of Polymer Solutions

Figure 2 represents schematically an apparatus in common use for osmotic pressure measurements. The membrane is permeable to solvent but not to high molecular weight solutes. The chemical potential of the solvent in the solution is less than that of the pure solvent and, consequently, if the system is to be at equilibrium, the chemical potential of the solvent μ_1 on either side of the membrane must be made equal. This may be done by applying excess pressure to the solution. The excess pressure required is called the osmotic pressure, Π, and is related to the change in the chemical potential by (1)

$$\Delta\mu_1 = -\Pi V_1 \tag{39}$$

where V_1 is the molar volume of the solvent (assumed independent of pressure for the small changes involved).

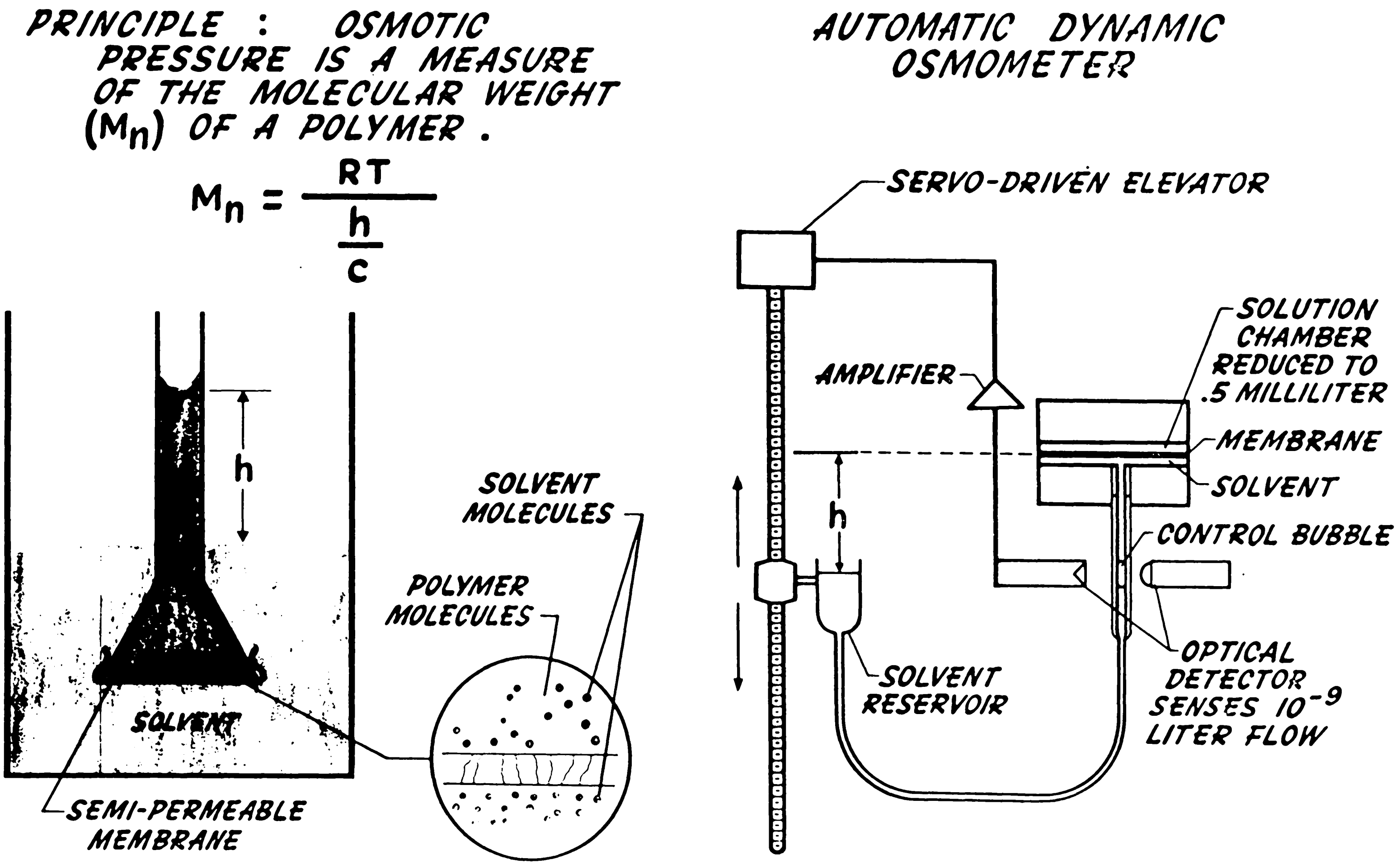

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FIGURE 2. POLYMER MOLECULAR WEIGHT FROM OSMOTIC PRESSURE

As the solutions become more dilute, the activity, a, of the solvent approaches its mole fraction, x. At infinite dilution, the solution is ideal and $a = x$. It follows that the depression of the activity of the solvent by a solute is equal to the mole fraction of the solute (3). Thus, for dilute solutions where x_2 approaches zero, Equation (38) becomes

$$\Pi V_1 = - R T \ln x_1 \approx R T x_2 \tag{40}$$

where x denotes mole fraction and subscripts 1 and 2 denote solvent and solute, respectively. At low concentrations, the approximation may be made that

$$x_2 \approx \frac{c_2 V_1}{M_2} \tag{41}$$

where M_2 and c_2 are the molecular weight and concentration of solute. Therefore, in the limit of infinite dilution

$$\lim_{c_2 \to 0} \left[\frac{\Pi}{c_2}\right] = \frac{RT}{M_2} \tag{42}$$

For finite concentrations of polymer in thermodynamically good solvent, (i.e., one in which polymer-solvent contacts are favored over polymer-polymer contacts) a plot of Π/c_2 versus c_2 results in a line of positive slope, becoming convex to the c_2 - axis with increasing c_2. This behavior can be described by expressing the reduced osmotic pressure, Π/c_2 with a power series in c_2.

$$\frac{\Pi}{c_2} = \frac{RT}{M_2} + Bc_2 + Cc_2{}^2 + \cdots \tag{43}$$

Usually, no more than two terms are required. The virial coefficients B and C are strongly dependent on polymer-solvent interactions. The intercept RT/M_2 has been found (as predicted by the thermodynamics) to be independent of the solvent.

III. EXPERIMENTAL

This section contains the purpose of the investigation, the plan of experimentation, and the results.

Purpose of Investigation

The purpose of this investigation was the development of an apparatus for measuring the thermal conductivity of polymer solutions at atmospheric pressure, the calibration of the apparatus with fluids of known thermal conductivity and the measurements of the thermal conductivities of solutions of polystrene in benzene as a function of concentration and molecular weight at 25° C.

Plan of Experimentation

The experimental work for this investigation consisted of the following phases: selection of method, design and construction of the apparatus, calibration of the apparatus, characterization of polymer, and polymer solutions, thermal conductivity determinations of the polymer solutions.

Selection of the experimental method.- The steady-state, concentric cylinder method was chosen for this investigation. Some of the factors influencing this selection are given below:

(a) Steady-state methods yield the thermal conductivity directly and do not necessitate the accurate determination of heat capacity and density (as in most unsteady-state methods). Steady-state methods give more reliable and accurate results than nonsteady-state methods (18).

(b) In the concentric cylinder apparatus end effects can be minimized with guard heaters. This can be done with more ease than in the parallel plate method.

(c) The concentric sphere apparatus completely eliminates end effects.but it requires special equipment and knowledge to construct. This specialized capability was not available.

Design and description of apparatus.- Only a brief description is given here. The interested reader is referred to Appendix C, p. 91, which contains detailed drawings and a full description of the construction of the thermal conductivity cell.

The cell consisted of three concentric cylinders. The inner-most cylinder is composed of the measuring cylinder with guard heaters at both ends (see Figure 3). These cylinders were made of copper and contained resistance heating elements. The guard heaters minimized the axial heat loss from the measuring cylinder. This was accomplished by keeping the temperature difference between the ends of the measuring cylinder and the guard heaters small.

Concentric with measuring cylinder is a brass outer cylinder (see Figure 3). The annular gap (0.052 inch) between the brass cylinder and the copper cylinders (measuring cylinder and guard heaters) contained the test fluid. The concentric cylinder system was contained in a 3-inch I.D. copper tube.

Calibrated differential thermocouples were embedded in the measuring cylinder and the brass cylinder (a total of six pairs). The

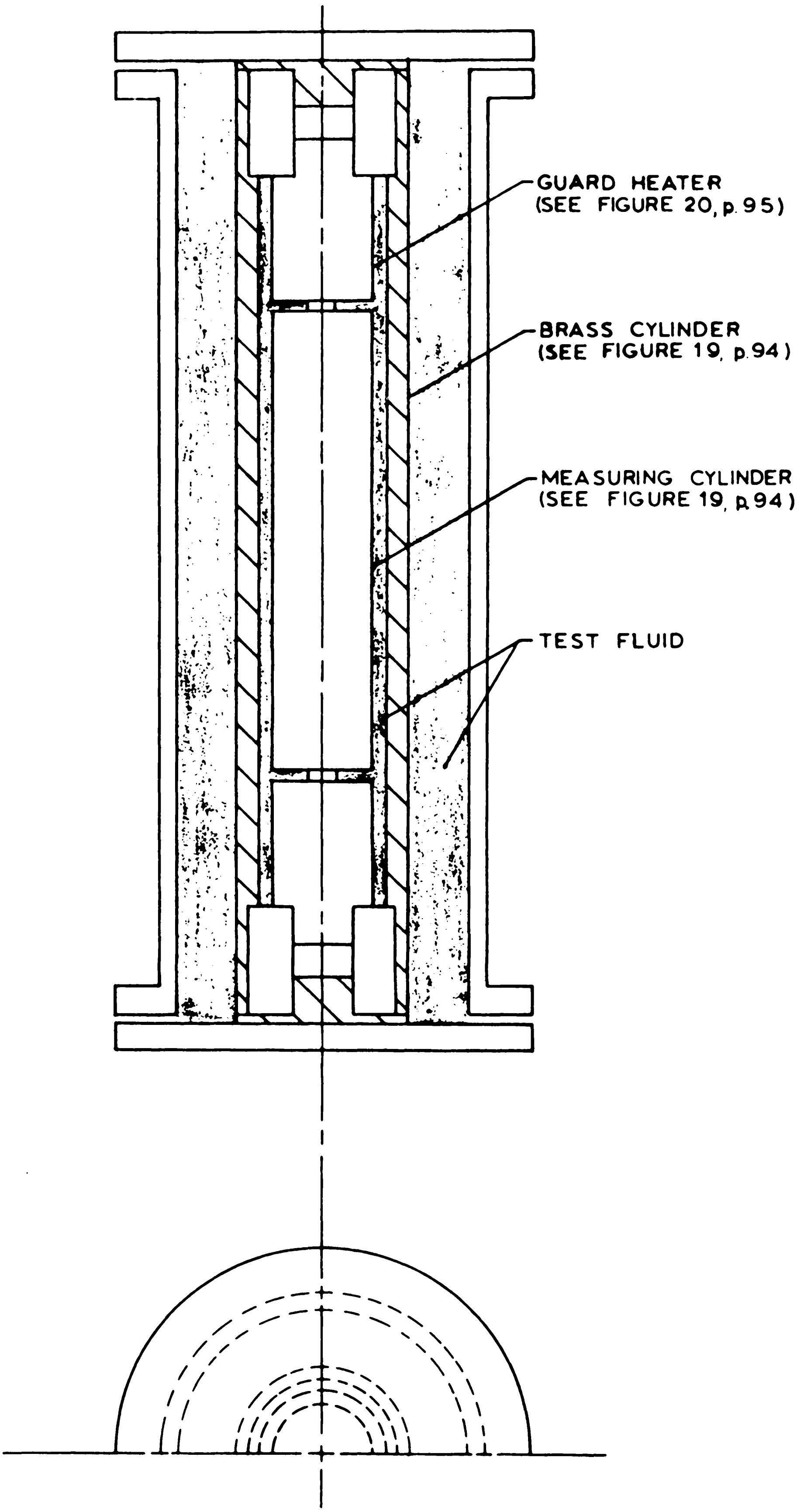

FIGURE 3 . THERMAL CONDUCTIVITY CELL

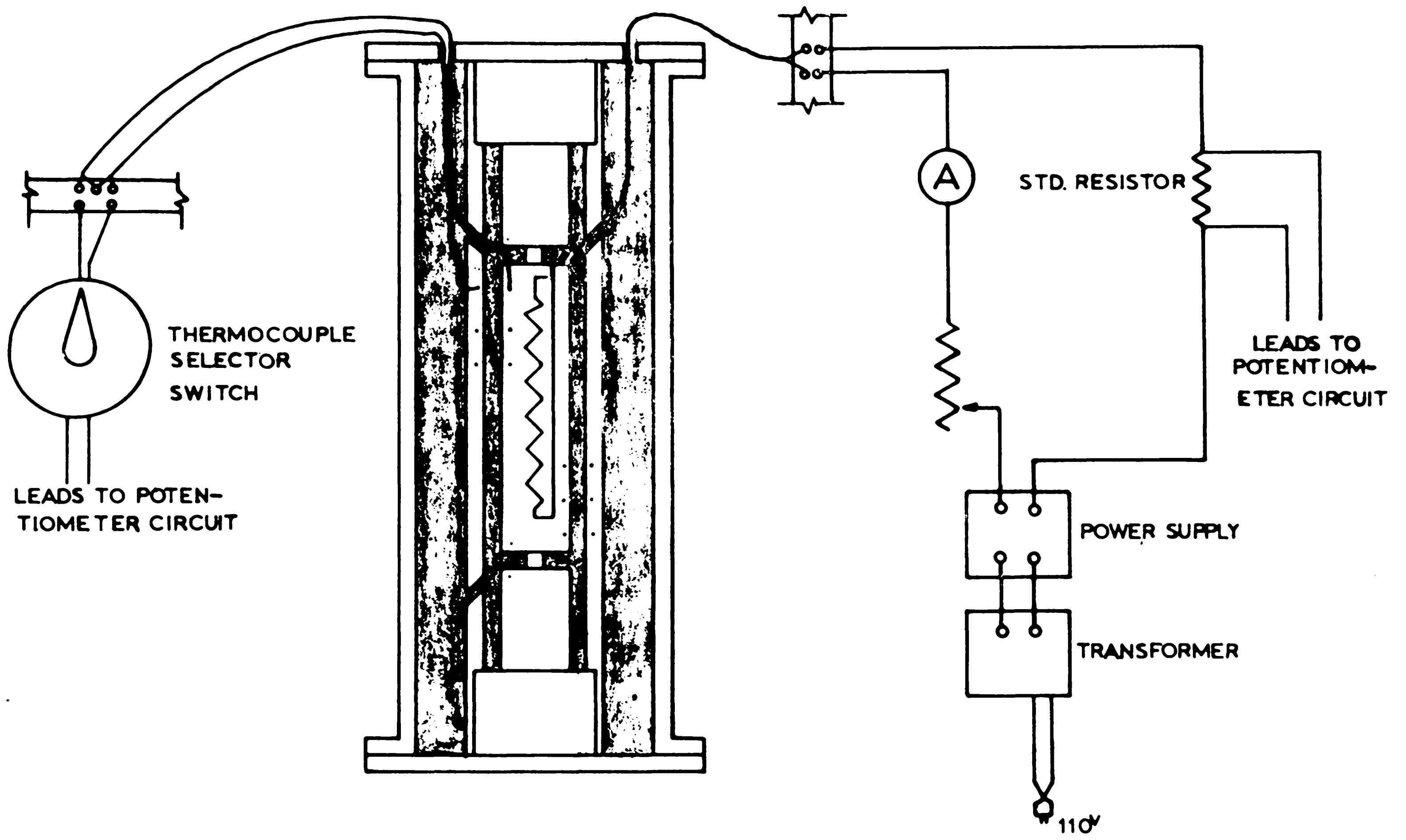

FIGURE 4. THERMAL CONDUCTIVITY MEASURING CIRCUIT

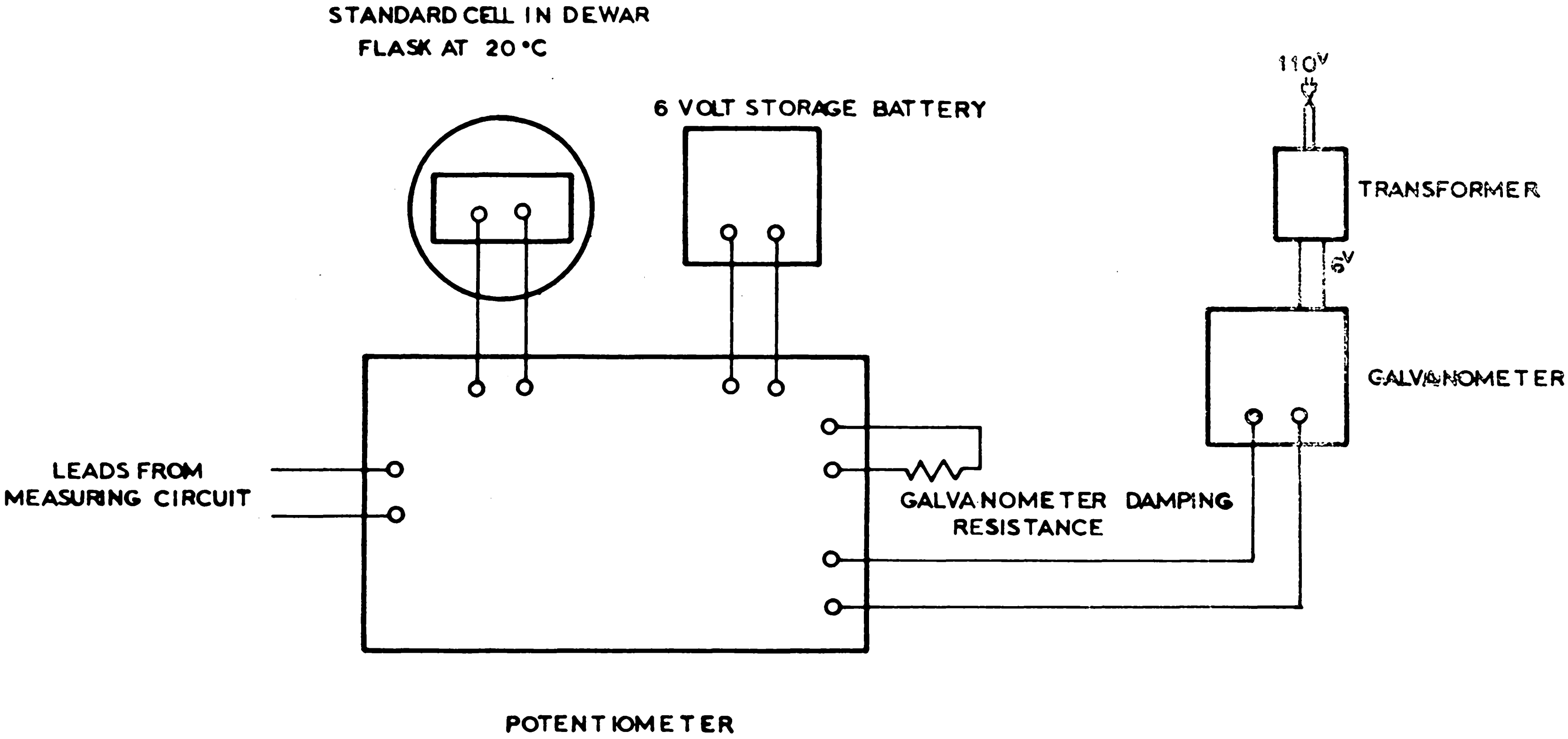

FIGURE 5. POTENTIOMETER CIRCUIT

temperature difference across the annular gap was calculated from the emf of the differential thermocouples.

The heat input to the measuring cylinder was calculated from the current and the resistance of the heater. The current in the measuring cylinder circuit was obtained by measuring the potential drop across a standard resistor with the potentiometer (see Figure 4). This resistor was maintained at a constant temperature and its resistance at that temperature was accurately known (see Appendix A, p. 76). The average temperature of the measuring cylinder was calculated from readings of the emfs generated by the thermocouples on the measuring cylinders paired with a thermocouple at 0° C. The resistance of the heater corresponding to this temperature could then be read from the calibration curve (Figure 18, p. 85).

The step by step procedure followed in making thermal conductivity measurements is given in Appendix E, p. 110).

Calibration of the apparatus.- In order to obtain an indication of the actual experimental error, the conductivity cell was calibrated with three fluids of known conductivity. These liquids were chosen with physical properties such that convection would be negligible. The fluids were: water, ethylene glycol, and cyclohexanol. The procedure followed in obtaining these measurements was the same as that followed in the polymer solution tests. The procedure is outlined in detail in Appendix E, p. 110.

Polymer characterization.- The intrinsic viscosities of the polymer samples were determined in benzene at 25° C. Samples for these determinations were obtained by a coning and quartering process which resulted in an approximately 100 gram sample of the 10-pound original sample. This procedure was performed twice on each polymer sample to obtain two representative samples of each original polymer sample. This was done to get an indication of the homogeneity of the respective samples. The procedure used in determining the intrinsic viscosity is outlined in Appendix B, page 86.

Osmotic pressure measurements of the polymer samples in toluene solution were made at 37° C. The results of these determinations were estimates of the number average molecular weights. These measurements were made in a high speed membrane osmometer with reconstituted cellulose membranes. The procedure followed was that recommended by the manufacturer in the instruction manual.

Results

This section contains the results of the polymer characterizations, cell calibration and polymer solution conductivity measurements.

Polymer characterization.- The results of the intrinsic viscosity determinations are shown on Figures 6 and 7. The data are tabulated in Tables XII and XIII on pages 88 and 89. The points for a given molecular weight represent different samples of a given molecular weight and different solutions made from those samples. In the case of the middle molecular weight, the points are also from different investigators. Despite all these various sources of variation, the results are within 1 percent. This indicated that the technique was reproducible and the polymer samples were homogeneous (this is not to say that the

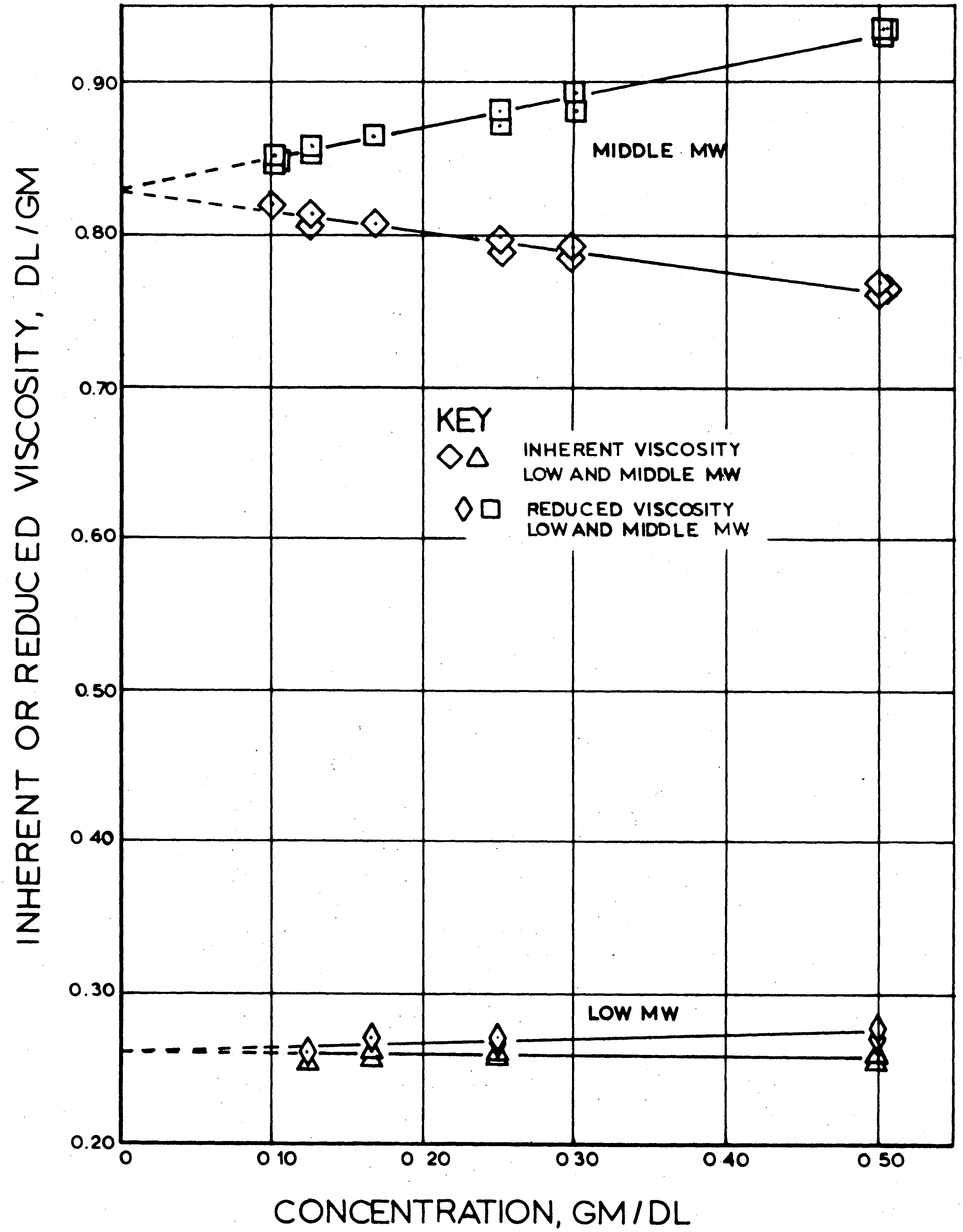

FIGURE 6 . DETERMINATION OF INTRINSIC VISCOSITY OF LOW AND MIDDLE MOLECULAR WEIGHT POLYSTYRENE IN BENZENE AT 25°C

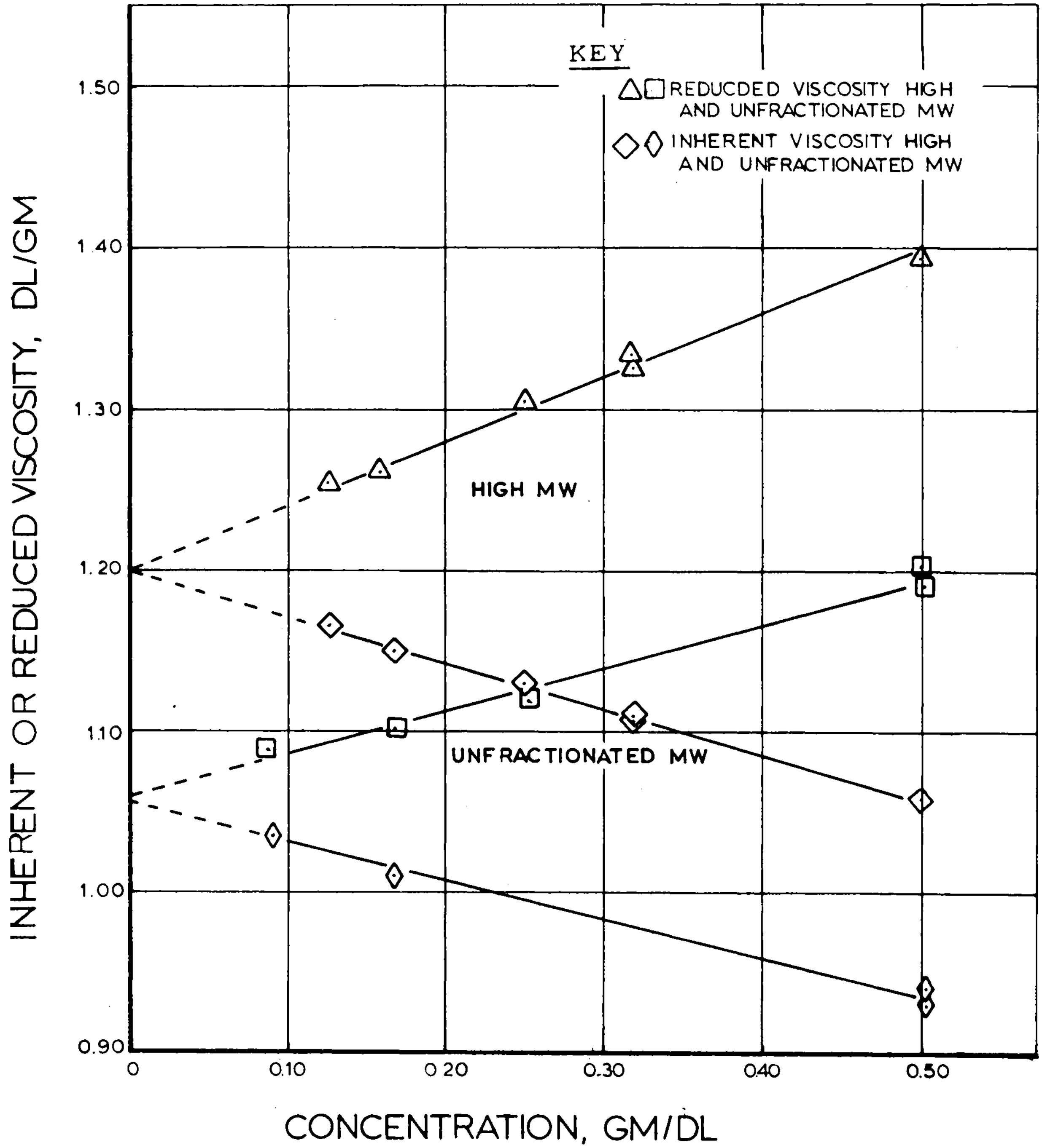

FIGURE 7. DETERMINATION OF INTRINSIC VISCOSITY OF UNFRACTIONATED AND HIGH MOLECULAR WEIGHT POLYSTYRENE IN BENZENE AT 25°C

samples were monodisperse). The data for each molecular weight are plotted in two ways: the specific viscosity and the inherent viscosity (see Table I, page 19). Both extrapolate to the intrinsic viscosity at infinite dilution. Therefore, plotting both these quantities provides a check on the extrapolation. The extrapolated values are given in Table II, page 40.

The results of the osmotic pressure measurements are shown on Figure 8, page 39. The data are extrapolated to infinite dilution and the number average molecular weight is calculated from the intercept (see Appendix D, page 98). The molecular weights calculated in this way are tabulated in Table II, page 40. It was not possible to make osmotic determinations on the low molecular weight polymer because diffusion of polymer through the membrane interfered with the equilibration.

Table II page 40 is a summary of all the characterization data resulting from the study for each polymer sample. Also included in the table are all the data provided by the manufacturer.

Calibration factor.- The thermal conductivity cell was calibrated with three fluids. The results revealed that it was necessary to apply a calibration factor to the results to compare them with the literature values. Three liquids (water, ethylene glycol, and cyclohexanol) whose thermal conductivities encompassed the range measured for polymer solutions were tested. The factor was found to be constant within the limits of experimental error (± 3.0 percent). It was thus assumed safe to apply the factor to the results. It was not possible to measure the conductivity of the solvent (benzene) because its physical properties indicate that convection would almost certainly have been present.

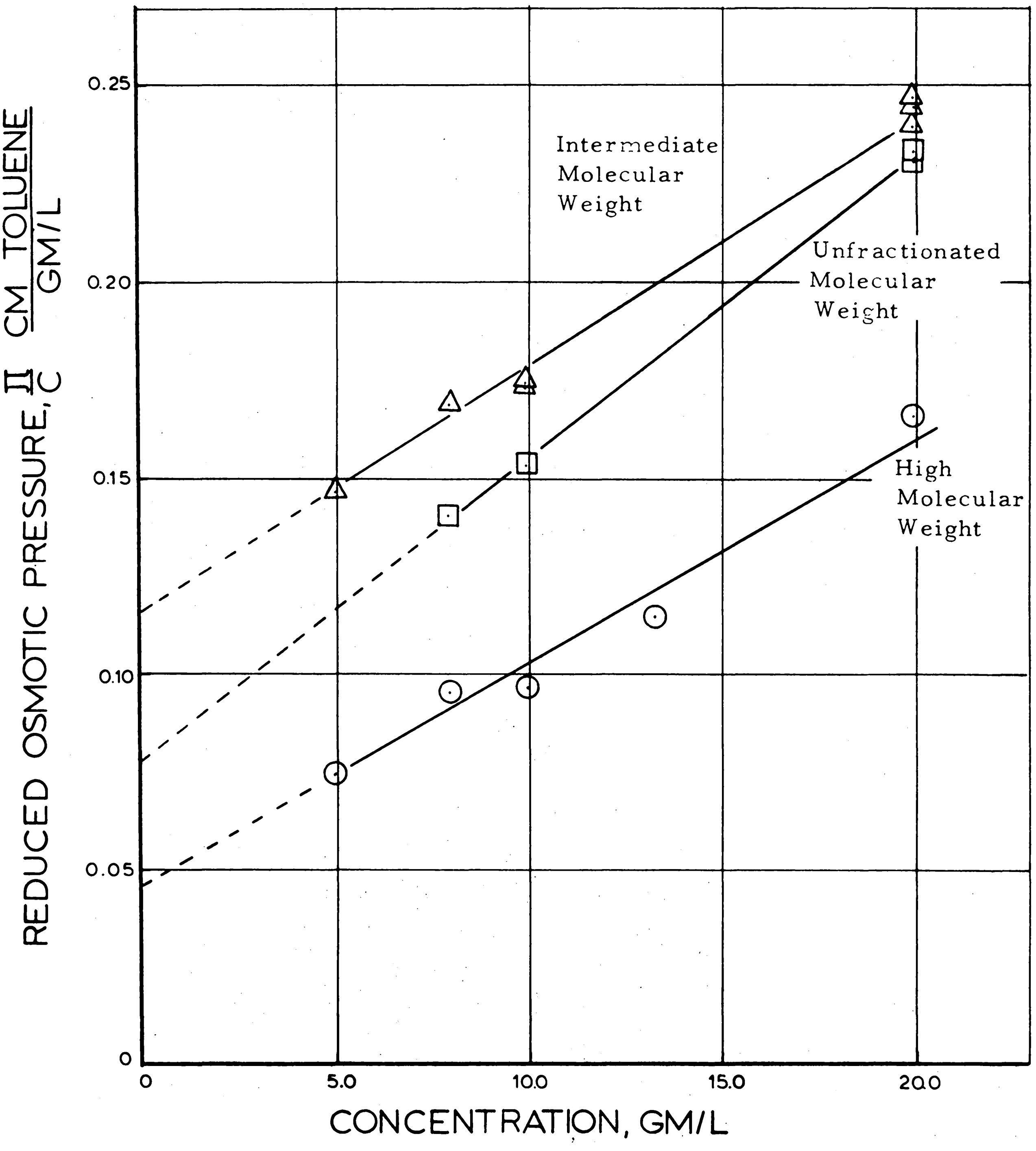

FIGURE 8. OSMOTIC PRESSURE OF POLYSTYRENE SAMPLES IN TOLUENE AT 37°C

TABLE II

RESULTS OF POLYMER CHARACTERIZATION

Sample	Method	Type of average	Average molecular weight gm-mole^{-1}	Intrinsic viscosity in C_6H_6 at 25° C dl - gm^{-1}
Low	GPC(a)	Number	21,000	0.265
	GPC(a)	Weight	61,000	——
Middle	Sedimentation(c)	Weight	245,000	0.830
	Osmometry(b)	Number	264,000	——
Unfractionated	Osmometry(b)	Number	389,400	1.06
High	Osmometry(b)	Number	660,000	1.20

(a) Gel Permeation Chromatography. Haynes, W. S., Pvt. Communication, Midland, Mich., April 1967.
(b) Membrane Osmometry (see Results, page).
(c) Ultracentrifugation. Parker, J. A., Pvt. Communication, Blacksburg, Va., October 1966.

The results of the thermal conductivity measurements for the calibration fluids (water, ethylene glycol, and cyclohexanol) are given in Table V page 44. The values of K in this table are corrected with the calibration factor (1.095) and are designated K_c. The uncorrected values are given in Appendix E with the experimental data.

The experimental data are plotted in Figure 9, page 45, with recommended values from the literature. The literature values are taken from literature surveys by various authors who have graded them according to the estimated experimental error. The data for water also include recommended values from McLaughlin (18).

Thermal conductivity of polymer solutions.- The results of the thermal conductivity measurements (corrected to reflect the calibration factor) are presented in Tables VI, VII, and VIII. The conductivities of solutions of the three molecular weights are plotted against concentration in Figures 10, 11, and 12. The curves drawn through the points in these figures are based on the results of a regression analysis of the data (see page 65). The dependence of the thermal conductivity on the number average molecular weight at 1 and 10 weight percent is shown in Figures 13 and 14. The lines through the points are curves of best fit in the least-square sense.

TABLE III

LITERATURE VALUES OF THE THERMAL CONDUCTIVITY OF CALIBRATION FLUIDS, CYCLOHEXANOL AND ETHYLENE GLYCOL

Liquid	T ^{o}F	K $\frac{Btu}{hr\text{-}ft\text{-}^{o}F}$	Investigator[(b)]	Grade[(a)]
Cyclo-hexanol	68	0.0791	Riedel(15)	B
	86	0.0796	Filippov(15)	B
Ethylene Glycol	68	0.1471	Riedel(28)	A
	86	0.1478		A
	68	0.1510		B
	104	0.1525		B
	122	0.1531		B
	68	0.1503	Slawecki(29)	B
	78	0.1505		B
	88	0.1507		B
	74.7	0.1460	Schmidt(29)	A
	86	0.1465		A
	68	0.1466	Grassmann(29)	B
	86	0.1478		B

(a) A grade of A or B indicates that the probable experimental error ≤ ± 2 percent or ≤ ± 5 percent, respectively. Grades assigned by authors cited.

(b) Literature references are found in Bibliography, p. 71.

TABLE IV

LITERATURE VALUES OF THE THERMAL CONDUCTIVITY OF CALIBRATION FLUIDS, WATER

Liquid	T ^oF	K $\frac{Btu}{hr\text{-}ft\text{-}^oF}$	Investigator[b]	Grade[a]
Water	68	0.3467	Powell(15)	A
	86	0.3551		A
	104	0.3631		A
	68	0.3460	McLaughlin(18)	- -
	86	0.3557		- -
	104	0.3641		- -
	68	0.3460	Riedel(15)	B
	104	0.3630		B
	64.4	0.3425	Smith(28)	B
	104	0.3660		B
	60.8	0.338	Van Der Held(28)	B
	103	0.360		B
	68	0.3470	Riedel(28)	B
	68	0.3460		B
	68	0.3440		B
	68	0.3594	Slawecki(28)	B
	78	0.3633		B
	88	0.3661		B

(a) A grade of A or B indicates that the probable experimental error $\leq \pm 2$ percent or $\leq \pm 5$ percent, respectively. Grades assigned by authors cited.

(b) Literature references are found in Bibliography, p. 71.

TABLE V

THERMAL CONDUCTIVITY OF CALIBRATION FLUIDS

Thermal conductivity K_c Btu-(hr-ft-$^\circ$F)$^{-1}$	Temperature $^\circ$F
Water	
0.353	76.8
0.356	78.3
0.354	76.1
0.354	78.1
0.354	77.9
Ethylene Glycol	
0.151	81.7
0.150	79.9
0.150	77.7
Cyclohexanol	
0.0815	79.0
0.0809	78.6
0.0821	79.7

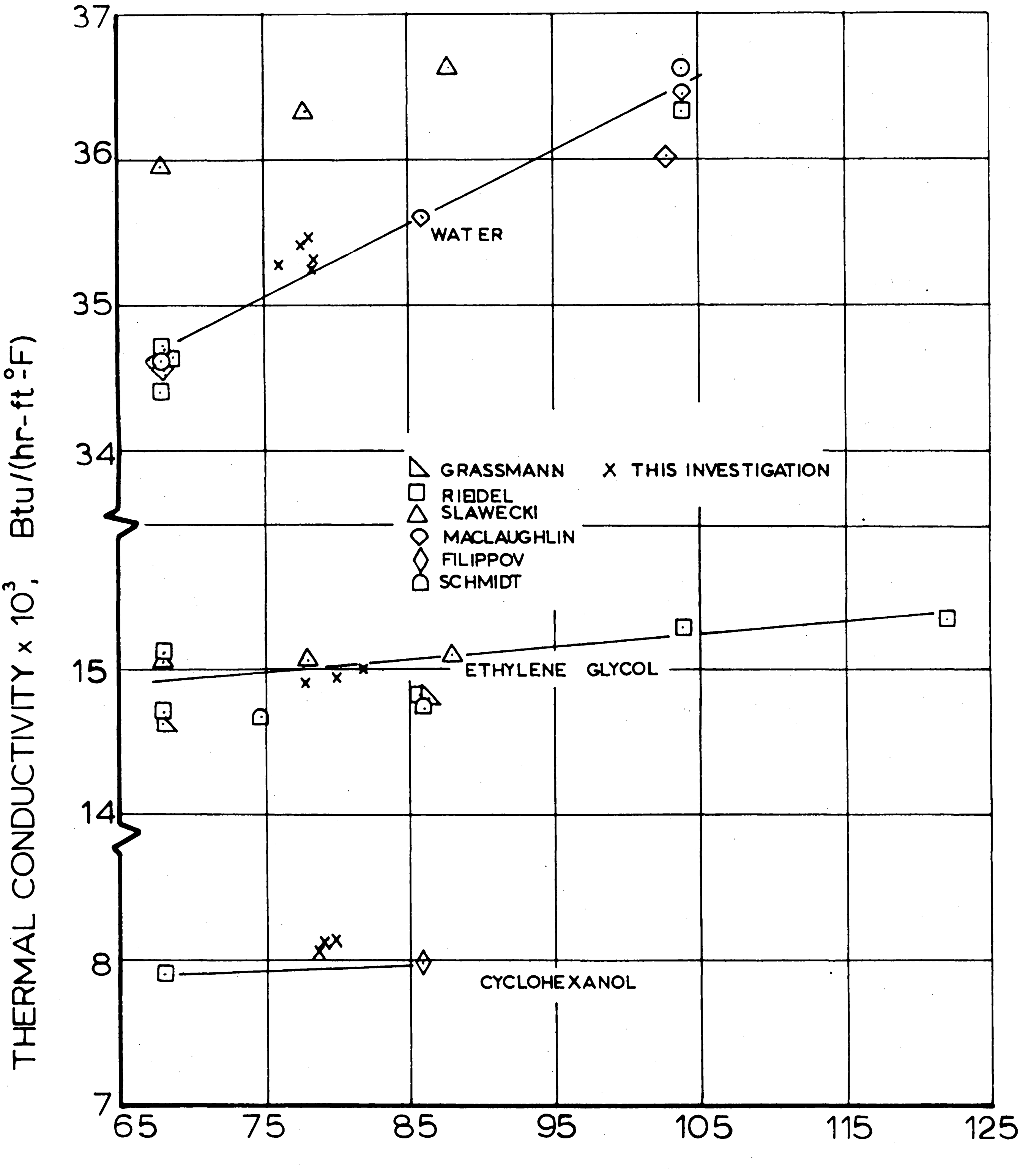

FIGURE 9. THERMAL CONDUCTIVITY OF CALIBRATION FLUIDS

TABLE VI

THERMAL CONDUCTIVITY OF SOLUTIONS OF LOW MOLECULAR WEIGHT POLYSTYRENE IN BENZENE

Concentration wt percent	Thermal conductivity K_C Btu/hr-ft-°F
1.0	0.0989
1.0	0.1010
10.0	0.0941
10.0	0.0942
15.0	0.0929
15.0	0.0936
15.0	0.0946

TABLE VII

THERMAL CONDUCTIVITY OF SOLUTIONS OF INTERMEDIATE MOLECULAR WEIGHT POLYSTYRENE IN BENZENE

Concentration wt percent	Thermal conductivity K_C Btu/hr-ft-^oF
1.0	0.0987
1.0	0.0981
1.0	0.0988
1.0	0.100
2.5	0.0962
2.5	0.0962
2.5	0.0975
10.0	0.0931
10.0	0.0929
15.0	0.0923
15.0	0.0923
15.0	0.0906

TABLE VIII

THERMAL CONDUCTIVITY OF SOLUTIONS OF HIGH MOLECULAR WEIGHT POLYSTYRENE IN BENZENE

Concentration wt percent	Thermal conductivity K_c Btu/hr-ft-°F
0.10	0.101
0.10	0.0996
0.10	0.0985
1.0	0.0954
1.0	0.0954
1.0	0.0959
5.0	0.0897
5.0	0.0901
5.0	0.0911
10.0	0.0883
10.0	0.0888
10.0	0.0890

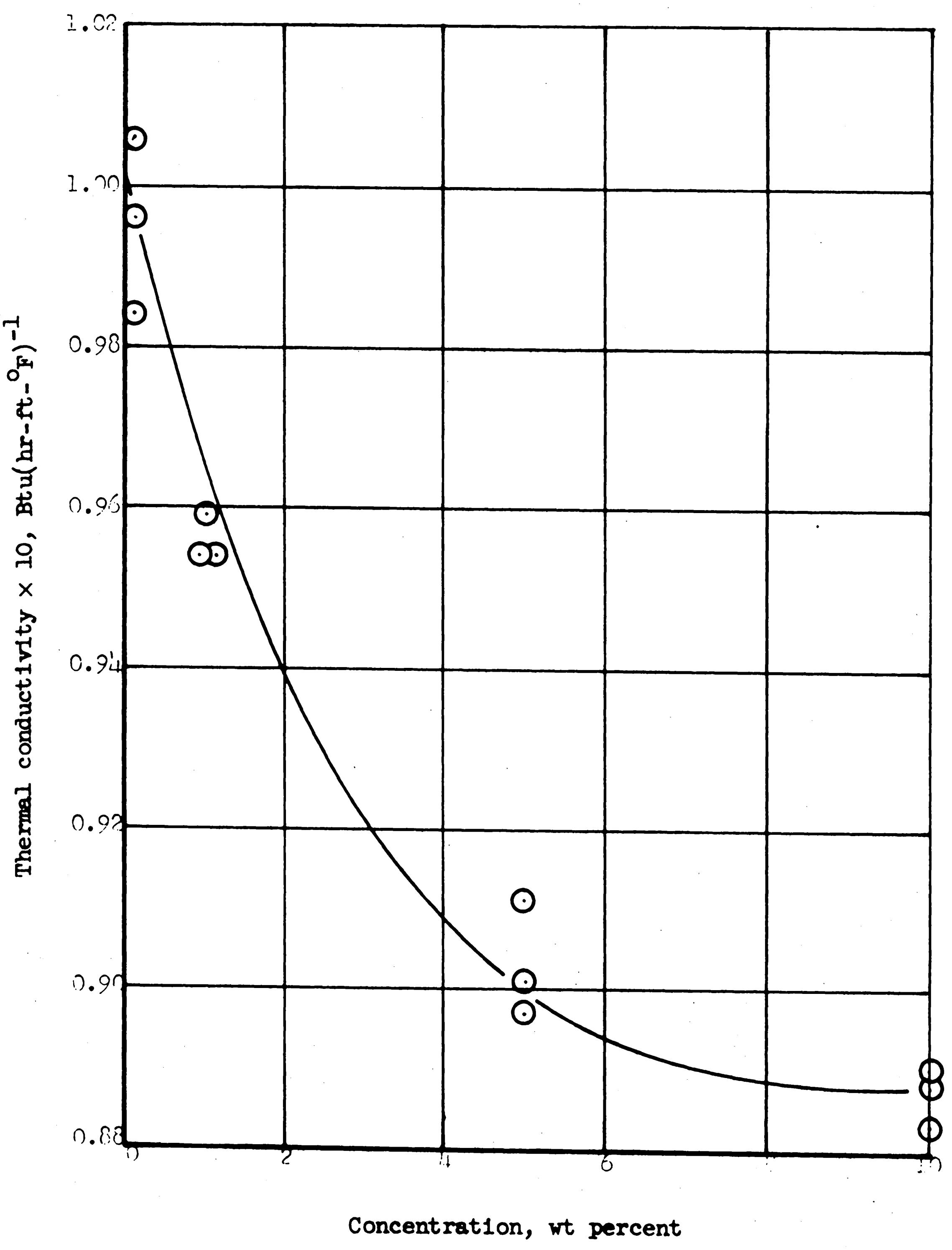

FIGURE 10. THERMAL CONDUCTIVITY VS CONCENTRATION HIGH MOLECULAR WEIGHT POLYSTYRENE IN BENZENE

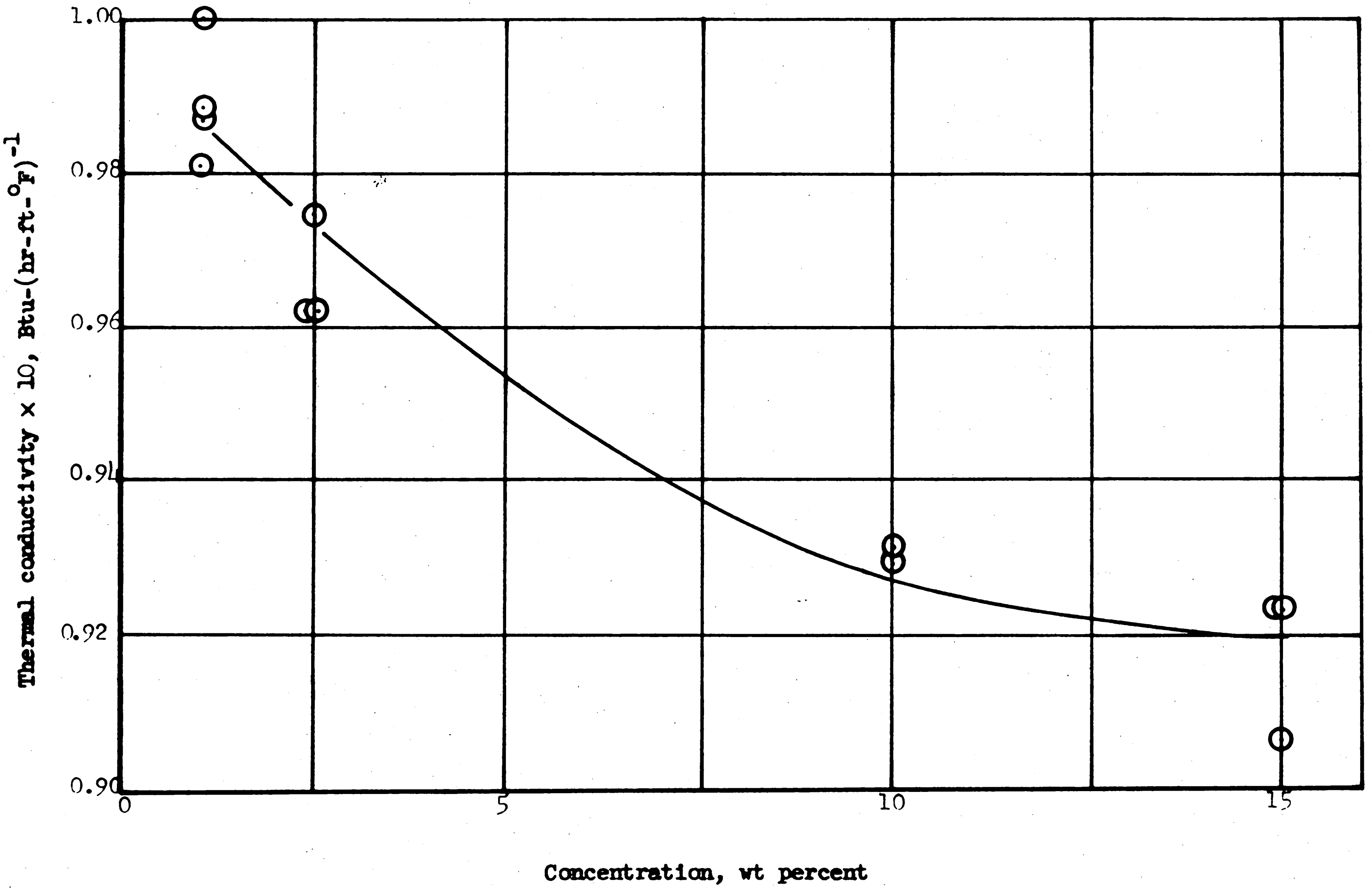

FIGURE 11. THERMAL CONDUCTIVITY VS. CONCENTRATION, INTERMEDIATE MOLECULAR WEIGHT POLYSTYRENE IN BENZENE

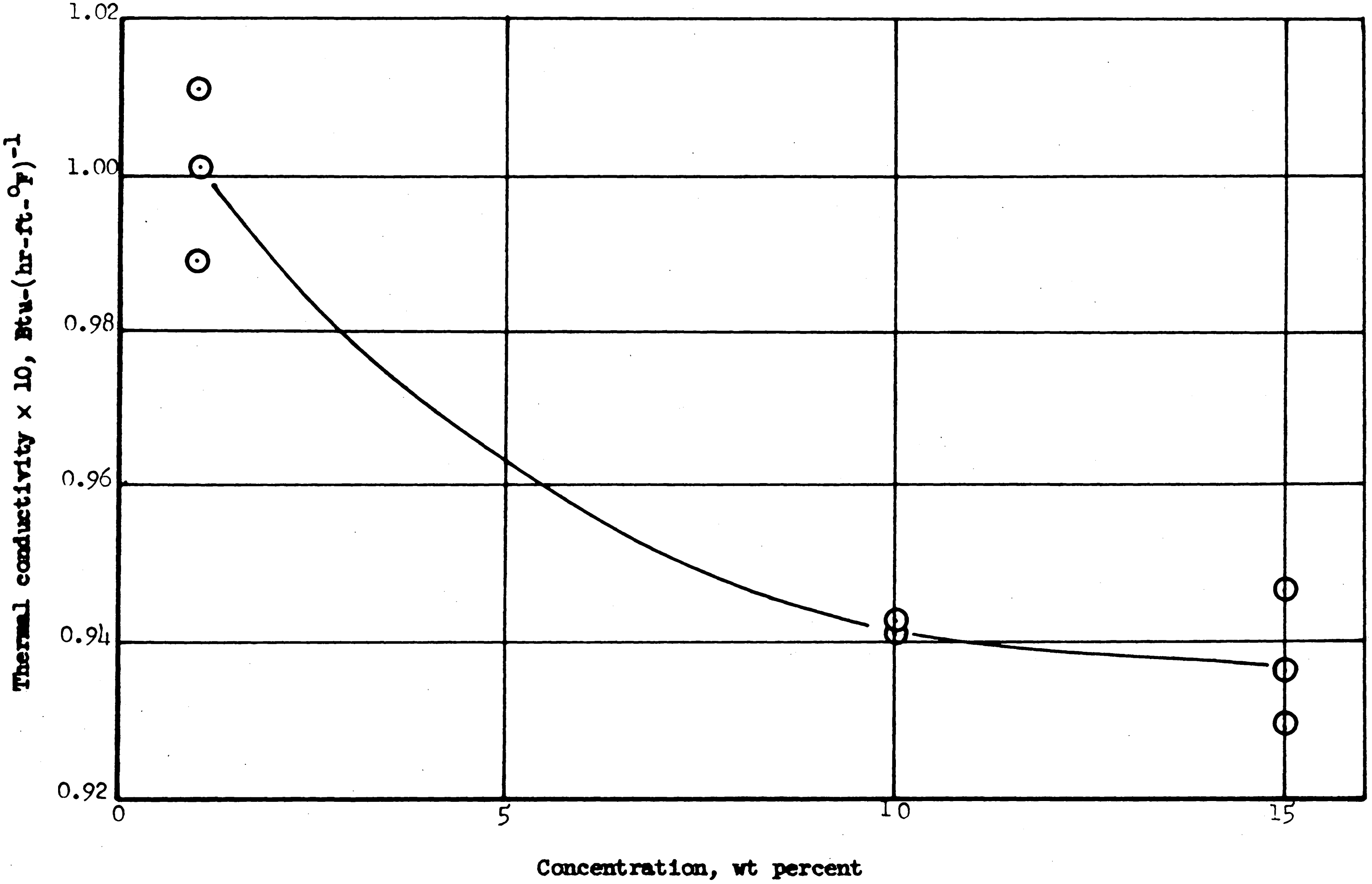

FIGURE 12. THERMAL CONDUCTIVITY VS. CONCENTRATION, LOW MOLECULAR WEIGHT POLYSTYRENE IN BENZENE

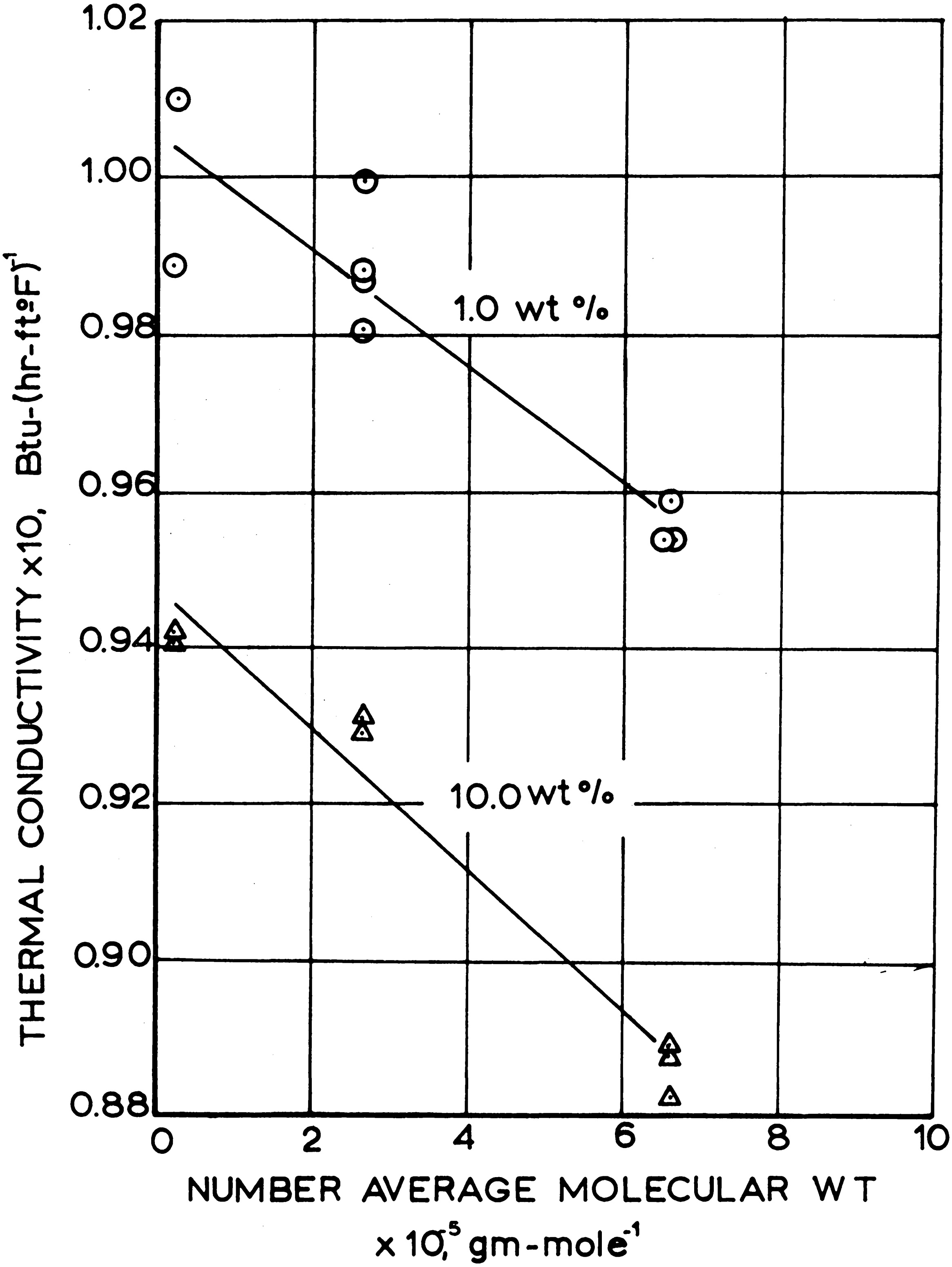

FIGURE 13. THERMAL CONDUCTIVITY VS. MOLECULAR WEIGHT AT ONE AND 10 WT PER CENT POLYSTYRENE IN BENZENE AT 25°C, LEAST SQUARES FIT

IV. DISCUSSION

This section contains a discussion of the experimental results, the limitations, and recommendations for future work.

Error Analysis

The sources of error in the experimental procedure are discussed and an estimate of the contribution of each source is given in the following paragraphs.

Temperature measurement.- The temperature difference across the annulus was measured with differential copper constantan thermocouples. The thermocouple emf was measured on a Rubicon potentiometer (see page 167). Appendix H). The limit of the accuracy of this device due to internal thermal emfs is 1 microvolt. The thermocouple calibration (see page 76, Appendix A) and subsequent statistical analysis of the results showed that the average error in estimating the temperature difference from the emfs at 99 percent confidence was $< \pm 0.01^\circ$ C. The error in temperature measurement was assumed to be $\pm 0.01^\circ$ C.

Heat input measurement.- The heat input was calculated by multiplying the square of current in the heater circuit I, by the resistance of the heater, R. The heater resistance was known as a function of temperature (see Appendix A). I was calculated as the quotient of the potential drop E across a standard resistor and its resistance, r. The standard resistor was maintained at 0° C in a Dewar filled with a crushed ice-water slurry. Its resistance at this temperature was measured with a calibrated Rubicon Kelvin bridge (see Appendix A). The resolution and limits of error of the Kelvin bridge in this range allow measurements to be made to ± 0.00005 ohm. The potential drop across the standard resistor E was measured on the potentiometer. The potentiometer was capable of measuring E to ± 0.00001 volt, but fluctuations in power source caused variations of as much as ± 0.00004 volt in some cases. Values of E ranged from 0.01 to 0.03 volts. The resistance of the heater R depended on the temperature of the particular test and varied from 42.610 to 42.620 ohms. R could be considered known to ± 0.001 ohm.

Geometric constant.- The diameters of the copper measuring cylinder D_1 and the outer brass cylinder D_2 were measured with micrometers at numerous points to within ± 0.0001 inch. The average value of D_1 was found to be 1.241 inches with standard deviation of 0.0005 inch and the average value of D_2 was found to be 1.345 inches with standard deviation of 0.0005 inch. The length of the measuring cylinder L was measured to the nearest 0.01 inch and found to be 4.78 ± 0.01 inch.

Radiation losses.- The measuring cylinder was nickel-coated and highly polished with jeweler's rouge on a polishing wheel. The inner surface of the brass cylinder was also polished. These measures should tend to minimize radiative heat transfer. The maximum radiation correction can be calculated for the case of perfect black bodies radiating in a transparent medium. The equations for this estimate were developed in the Literature Review (see page 9). The ratio of the radiative heat transfer to the conductive heat transfer was 0.002 percent. This is small compared to errors from other sources and was neglected.

Convection.- The theory underlying Kraussold's convection criterion was developed in the Literature Review. The reservations held by various investigators in the field were also indicated. The criteria for the onset of convection of both Kraussold and Ellington (see Literature Review, page 12) were applied to the data of this investigation. The quantities entering the Rayleigh number were, insofar as possible, determined from measurements of the test solutions. The thermal expansivity, density, and viscosity data for selected polystyrene solutions are given in Appendix D. The heat capacities of the solutions were calculated on a weight average basis. The heat capacity of benzene was taken as 0.419 cal-gm^{-1} - $^{o}C^{-1}$ (35) and that of polystyrene as 0.288 cal-cm^{-1} - $^{o}C^{-1}$ (33). The values of solution heat capacities calculated in this way are only approximate, but they should be good estimates.

By correlating the value of the Rayleigh number at which the Q versus ΔT plots began to deviate from linearity for several solutions, it was possible to estimate a critical value of N_{Ra}. A typical Q versus ΔT plot is given in Figure 14. The critical value of N_{Ra} estimated in this way was approximately 200. This is appreciably lower than the value of 700 recommended by Tsederberg. The discrepancy can be attributed to one principal cause. The existence of a small vertical gradient in the temperature of the brass cylinder was doubtlessly a

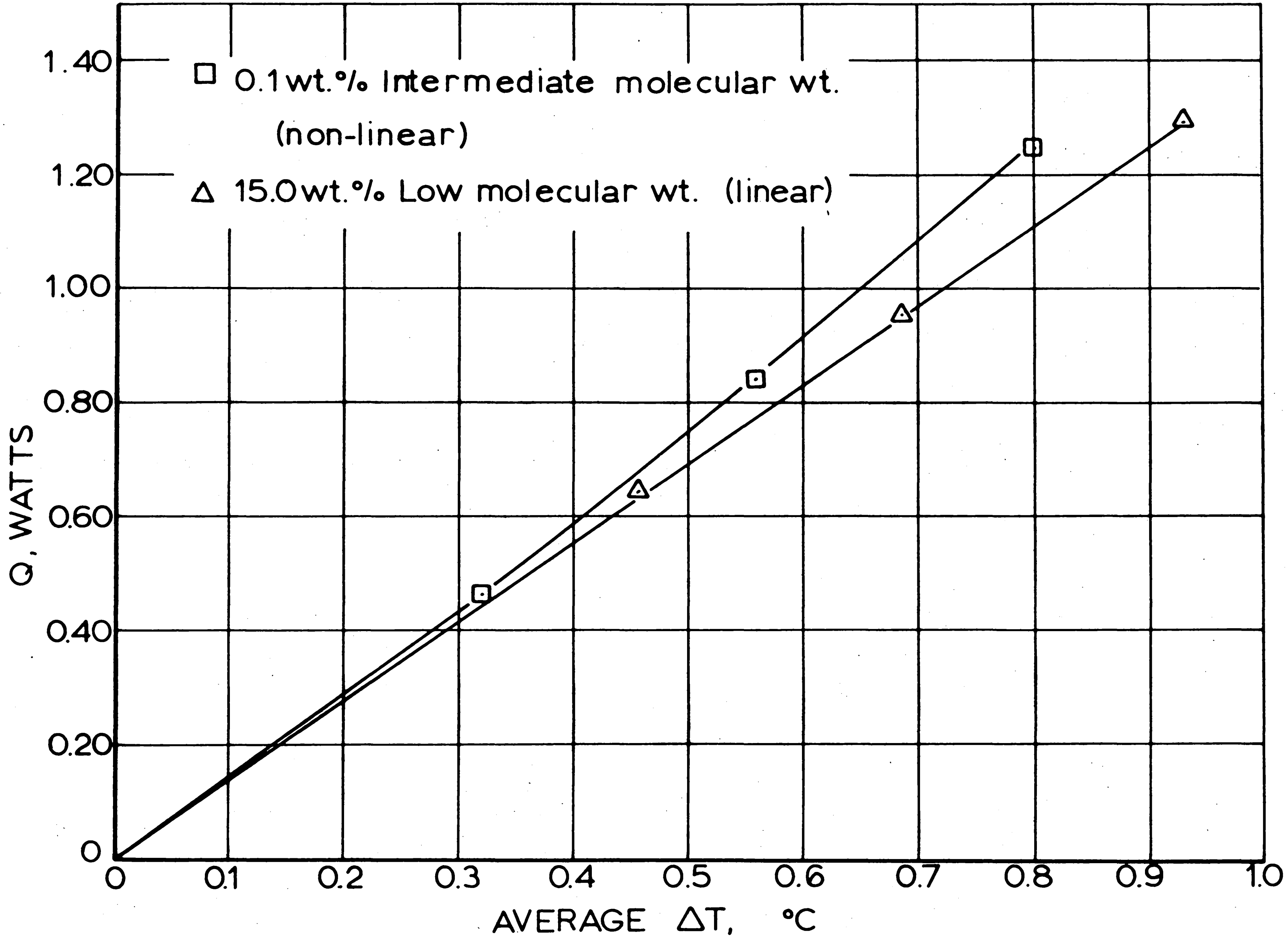

FIGURE 14. PLOT OF Q vs. ΔT FOR TWO SAMPLES OF POLYSTYRENE IN BENZENE SHOWING THE ONSET OF CONVECTION

major factor in producing convective flow. It was thought that the gradient was produced by convective flow in the large outer annulus. In an effort to break up any flow pattern in this outer space, it was filled with 6-mm-diameter glass balls. This was found to have no effect on the gradient. An analysis of the effect of the gradient on the results was carried out. The actual temperature distribution in the annulus was calculated by a numerical relaxation technique for a typical measurement. The actual gradient was then calculated via graphical differentiation of the data. The average temperature difference calculated in this way was within 0.3 percent of that calculated as the average of the thermocouple readings in the normal manner.

Conduction heat losses.- All tests were run at approximately 25° C which was always within 1° or 2° of room temperature. Thus, conduction losses through thermocouples and heater leads were negligible. Axial heat conduction in the measuring cylinder was minimized by the guard heaters. For a net temperature difference across the ends of the measuring cylinder, that is, the algebraic sum (considering the directions of the differences) of the temperature difference between the measuring cylinder and the guard heaters of 0.5° C, the axial heat transfer was calculated to be less than 1 percent. During actual measurements, the net temperature difference was kept to less than ~ 0.06° C, so that this correction was negligible.

Differential error analysis.- The equation for calculating the thermal conductivity in concentric cylinders is

$$K = \frac{Q \, ln\left(\frac{D_2}{D_1}\right)}{2\pi \, L \, \Delta T} \tag{1}$$

where: K = thermal conductivity

Q = heat input

D_2, D_1 = diameters of outer and inner cylinders, respectively

L = length of cylinders

ΔT = temperature difference across annular gap

Differentiating Equation (1) and dividing the result by K gives the relative error dK/K

$$\frac{dK}{K} = \frac{dQ}{Q} + \frac{d\left(\frac{D_2}{D_1}\right) D_1}{ln\left(\frac{D_2}{D_1}\right) D_2} + \frac{dL}{L} + \frac{d(\Delta T)}{\Delta T} \qquad (2)$$

However, Q was measured as

$$Q = I^2 R = \frac{E}{r}^2 R \qquad (3)$$

$$\frac{dQ}{Q} = \frac{dR}{R} + \frac{2dE}{E} + \frac{2dr}{r} \qquad (4)$$

where: R = resistance of heater

r = resistance of standard resistance

E = voltage drop across standard resistance

I = current flowing in heater

The term involving the diameters D_1 and D_2 in Equation (2) must also be further broken down

$$d\left(\frac{D_2}{D_1}\right) = \frac{d(D_2)}{D_1} + D_2 \frac{d(D_1)}{D_1^2} \qquad (5)$$

$$\frac{d\left(\frac{D_2}{D_1}\right) D_1}{ln\left(\frac{D_2}{D_1}\right) D_2} = \frac{\frac{d(D_2)}{D_2} + \frac{d(D_1)}{D_1}}{ln\left(\frac{D_2}{D_1}\right)} \qquad (6)$$

Substituting Equations (4) and (6) into Equation (2) results in

$$\frac{dK}{K} = \frac{dR}{R} + \frac{2dE}{E} + \frac{2dr}{r} + \frac{\frac{d(D_2)}{D_2} + \frac{d(D_1)}{D_1}}{ln\left(\frac{D_2}{D_1}\right)} + \frac{dL}{L} + \frac{d(\Delta T)}{\Delta T} \qquad (7)$$

It will be noted that negative signs which would ordinarily result from the differentiation have been replaced with positive signs so that the estimate of the maximum experimental error will result. Substituting the numerical values given in the preceding paragraphs for the differentials in Equation (7), the measured values of r, D_2, D_1, and L, and typical values of E and R gives

$$\frac{dK}{K} = 0.00425 + 0.00963 + 0.00209 + \frac{0.01}{\Delta T}$$

$$\frac{dK}{K} = 0.01595 + \frac{0.01}{\Delta T} \qquad (8)$$

It can be seen from Equation (8) that the estimate of experimental error is quite sensitive to the value of ΔT. The ΔT's used in this investigation range from a low of $\sim 0.4^\circ$ C to a high of $> 2.0^\circ$ C, depending on the physical characteristics of the test fluids. The average ΔT was 0.8° C; using this to estimate the average experimental error gives

$$\frac{dK}{K} = 0.01595 + 0.0125 = 2.85 \text{ percent} \qquad (9)$$

The above calculations have not considered any contribution of eccentricity. Such contributions would not be random (as errors considered above are assumed to be) but consistent. Since the apparatus was of necessity always assembled in the same way, any eccentricity would be expected to appear as a constant factor in the results. The estimate of error which would result from an eccentricity of 0.002 inch due to simple translation of the axis is < 0.1 percent (calculated with the formula given in the Literature Review). As was mentioned in the Literature Review, there is no analytical expression for any other deviation from the concentric configuration.

Polymer Characterization

The results of the intrinsic viscosity and molecular weight determinations are presented as a plot of $\log [\eta]$ versus $\log \overline{M}_N$ in Figure 16. The data are remarkably consistent, considering that these are industrial samples and were probably prepared under widely differing conditions (temperature, method of polymerization, etc.).

The data were fitted to the Mark-Houwink relation

$$[\eta] = K' M^{\nu}$$

and values of $K' = 8.4 \times 10^{-3}$ and $\nu = 0.38$ were obtained. The value of ν lies well outside the theoretical limits $(0.50 \leq \nu \leq 0.80)$. It must be remembered, however, that the constants in the Mark-Houwink relation should be evaluated for a series of fractions of the same polymer and that these constants were obtained from measurements on polydisperse samples of different polymers.

Calibration Factor

A calibration factor of 1.095 was applied to the results of the thermal conductivity measurements of water, ethylene glycol, and cyclohexanol. The resulting values of thermal conductivity K_c were within ± 3 percent of the "best" literature values for these

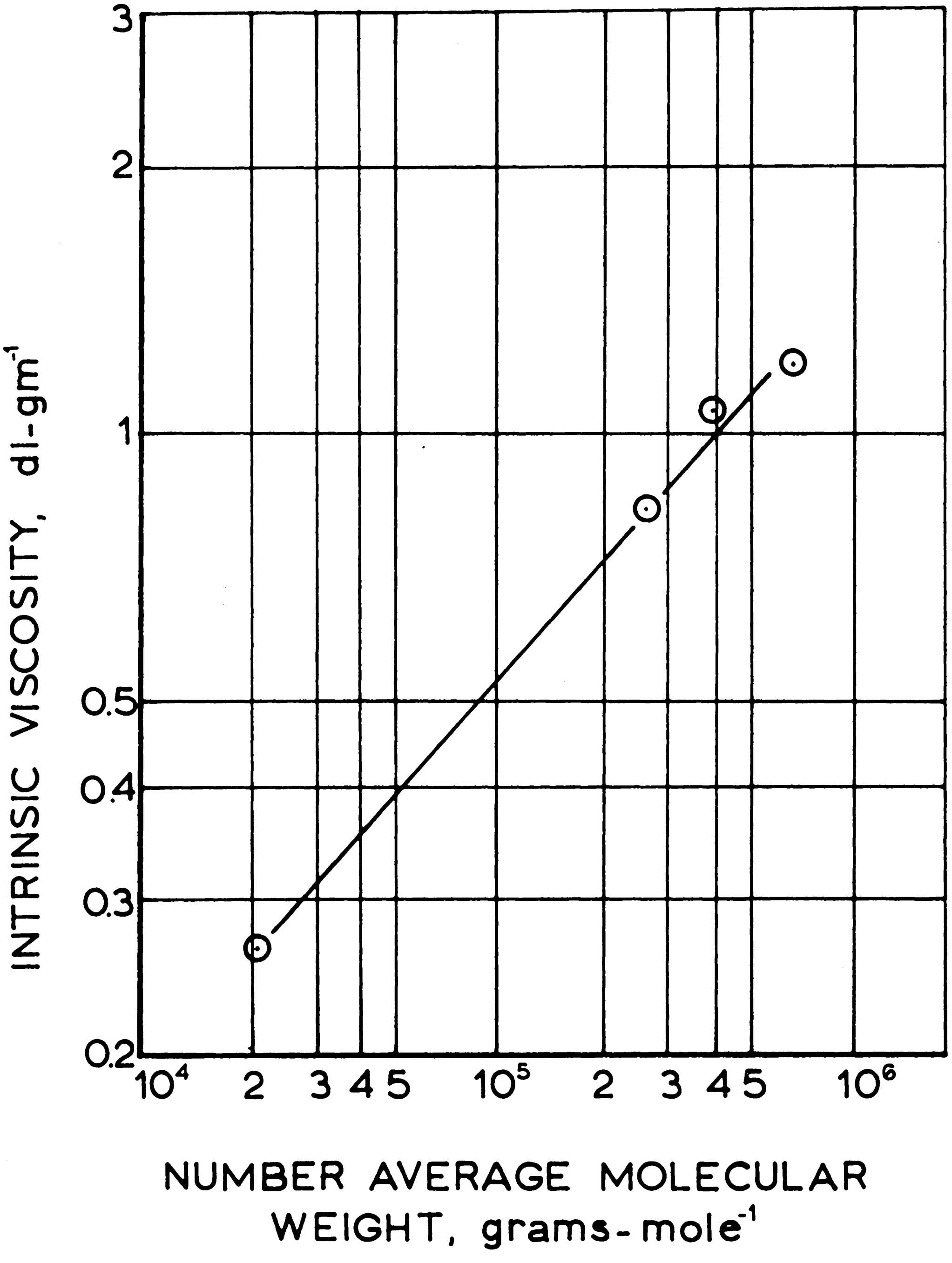

FIGURE 15. INTRINSIC VISCOSITY VS. NUMBER AVERAGE MOLECULAR WEIGHT FOR APPROXIMATING MARK-HOUWINK CONSTANTS

liquids. The estimated experimental error in this investigation is ± 3 percent so the factor could be considered constant in the range of interest to within experimental error.

The factor is almost certainly a geometric one since it showed no consistent variation with heating rate, thermal conductivity or temperature difference. Its source could well lie in the uncertainty described in Detailed Description of Apparatus, Appendix C, p.98. It was not possible to be sure that the counterbores on either end of the brass outer cylinder were concentric. The result of such an eccentricity would be that the measuring cylinder would be inclined from the vertical. The Delrin spacers should tend to minimize this effect but could not preclude it.

Thermal Conductivity of Polymer Solutions

Solutions of polystyrene of all three molecular weights exhibited a parabolic dependence of K on concentration. The conductivity decreased with increasing concentration. This is similar to the parabolic dependence found by Filippov (8) and others for mixtures of organic liquids.

The results obtained for the dilute solutions are the least reliable. This is a result of the fact that temperature differences had to be kept low in order to prevent convection in these low viscosity solutions. Operating at low temperature differences increases the experimental error. Convection is also more likely to occur in dilute solutions because of their high Rayleigh numbers.

The conductivity of the polymer solutions was higher than that of the solvent. An average of the best literature values (15) for benzene at 77° F is 0.0833 Btu/hr-ft-°F ± 5 percent. This value is from 6 to 10 percent below the lowest conductivity measured for any solution. This anomaly has not been previously reported, and certainly should receive further study. Several avenues of attack suggest themselves. The limit of low molecular weight should be investigated. This could be conveniently done by testing mixtures of solvent and styrene monomer. The behavior of this simple system should be understood before any attempt is made to explain the complexities of the polymer system.

There appear to be two mechanisms operative in the concentration dependence of K for these solutions. The conductivity is apparently enhanced in dilute solutions. This enhancement is increasingly surpressed with increasing concentration and the conductivity seems to approach a lower limit. The model for a dilute polymer solution is an approximately spherical distribution of the segments of a single molecule surrounded by an "infinite sea" of solvent. For concentrated solutions the segment density (to which many molecules may contribute) is nearly uniform throughout the solution. Flory has estimated that this uniform density may exist for concentrations of a few percent for molecular weights $\gtrsim 10^5$ (38). The conductivity behavior should be interpreted in terms of these physical models. Such interpretation would require that conductivities be measured over the full range of concentrations from very dilute solutions to the most concentrated solution obtainable with a given molecular weight.

The data of Nychas (22) for aqueous polyethylene glycol solutions are insufficient to lend any but qualitative support to the results of this study. Nychas's data do show a decrease in K with increasing concentration and molecular weight. The data of Parker (24) provide quantitative support for the observed concentration dependence and the anomalous behavior noted above. Parker's data show this anomaly for the middle molecular weight polystyrene in carbon tetrachloride and styrene monomer.

The data for K versus $\bar{M}_N$ were found by regression analysis to fit the following equation

$$K = a + b\left(\bar{M}_N \times 10^{-5}\right)$$

The intercept a and the coefficient b were obtained via least squares estimation. Their values are given in Table IX for one and 10 wt percent concentrations. The regression analysis revealed that a quadratic equation did not give a significantly better fit of the data.

Multiple regression analysis showed that the data for the concentration (C) dependence of K were best fit by a relation of the form

$$K = a + b_1 C + b_2 C^2$$

The values of the coefficients are given in Table IX for $\bar{M}_N$ = 21,000; 264,000; 660,000.

TABLE IX.- RESULTS OF REGRESSION ANALYSIS OF POLYMER SOLUTION THERMAL CONDUCTIVITY DATA[a]

Equation	Conditions	a	Parameters			
			b_1	b_2	b_3	b_4
$K = a + b \bar{M}_N'$	C = 1.0 wt %	0.1005	-7.3×10^{-4}	--	--	--
	C = 10.0 wt %	.0947	-8.9×10^{-4}	--	--	--
$K = a + b_1 C + B_2 C^2$	$\bar{M}_N' = 0.21$	.1010	-0.1090	0.4000	--	--
	$\bar{M}_N' = 2.64$	.0996	- .1049	.3536	--	--
	$\bar{M}_N' = 6.60$	.0991	- .2612	1.5836	--	--
$K = a + b_2 C^2 + b_1 C + b_3 \bar{M}_N' + b_4 \bar{M}_N'^2$	--	.1009	- .1311	.5763	-4.2×10^{-3}	-6.40×10^{-5}

(a) $\bar{M}_N' = \bar{M}_N \times 10^{-5}$

The regression analysis for the dependence of K on the significant variables showed that the best fit was obtained with the following equation

$$K = a + b_1 C + b_2 C^2 + b_3 C M_N' + b_4 M_N'^2$$

The least squares estimates of these coefficients are given in Table IX. The conductivities calculated from these equations are within ± 2 percent of the experimental values.

Recommendations

1. The thermal conductivities of various concentrations of styrene and solvent should be measured to investigate the limit of low molecular weight. The molecular weight range should be increased in the other direction to molecular weights $> 10^6$.

2. An apparatus should be designed so that solvents and dilute solutions can be studied. This can be accomplished on the existing equipment by machining another brass outer cylinder such that the dimension of the annular gap is decreased to 0.040 inches. Computer analysis of the variables has shown that the Rayleigh Number will be less than 200 for Toluene at 25° C with a temperature difference of 0.8° C. Under these conditions the estimated experimental error would be 3.1 percent and the uncertainty due to possible eccentricity would be on the order of 0.1 percent.

3. A more sensitive potentiometer should be used to measure the temperature differences as this is the largest single source of error in the present work.

4. The apparatus should be designed so that the geometric constant can be measured independently of the mechanical measurements (e.g., capacitance of the evacuated annulus) as a check on these measurements.

Limitations

1. The average experimental error was estimated at approximately 3 percent. The calibration factor was found to be constant over the range of experimental values within the limits of experimental error.

2. The measurements were made at an average temperature of 25° C.

3. The thermal conductivities of the dilute solutions (< 1.0 wt percent) of the low and intermediate molecular weight polymers could not be investigated because of convection. The same limitation precluded any measurements on the solvent.

V. CONCLUSIONS

The following conclusions can be drawn from the experimental results:

1. The apparatus, as designed, is suitable for measuring the thermal conductivities of viscous liquids and solutions with Rayleigh numbers less than approximately 200.

2. The thermal conductivity of solutions of polystyrene in benzene decreases linearly with molecular weight and parabolically with increasing concentration in the range of concentration 1 to 10 weight percent and number average molecular weight 21,000 to 660,000 grams per mole.

3. The following equations were obtained from regression analysis of the results. They predict the measured thermal conductivities within ± 2 percent in the range of variables: wt fractions of 0.01 to 0.15 and molecular weights from 21,000 and 660,000.

$$K = 0.1005 - 7.3 \times 10^{-4}\, \overline{M}_n' \quad \text{for} \quad C = 0.01$$

$$K = 0.0947 - 8.9 \times 10^{-4}\, \overline{M}_n' \quad \text{for} \quad C = 0.10$$

$$K = 0.1010 - 0.109\, C + 0.400\, C^2 \quad \text{for} \quad \overline{M}_n' = 0.21$$

$$K = 0.0996 - 0.1049\, C + 0.3536\, C^2 \quad \text{for} \quad \overline{M}_n' = 2.64$$

$$K = 0.0991 - 0.2612\, C + 1.5836\, C^2 \quad \text{for} \quad \overline{M}_n' = 6.60$$

$$K = 0.1009 - 0.1311\,C + 0.5763\,C^2 - 4.2 \times 10^{-3}\,C\,\bar{M}_n' - 6.40 \times 10^{-5}\,\bar{M}_n'^2$$

where: K = thermal conductivity, Btu/hr-ft-°F

$\bar{M}_n'$ = number average molecular weight × 10^{-5}

C = polymer concentration, weight fraction

VI. SUMMARY

The thermal conductivities of polystyrene in benzene solutions at concentrations of 0.1 to 15 weight percent were measured at 25° C and atmospheric pressure. Osmotic pressure measurements and information supplied by the manufacturer indicated number average molecular weights $\bar{M}_N$ of 21,000, 264,000, and 660,000 for the three polystyrene polymers studied. The following equation was obtained by regression analysis of the results and predicts the measured thermal conductivity within ± 2 percent in the range of variables studied.

$$K = 0.1088 - 0.1311\ C + 0.57629\ C^2 - 6.40 \times 10^{-5} \left(\bar{M}_N \times 10^{-5}\right)^2 - 4.2 \times 10^{-4}\ C\left(\bar{M}_N \times 10^{-5}\right)$$

where: K = thermal conductivity of solution, Btu/hr-ft-°F

C = weight fraction polymer

$\bar{M}_N$ = number average molecular weight

The conductivities were measured in a steady-state concentric cylinder apparatus developed for measuring the thermal conductivity of viscous liquids. The annular gap was 0.052 inch and guard heaters were employed to minimize end losses and distortion of the steady-state temperature distribution at the ends. The apparatus was calibrated with three liquids of known thermal conductivity, water, cyclohexanol. and ethylene glycol. The calibration factor was found to be constant to within experimental error (± 3 percent) over the range of measurements.

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VIII. ACKNOWLEDGMENTS

The author would like to express his appreciation to Dr. R. A. Mischke, Associate Professor in the Department of Chemical Engineering, who was thesis advisor for this investigation. The author is indebted to him for his advice, guidance, and interest throughout this investigation.

The design, construction and calibration of the apparatus was a cooperative effort between the author and . The author is indebted to not only for his part of these earlier phases of the study, but also for his advice and assistance throughout the latter stages of the author's research.

Thanks are also due the Chemical Engineering Department and Research Division machine shops for the construction and modification of the apparatus.

The author would like to thank Professor N. F. Murphy, acting Head of the Chemical Engineering Department at V.P.I. for the use of his electro-plating facility, and Dr. George Sands of the NASA's Langley Research Center for the use of his high-speed membrane osmometer.

The author wishes to acknowledge the National Science Foundation for its financial support of this project.

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APPENDIX A

CALIBRATION PROCEDURES

DETAILED OUTLINE OF PROCEDURE

THERMOCOUPLE CALIBRATION

Copper-Constantan thermocouples were made by arc welding junctions in air. The junctions were approximately spherical and less than 0.05 inch in diameter. The wire used was Honeywell No. 9B188 (see Materials, page 163) which was then covered with heat-shrinking irradiated polyolefin insulation to increase its resistance to organic solvents.

The thermocouples were paired and connected to the Rubicon Potentiometer (see Apparatus, page 167) through a Lewis Engineering thermocouple selector switch (see Apparatus, page 168). The connections were screw connections on a terminal board such that the Constantan leads were joined together and the copper leads were connected to the switch with copper wire. This switch was, in turn, connected to the potentiometer with copper wire.

One junction from each pair was attached via a rubber band to the bulb of a Beckman thermometer. The thermometer with attached junctions (radially dispersed about the bulb) was placed in an oil-filled test tube which was, in turn, placed in an oil-filled 500 ml graduated cylinder. The cylinder _et al_. was then placed in the bath water. The same procedure was followed for the remaining junction of each pair. The temperature in the Cannon constant temperature baths (see Apparatus, page 166) was constant to ± 0.01° C. The Beckman thermometers were graduated in 0.01° C graduations, and the temperature difference was estimated to ± 0.0025° C.

The temperatures of the two baths were set so that the difference was approximately 2.0, 1.5, 1.0, and so forth, and the exact ΔT was inferred from the readings of the Beckmans. The bath temperatures drifted slightly with time ($< 0.01^\circ$ C), but this drift was easily monitored by reading the thermometers after each thermocouple reading was taken. At each ΔT, several readings were taken on each thermocouple pair. After a set of readings had been taken at a given ΔT, the Beckman thermometers were placed in the same bath and readings were taken so that the two were calibrated with respect to each other. Then, by assuming linearity between the two thermometers over the range of 1° or 2°, the ΔT's could be calculated for each thermocouple reading. The calibration data for several ΔT's indicated that as long as the amount of mercury in the column remained constant, the thermometers were linear to within $\pm\ 0.001^\circ$ C (estimated).

The calibration data were analyzed by regressions of potentiometer reading (emf in millivolts) against ΔT in $^\circ$C. The data were fit with both linear and quadratic equations and statistical analysis showed that the quadratic fit was not significantly better than the linear. This was true for all thermocouples.

The linear regression coefficients were then used to determine the maximum residual which could be expected at 99 percent confidence. The results for a typical thermocouple (number 4) are shown in Table XI on page 80. The linear regression coefficients for all thermocouples are shown in Table X, page 79.

TABLE X

RESULTS OF REGRESSION ANALYSIS OF THERMOCOUPLE CALIBRATION DATA

Thermocouple pair number	Intercept °C	Slope $\frac{^\circ C}{\text{Volts}} \times 10^4$
6	-0.004190	2.44910
5	-0.00023	2.64268
4	0.00023	2.44184
3	-0.004250	2.4591
2	0.00128	2.45711
1	-0.00086	2.44120
20	-0.00179	2.45380
19	-0.00149	2.44513
18	0.00128	2.44473
17	-0.00663	2.46105

TABLE XI

RESIDUAL ERROR AT 99 PERCENT, CONFIDENCE FOR THERMOCOUPLE NO. 4

ΔT °C	EMF × 10^4 Volts	Error at 99% Confidence °C
0.100	0.041	0.0051
0.300	0.123	0.0045
0.500	0.205	0.0040
0.700	0.287	0.0035
0.900	0.369	0.0032
1.10	0.450	0.0031
1.30	0.533	0.0032
1.51	0.618	0.0034
1.70	0.696	0.0038
1.90	0.778	0.0043
2.00	0.819	0.0045

CALIBRATION OF STANDARD RESISTOR

The standard resistor was made by winding approximately 1 foot of 30-gauge copper wire on a ceramic core. The potential taps are of 10-gauge copper wire so that the potential drop through these leads was negligible. The standard resistor was maintained at 0° C in a Dewar flask filled with crushed ice water mixture.

The resistance of the standard resistor was measured on a Rubicon Kelvin Bridge (see Apparatus p.168). The Kelvin Bridge was checked with a Leeds and Northrup 0.1Ω Shunt (see Apparatus p. 168) and found to be accurate in this range. Figure 17 is a schematic of the circuit used in this measurement. The standard resistor is also a four-lead resistor and the circuit diagram for its calibration is identical with the exception that the potential taps were joined to the matched leads of the Kelvin Bridge $\left(P_1 \text{ and } P_2\right)$ via screw connections on a terminal block.

The resistance of the standard resistor at 0° C was found to be 0.9538 ± 0.00005 ohms. A check on this determination was obtained by placing the standard resistor in series with the L and N shunt and comparing the potential drops across them with the Poteniometer. The resistance calculated in this way was 0.95377 ohm.

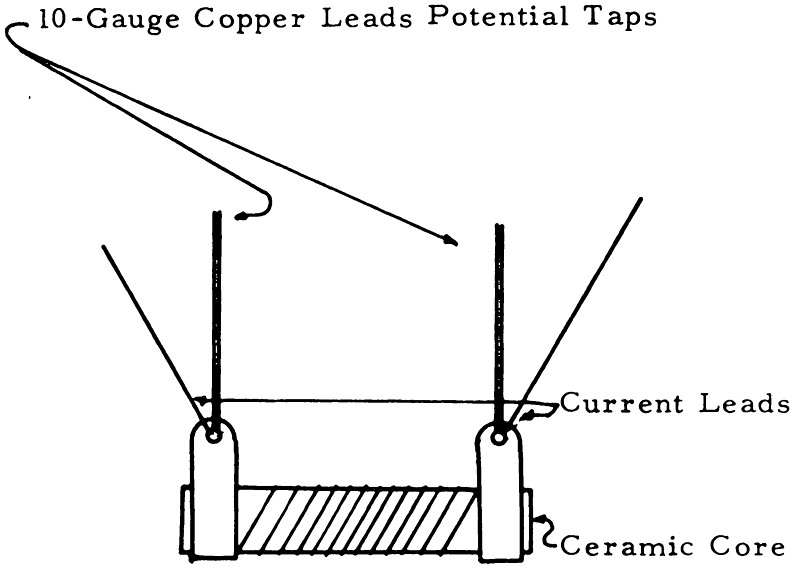
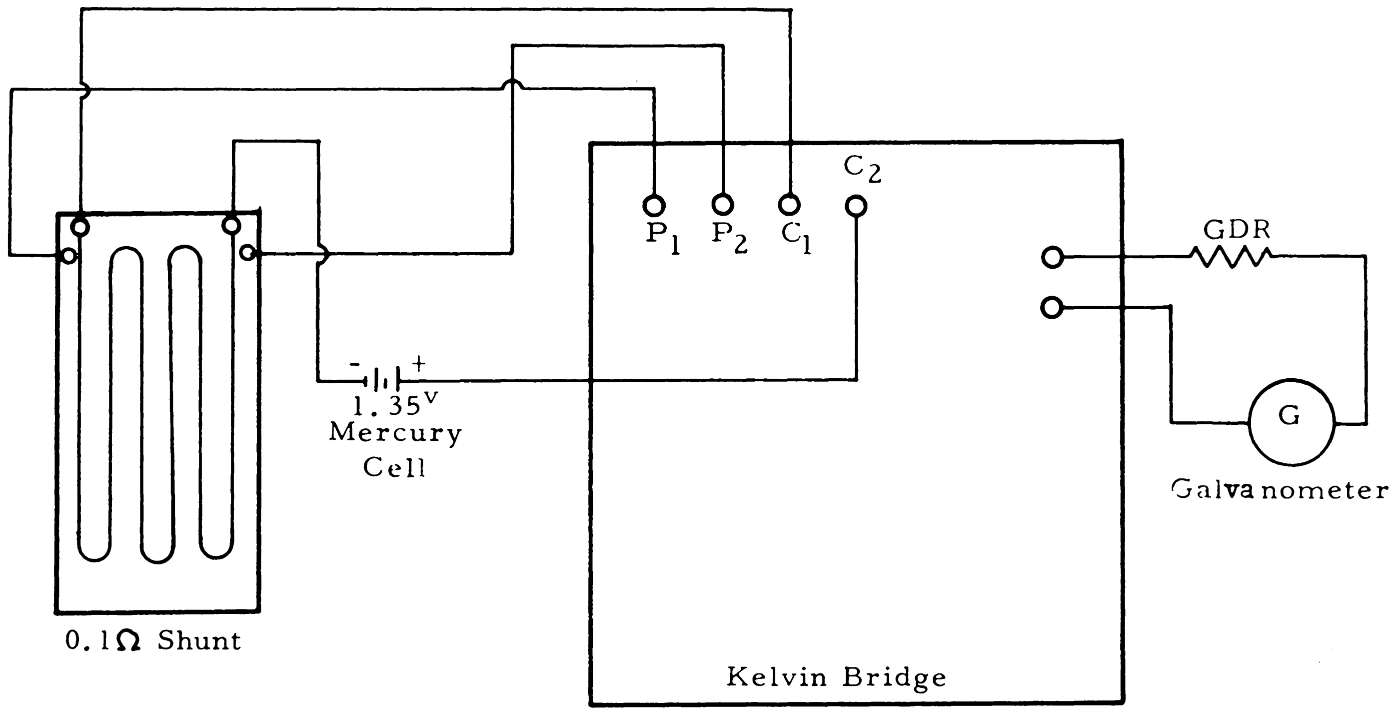


FIGURE 16 . SKETCH OF WIRE WOUND STANDARD RESISTOR



P_1 and P_2 are Matched Resistance Leads

FIGURE 17. PICTORAL CIRCUIT FOR CALIBRATION OF KELVIN BRIDGE

CALIBRATION OF RESISTANCE OF MAIN HEATER AS A FUNCTION OF TEMPERATURE

The main heater was made by winding 30-gauge Constantan wire on a threaded brass cylinder. The resistivity of Constantan is a slightly decreasing function of temperature.

The resistance heater was allowed to equilibrate in the constant temperature bath at three different temperatures. The resistance was measured at each temperature with a Rubicon Wheatstone Bridge. The results are presented on Figure 18, page 85. The average temperature coefficient of resistance $\left(\frac{1}{R}\frac{dR}{dT} \approx \frac{1}{R_{avg}}\frac{\Delta R}{\Delta T}\right)$ was found to be $3.1 \times 10^{-5}\ {}^{o}C^{-1}$.

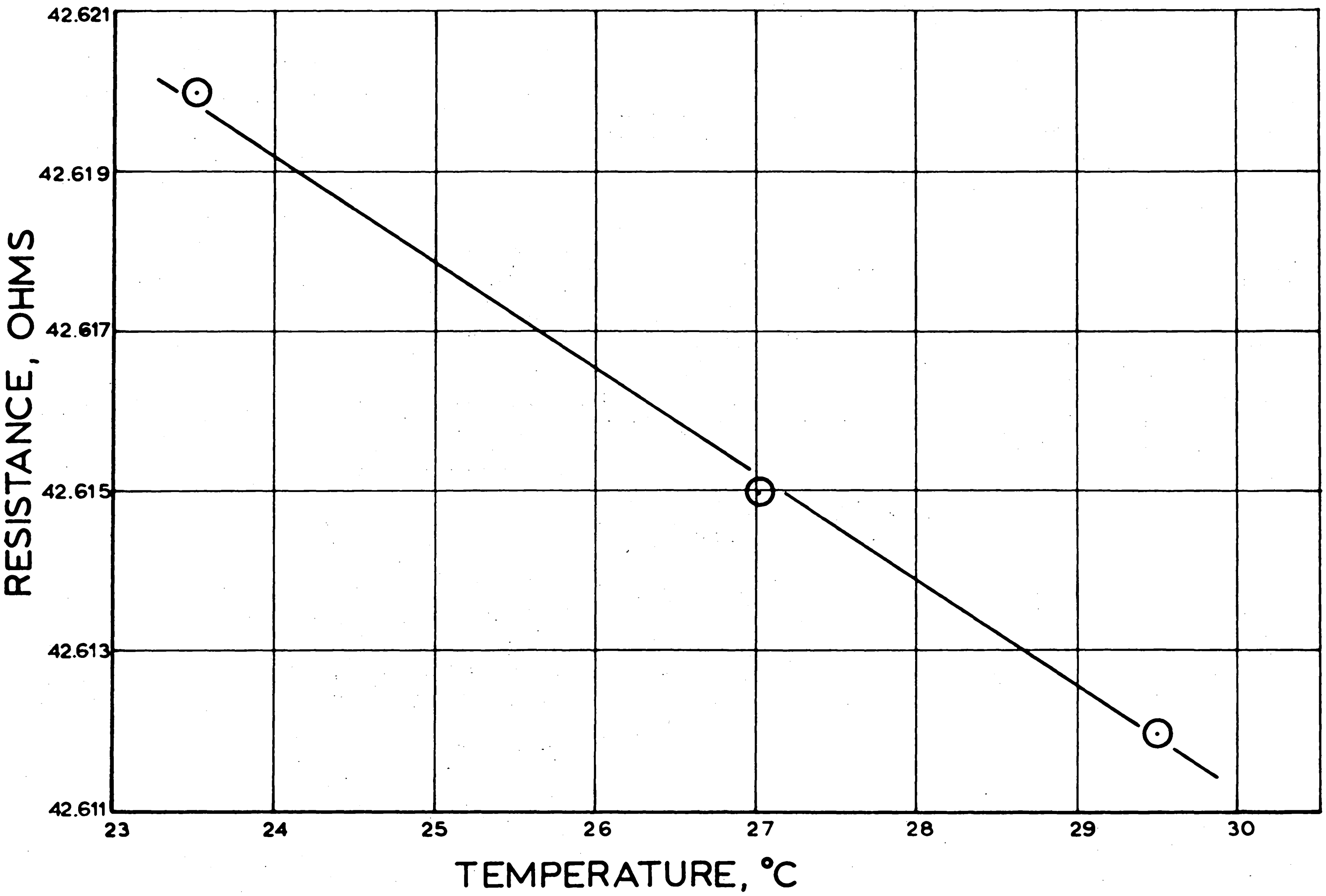


FIGURE 18. RESISTANCE OF MAIN HEATER AS A FUNCTION OF TEMPERATURE

APPENDIX B

POLYMER CHARACTERIZATION

DETERMINATION OF INTRINSIC VISCOSITIES

The solutions for these determinations were made by weighing 0.5000 grams of polymer on the analytical balance. This known weight was transferred to a 100 milliliter volumetric flask which was then filled to the mark with solvent. Solutions were allowed to stand overnight before using.

Successive dilutions were accomplished by pipetting 10 mililiter aliquots of the stock solution (0.50 grams per deciliter) into flasks and diluting with 10, 20, and 30 milliliters of solvent. The same 10 milliliter pipette was used throughout, so that any error in its volume should have cancelled.

Ten milliliters of each of these solutions were pipetted into Cannon-Fenske Routine, size 50, viscometers in which the efflux time of the solvent had been previously determined. Each solution was then run until at least three efflux times within 0.3 percent of each other were obtained. An average of these times were used to determine the viscosity number at that concentration. The results are shown on Figures 6 and 7, pages 36 and 37. The data are tabulated in Tables XII and XIII on the following pages.

TABLE XII

INTRINSIC VISCOSITY OF HIGH, UNFRACTIONATED, AND LOW MOLECULAR WEIGHTS POLYSTYRENE IN BENZENE AT 25° C

Molecular weight	Concentration gm-dl^{-1}	Reduced viscosity dl-gm$^{-1}\Omega$
High[(a)]	0.500	1.394
	0.316	1.323
	0.316	1.333
	0.250	1.305
	0.158	1.262
	0.125	1.255
Unfractionated[(b)]	0.503	1.189
	0.501	1.202
	0.252	1.119
	0.168	1.101
	0.0875	1.090
Low[(c)]	0.500	0.277
	0.500	0.279
	0.250	0.274
	0.250	0.270
	0.167	0.272
	0.167	0.267
	0.125	0.261

(a) Number average molecular weight = 660,000 gm-mole^{-1}.
(b) Number average molecular weight = 389,400 gm-mole^{-1}.
(c) Number average molecular weight = 21,000 gm-mole^{-1}.

TABLE XIII

INTRINSIC VISCOSITY OF INTERMEDIATE[(a)] MOLECULAR WEIGHT POLYSTYRENE IN BENZENE AT 25° C

Concentration $gm\text{-}dl^{-1}$	Reduced viscosity $dl\text{-}gm^{-1}$
0.501	0.926
0.500	0.934
0.500	0.927
0.500	0.934
0.300	0.880
0.300	0.894
0.250	0.871
0.250	0.882
0.167	0.865
0.125	0.858
0.125	0.854
0.100	0.831
0.100	0.845
0.100	0.854

(a) Number average molecular weight = 264,000 $gm\text{-}mole^{-1}$.

OSMOTIC PRESSURE MEASUREMENTS

The solutions for these determinations were prepared by successive dilutions of a stock solution in the same manner as intrinsic viscosity solutions.

The determinations were made in a dynamic membrane osmometer. The membrane used was of reconstituted cellulose. This membrane was not suitable for measurements of the low molecular weights. This was evidenced by diffusion of the polymer through the membrane. The results of the measurements on the other molecular weights are shown in Figure 8 p. 39. The determinations were made in toluene at 37° C.

The osmotic pressure was measured in centimeters of solvent h. This height was then converted to pressure units via the ratio of solvent density ρ_s to the density of Hg, ρ_{Hg}.

The molecular weight was calculated from the following formula:

$$\bar{M}_N = \frac{R\,T}{\left[\frac{h}{c}\right]_0 \frac{\rho s}{\rho_{Hg}}}$$

Where T is temperature and R is the universal gas constant in appropriate units.

APPENDIX C

DETAILED DESCRIPTION OF APPARATUS

DETAILED DESCRIPTION OF APPARATUS

The heaters in the guard heaters and measuring cylinder were made by winding 30-gauge Constantan wire on brass cylinders which were grooved to accommodate the wire. The brass heater cylinder was machined to within ± 0.001 inch and was a force fit with the hole bored in the copper (tolerance ± 0.001 inch). The temperature drop through a possible gap of ± 0.002 inch was estimated to be 0.0002° F. Thus, the brass was assumed to be in good thermal contact with the copper.

The guard heaters were threaded and screwed into a "Delrin" (a polyoxymethylene polymer made by DuPont) cylinder. The Delrin cylinder was screwed onto a brass cylinder which was bolted onto the copper flange which forms the top of cell. The flange was chucked in the lathe and the outside diameters (O.D.) were machined in sequence. Integral machining of this assembly assured that all cylinders would be concentric.

The counter-bores at either end of the brass cylinder were machined to fit over the Delrin cylinders. The machining of the brass cylinder was accomplished as follows: 1. The O.D. was machined, the 1.345-inch-diameter hole bored and the counter-bore at one end bored, 2. the cylinder was removed from the lathe and the counter-bore at the other end bored. It was thus impossible to be absolutely sure that the last counter-bore was on the same center as the other counter-bore and the 1.345-inch bore. Every effort was made, however, to assure that the bores were concentric.

A hole was bored through the centers of the brass heater cylinders of the guard heaters and measuring cylinder. This hole accommodated a teflon centering rod. To assure that the holes for the rod were centered with respect to the guard heaters, a brass insert was machined (see Detail A, Figure 20). The heater cylinders of the guard heaters were drilled to accommodate the insert which was then driven into place. The hole for the centering rod was redrilled and at the same time all O.D.'s on the guard heater assembly were remachined.

Thus, when the cell was assembled, the guard heaters were centered with respect to the outer brass cylinder via the fit of the Delrin with the counter-bore. The measuring cylinder was centered with respect to the guard heaters (and consequently concentric with the outer brass cylinder) by virtue of the centering rod. As a further check on the centering, Delrin spacers were machined to the dimensions of the annular gap. They were inserted at the top and bottom of the measuring cylinder (see Detail B of Figure 20).

The annular gap was originally designed to be 0.047 inch. Because of gross variation in the dimensions of the original apparatus, remachining was required. The final dimension was 0.052 inch as shown on the drawings.

The outside of the cell is formed by a section of copper pipe to which flanges were attached. These flanges bolted to the flanges which form the bottom of the guard heaters and were grooved for an O-Ring, thus sealing the cell.

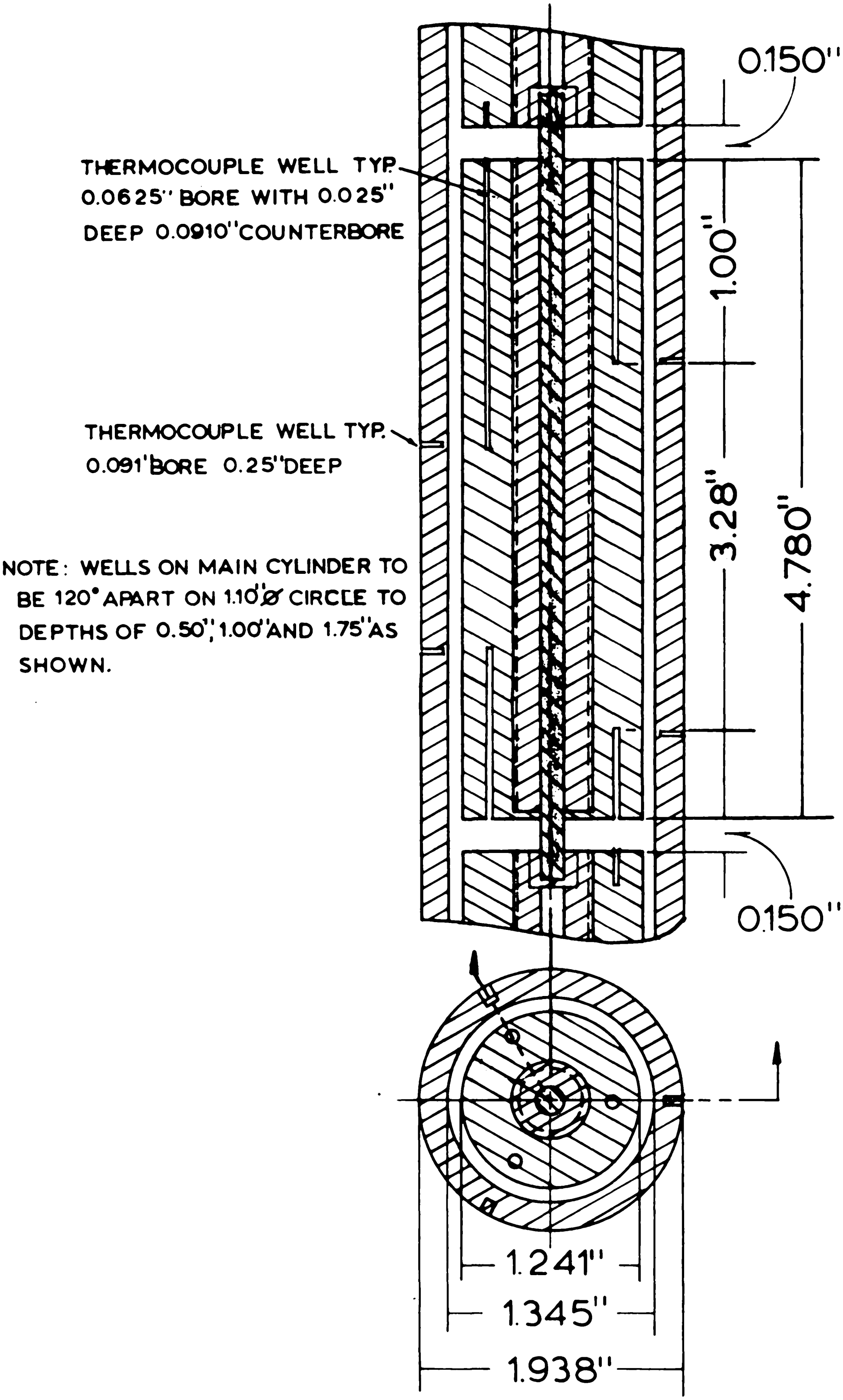
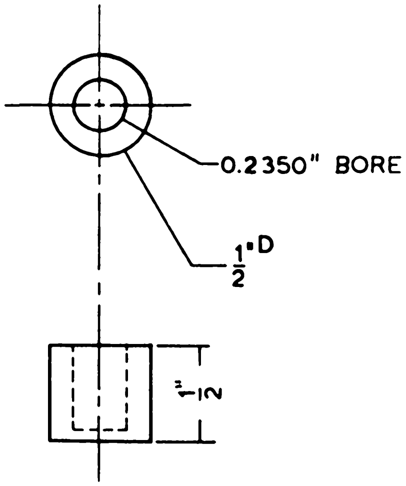
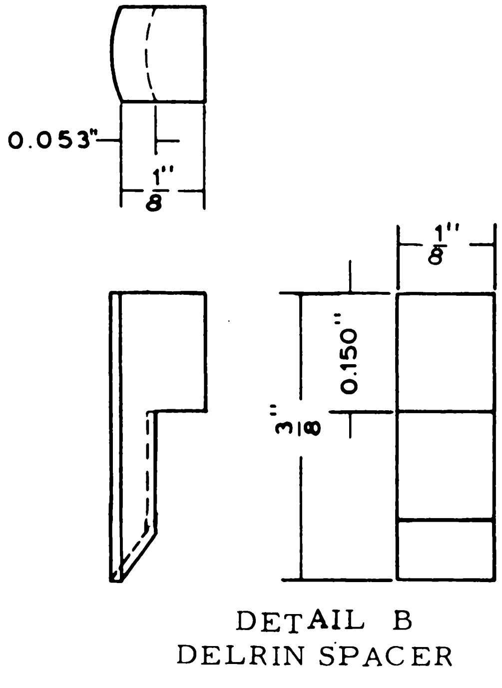


FIGURE 19. DETAILS OF THE THERMAL CONDUCTIVITY CELL



DETAIL A
BRASS INSERT



DETAIL B
DELRIN SPACER

FIGURE 20. DETAILS OF THERMAL CONDUCTIVITY CELL

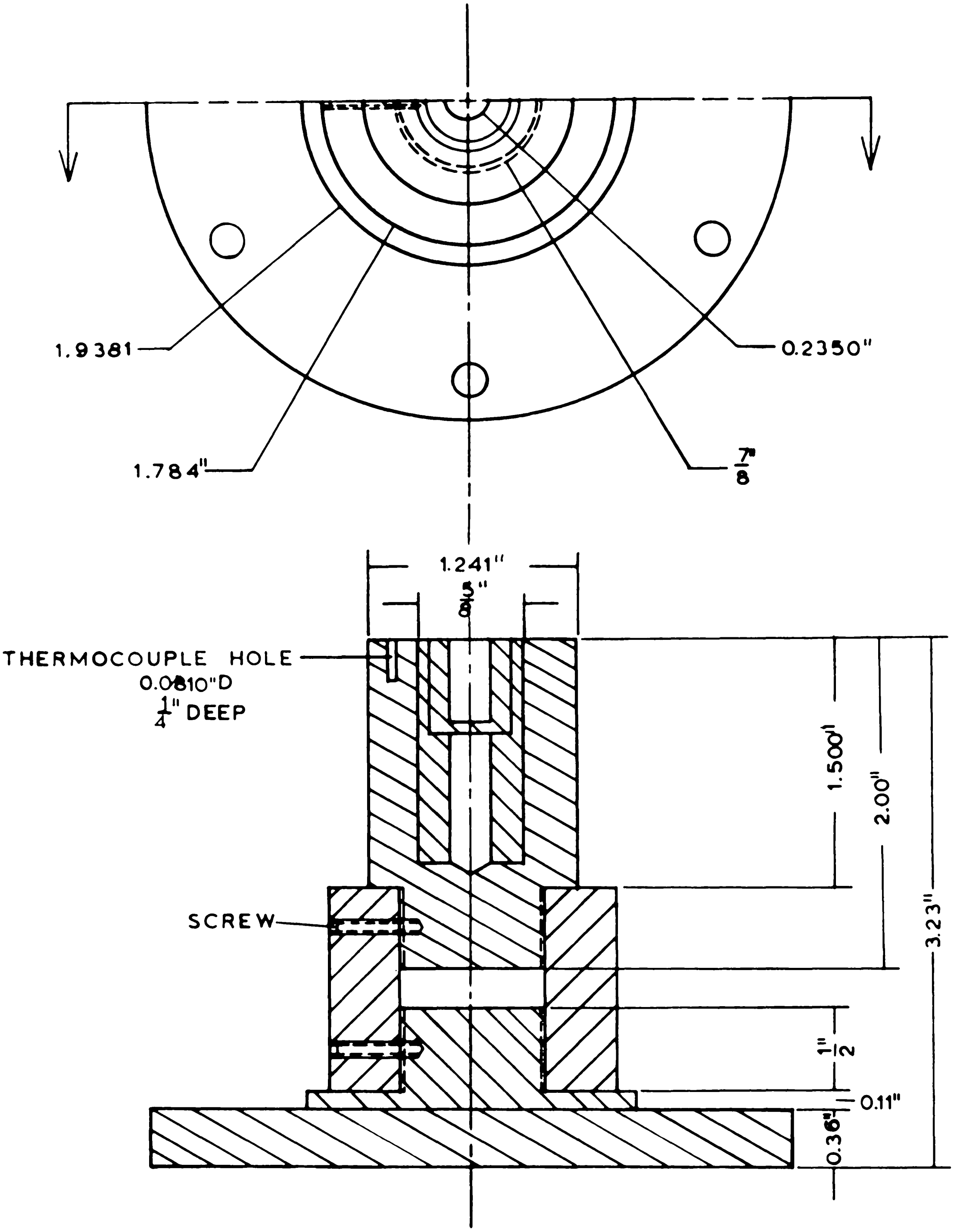


FIGURE 21. DETAILS OF GUARD HEATER

The copper guard heaters and the measuring cylinder were electroplated with nickel to a thickness of < 0.002 inch. This was necessary in order to prevent the contamination of the test fluids with the products of copper corrosion. The polished nickel surface minimized the radiation error and prevented the possibility of interaction of the large organic molecules with an active copper surface.

APPENDIX D

DATA FOR POLYMER SOLUTIONS

DENSITY AND THERMAL EXPANSIVITY OF POLYMER SOLUTIONS

The densities of selected polymer solutions were determined as a function of temperature in a pycnometer. The pycnometer contained a thermometer which allowed density measurements at various temperatures on the same samples.

The thermal expansivity β is defined as

$$\beta = -\frac{1}{\rho}\frac{\partial\rho}{\partial T} \tag{1}$$

where ρ is density and T is temperature. This can be approximated by

$$\beta \approx -\frac{1}{\rho}\frac{\Delta\rho}{\Delta T} \tag{2}$$

where $\bar{\rho}$ is an average density in the interval of the Δ's.

The density data obtained for solutions of the low molecular weight Polystyrene are typical and are given in Table XIV and plotted in Figure 22. Density was found to be a strong function of concentration and a slight function of molecular weight.

A summary of density and expansivity data for the solutions on which these determinations were made is given in Table XV, on page 102.

TABLE XIV

DENSITY OF SOLUTIONS OF MIDDLE MOLECULAR WEIGHT POLYSTYRENE AS A FUNCTION OF TEMPERATURE

Concentration weight percent	Temperature °C	Density gm/ml
0.1	21.2	0.8795
	21.9	.8783
	22.4	.8772
	24.2	.8750
	25.2	.8736
	26.2	.8728
	26.9	.8714
	27.9	.8710
	28.8	.8701
1.0	21	.8794
	22	.8784
	23	.8771
	24	.8763
	25	.8752
	26.3	.8739
	27	.8731
10.0	22	.8950
	23	.8942
	23.6	.8931
	24.2	.8929
	25.0	.8924
	25.2	.8921
	26.0	.8909
	29.2	.8884
	29.4	.8879
	30.3	.8868

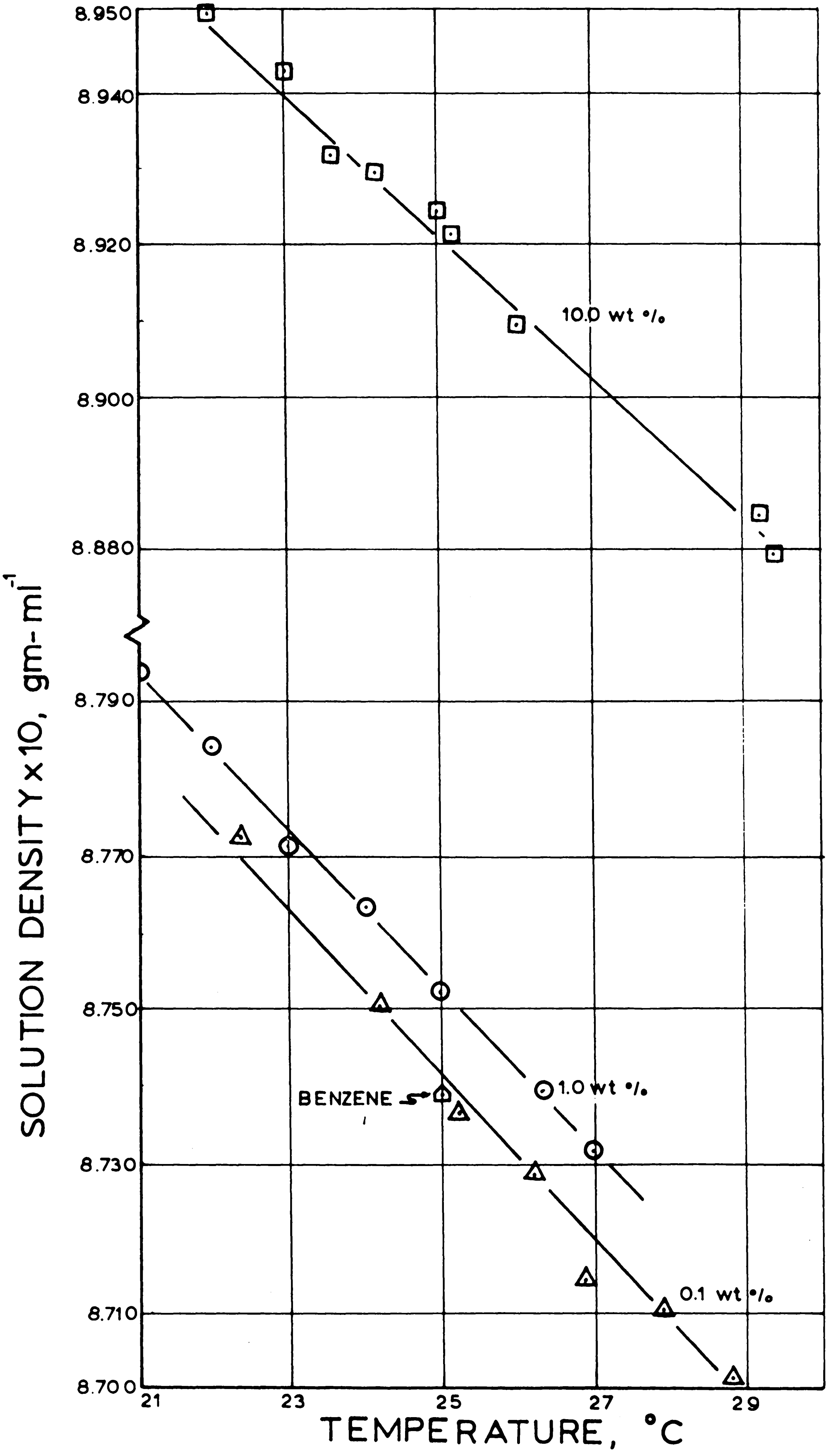


FIGURE 22. DENSITY vs. TEMPERATURE, LOW MW IN BENZENE

TABLE XV

DENSITY AND THERMAL EXPANSIVITY OF POLYMER SOLUTIONS

Molecular weight	Concentration weight percent	Density at 25° C gm/ml	Thermal expansivity $\times 10^{+3}$ $^{o}C^{-1}$
Low	1.0	0.8752	1.14
Low	15.0	.9014	1.20
Middle	0.1	.8743	1.26
Middle	1.0	.8752	1.14
Middle	10.0	.8924	1.06
High	10.0	.8929	1.18

VISCOSITIES OF POLYMER SOLUTIONS

The viscosities of selected polymer solutions were measured in capillary viscometers. The equation which describes fluid flow in capillaries is (7)

$$\mu = \frac{\pi r^4 hgt}{8VL} - \frac{mV}{8Lt\pi} \qquad (1)$$

where: μ = kinematic viscosity

h = mean hydrostatic head

t = efflux time

V = efflux volume

L = length of capillary

m = kinetic energy correction coefficient

The above equation may be rewritten as

$$\mu = Ct - \frac{B}{t} \qquad (2)$$

C is a constant for a particular viscometer and is usually obtained by calibration with a fluid known viscosity. The term B/t is a kinetic energy correction and is negligible for efflux times greater than 200 seconds. This minimum efflux time is greater than the minimum recommended for intrinsic viscosity determinations (see page 18) for the following reasons. In calculating the reduced viscosity, the solution viscosity is ratioed with the solvent viscosity measured in the same viscometer. Since the solutions are dilute the solution viscosity does not differ greatly from the solvent viscosity. Thus the kinetic energy corrections (which are a function of Reynold's number (7)) tend to cancel.

The viscometers used in this investigation were calibrated in accordance with ASTM specifications with National Bureau of Standards Viscosity Oils (7).

The polymer solutions of this study are non-Newtonian fluids, with increasing shear rate γ, the viscosity decreases and approaches a lower limiting value, η_∞. As the shear rate is decreased, the viscosity approaches an upper limiting value, the zero-shear viscosity η_o (see Figure 23). In these two limiting regions, the fluids are Newtonain (i.e., their viscosities are constant).

Equation (2) is valid only for Newtonian fluids. Thus, for the polymer solutions, it can give meaningful results only in the η_o regime. The shear rate, γ is inversely proportional to efflux time, t. Therefore, the efflux time of the solutions were measured in capillary viscometers of decreasing capillary diameters and an estimate of η_o was obtained by extrapolation to $1/t = 0$ (corresponding to $\gamma = 0$) (7).

The apparent viscosities of the dilute solutions did not change significantly with shear rate and η_o was taken as an average of the viscosities measured at various shear rates. For the more concentrated solutions, η was only a slight function of shear rate (change in η of < 1.0 percent for a change in $1/t$ of 10^1) so that η_o could be approximated as η at the highest efflux time.

The data are given in Tables XVI, XVII, and XVIII. Figure 24 is a plot of estimated η_o versus concentration for the three molecular weights. The plot is made on logarithmic paper for convenience.

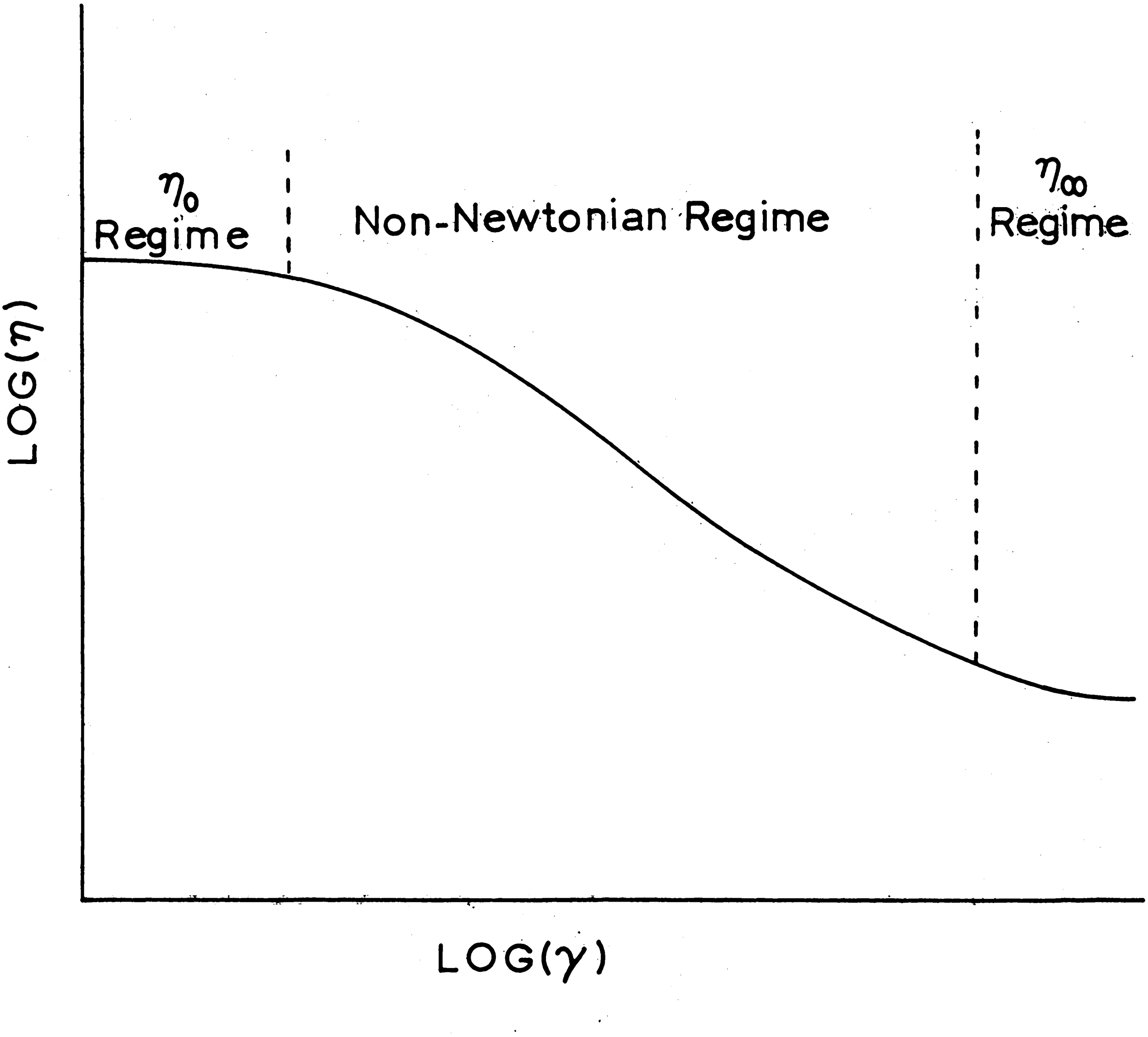


FIGURE 23.- TYPICAL VISCOSITY CURVE FOR A POLYMER SOLUTION.

TABLE XVI

APPARENT VISCOSITY OF LOW MOLECULAR WEIGHT POLYSTYRENE IN BENZENE SOLUTIONS AT 25° C[(a)]

Concentration weight percent	Efflux time, seconds	Apparent viscosity centipoise
0.55	272.2	0.72
1.00	116.2	0.764
1.00	244.2	0.760
2.05	292.9	0.95
2.30	304.9	0.49
4.07	526.5	1.40
5.21	652.9	1.74
9.62	193.6	3.47
15.00	226.4	7.60
15.00	548.5	7.63
22.5	1067.9	20.8

(a) Viscosities measured in Cannon-Fenske routine viscometers of various sizes.

TABLE XVII

APPARENT VISCOSITY OF INTERMEDIATE MOLECULAR WEIGHT POLYSTYRENE IN BENZENE SOLUTIONS AT 25° C(a)

Concentration weight percent	Efflux time, seconds	Apparent viscosity centipoise
0.10	208.5	0.649
0.10	99.45	0.653
1.00	174.8	1.15
1.00	369.7	1.15
2.03	600.8	1.92
2.49	906.8	2.40
4.91	684.0	6.04
10.00	3707.5	24.88
10.00	782.6	25.05
10.00	118.5	25.0
10.00	1892.8	26.1
22.5	4384.5	39.3

(a) Viscosities measured in Cannon-Fenske routine viscometers of various sizes.

TABLE XVIII

APPARENT VISCOSITY OF HIGH MOLECULAR WEIGHT POLYSTYRENE IN BENZENE SOLUTIONS AT 25° C(a)

Concentration weight percent	Efflux time, seconds	Apparent viscosity centipoise
0.10	217.4	0.677
0.10	103.1	0.678
0.10	216.4	0.673
1.01	460.7	1.50
1.99	154.7	2.72
1.99	1039.4	2.74
4.93	619.7	11.0
10.00	2198.6	73.1
10.00	334.1	73.2
10.00	84.9	70.1

(a) Viscosities were measured in Cannon-Fenske routine viscometers of various sizes.

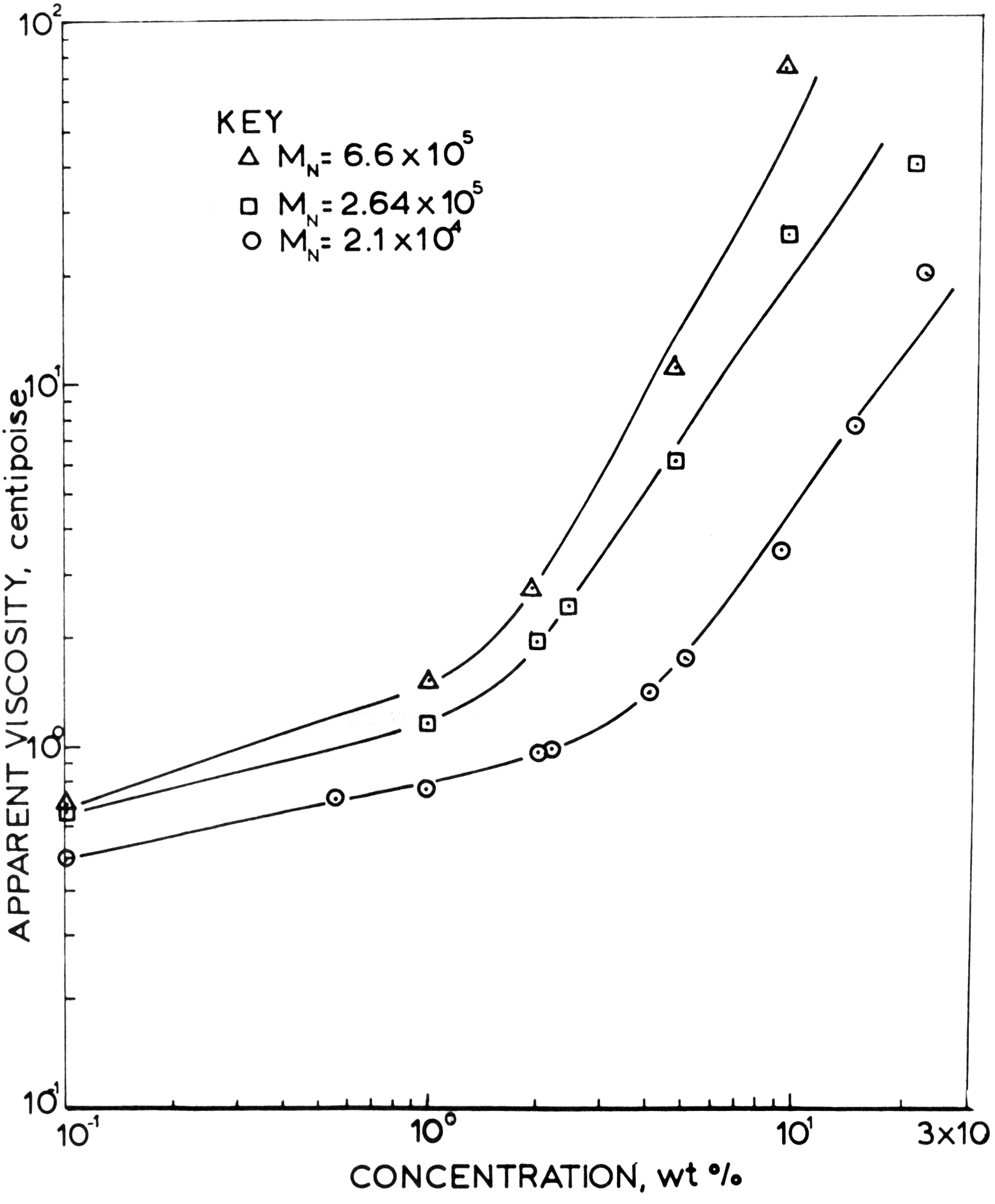


FIGURE 24.- ZERO-SHEAR VISCOSITY OF POLYMER SOLUTIONS AS A FUNCTION OF CONCENTRATION.

APPENDIX E

OPERATION OF EXPERIMENTAL EQUIPMENT

OPERATION OF EXPERIMENTAL EQUIPMENT

The apparatus was filled through a nipple at the bottom. The solutions were transferred to the apparatus directly from the container in which they were prepared. Filling from the bottom decreased the probability that air would be trapped in the annular gap.

After the conductivity cell was filled, it was transferred to a constant temperature bath. It was suspended in the bath from an angle-iron frame on which was mounted the thermocouple selector switch and terminal blocks for thermocouple and heater connections. The electrical connections were made and the approximate heating rates set on the control board. After a period of 20-30 minutes, the temperature difference between the guard heaters and the measuring cylinder was checked and suitable adjustments made in the current to the guard heaters. It was often necessary to repeat this process two and three times in order to make the temperature differences negligible.

After the end temperatures had been adjusted, it was necessary to achieve steady-state. This was done by taking thermocouple readings at 30-minute intervals (after an initial waiting period of 1 hour, following the adjustment of the end temperatures) until the readings repeated. This usually happened within 3 to 4 hours. After all the necessary readings had been taken, a new heating rate was set and the whole procedure repeated. A plot of heat flux $\dot{Q}$ versus average temperature difference ΔT was made. When the results of two or three of the above determinations were found to lie on a straight line through the origin (indicating the absence of convection), the determination of the thermal conductivity of that solution was considered complete. Thus, the determination of a single data point required no less than 4 hours and as long as 10 hours for some points, with an average time per point of about 8 hours.

After at least two "convection free" points had been taken, the apparatus was drained. The cell was flushed several times with solvent (technical grade Benzene), using air agitation, and then filled with fresh solvent and allowed to stand several hours. The cell was then drained and the top removed for visual inspection. Following this, the cell was rinsed with acetone and dried by blowing filtered compressed air through it.

APPENDIX F

SAMPLE CALCULATIONS

SAMPLE CALCULATIONS

The table on the following page is a thermal conductivity data sheet typical of those found in Appendix G. On it are recorded only those numbers which represent experimental observations.

Under the column headed "Thermocouple Pair" the numbers 6-6', 5-5', 4-4', and so forth, designate the differential thermocouple (DT) pairs. The readings of these thermocouples are given in the column headed "emf" and correspond to the temperature drop (ΔT) across the test fluid in the annulus or in the case of 6-6' and 18-18', the ΔT across the space between the measuring cylinder and the guard heaters. The ΔTs were calculated from the following equation

$$\Delta T_i = a_i + b_i \, (\mathrm{emf}_i) \quad (10)$$

where: $\Delta T_i = \Delta T$ indicated by the ith DT

b_i, a_i = slope and intercept respectively from the linear regression equation of the ith DT

The coefficients for all the DT's are given in Table X, page 79.

In order to calculate the ΔT indicated by DT 4-4', the following procedure would be followed. The coefficients obtained from Table X are

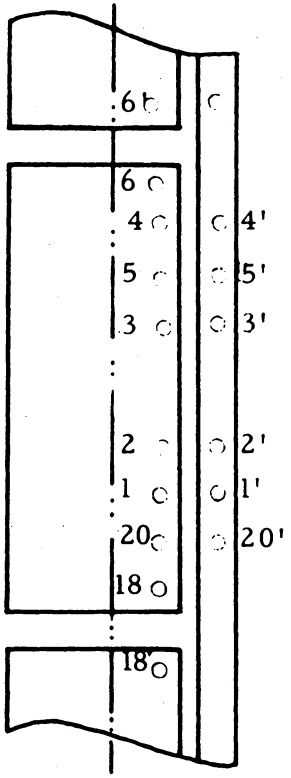
$$a_4 = 0.00023^\circ \text{ C}, \; b_4 = 2.44184^\circ \text{ C/v} \times 10^{-4}$$

The emf for DT 4-4' as obtained from the data sheet is

$$\mathrm{emf}_4 = 0.529 \text{ mv} = 5.29 \times 10^{-5} \text{ v}$$

Date 11-8-67	Ethylene glycol -1	Thermo-couple Pair	emf mv	ΔT's, °C	Heat Input to Measuring Cylinder

Thermocouple Location



Thermo-couple Pair	emf mv	ΔT's, °C
6 - 6'	0.007	
6' - ice	1.1348	
6 - ice	1.1340	
4 - 4'	.529	
4 - ice	1.1357	
5 - 5'	.620	
5 - ice		
3 - 3'	0.685	
3 - ice	1.1351	
2 - 2'	.677	
2 - ice		
1 - 1'	.775	
1 - ice		
20 - 20'	.786	
20 - ice	1.1290	
18 - 18'	.003	
18 - ice	1.1145	
18' - ice	1.1143	
20' - ice	1.0506	

Avg. Copper Temp, T_c = °C

$R_{\text{main heater}} = R_m =$ Ω

$\text{emf}_{\text{std resistor}} = V_{sr} = 28.51$ mv

$r_{\text{std resistor}} = r = 0.9538$ Ω

Current

$I = \frac{V_{sr}}{r} =$ ma

Power

$Q = I^2 R_m =$ watt

Avg. $\Delta T = \overline{\Delta T} =$ °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

$A = 10.549 \times 10^{-4}$ cm^{-1}

K = $\frac{\text{watt}}{\text{cm-°C}}$

$T_{\text{reference}} =$ °C

T_{bath} °C	$T_{\text{std cell}}$ °C
23.5	20 ± 1

Thus ΔT_4 is given by

$$\Delta T_4 = 0.00023 + (5.29 \times 10^{-5})\ (2.44184)\ (10)$$

$$\Delta T_4 = 1.44^{\circ}\ C$$

This procedure is followed for all the DT readings. The ΔT's which correspond to temperature drops across annulus are averaged arithmetically and the average value is entered opposite "Avg. $\Delta T = \overline{\Delta T}$."

In addition to the DT's, the Thermocouple Pair column contains designations such as 6-ice, 6'-ice, 4-ice, and so forth. The readings opposite these designations correspond to estimates of the absolute temperature in a given location. The readings are obtained by pairing one thermocouple of a DT pair with a copper-Constantan thermocouple maintained at 0° C in an ice-water slurry. The emf reading thus obtained is converted to an estimate of the absolute temperature via standard emf-temperature tables for copper-Constantan thermocouples (e.g., Leeds and Northrup Standard Number 31031, p. 35). These estimated temperatures were considered to be within ± 0.1° C of the actual temperature. The "Avg. Copper Temp., T_c" is calculated from temperatures measured in this way at various points on the measuring cylinder.

The potential drop across the standard resistors measured by the potentiometer is entered opposite "V_{sr}." This resistor is maintained at 0° C and its resistance, r is constant at 0.9538 ohm. The only other experimental observation is the temperature of the constant temperature bath as read from a calibrated mercury in glass thermometer.

The resistance of the main heater (the resistance heater in the measuring cylinder) was a function of temperature. It was considered to be at the same temperature as the measuring cylinder (T_c). Its resistance was read from the calibration curve of Figure 18, page 85 at temperature equal to T_c. The calculation of the thermal conductivity from these quantities is a straight forward procedure and is clearly outlined on the data sheets. This value of the thermal conductivity must then be multiplied by the calibration factor of 1.095. The reference temperature is simply the average temperature in the annulus. It is calculated by subtracting half of the average ΔT from the temperature of the measuring cylinder, T_c.

APPENDIX G

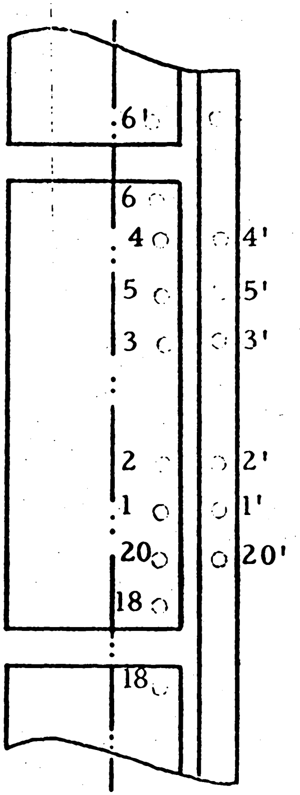
THERMAL CONDUCTIVITY DATA SHEETS

THERMAL CONDUCTIVITY DATA SHEETS

This section contains the data and partial calculations for all the thermal conductivity measurements reported herein. The calculations and nomenclature used in these tabulations are explained in Appendix F, page 116. The conductivity values in these tables have not been corrected with the calibration factor (1.095).

Date 4-8-67	Water

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.5	20± 1

Thermo-couple Pair	emf mv	ΔT's, °C
6 - 6'	0.0×10^{-1}	
6' - ice	1.035	26.12
6 - ice		
4 - 4'	0.321×10^{-1}	0.784
4 - ice		
5 - 5'	0.330×10^{-1}	0.819
5 - ice		
3 - 3'	0.354×10^{-1}	0.864
3 - ice		
2 - 2'	0.367×10^{-1}	0.903
2 - ice		
1 - 1'	0.418×10^{-1}	1.021
1 - ice		
20 - 20'	0.430×10^{-1}	1.053
20 - ice		
18 - 18'	0.012×10^{-1}	0.031
18 - ice		
18' - ice	1.029	25.97

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 26.05 °C

$R_{main\ heater} = R_m$ = 42.616 Ω

$emf_{std\ resistor} = V_{sr}$ = 31.995 mv

$r_{std\ resistor}$ = r = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r}$ = 335.4 ma

Power

$Q = I^2 R_m$ = 4.794 watt

Avg. $\Delta T = \overline{\Delta T}$ = 0.907 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

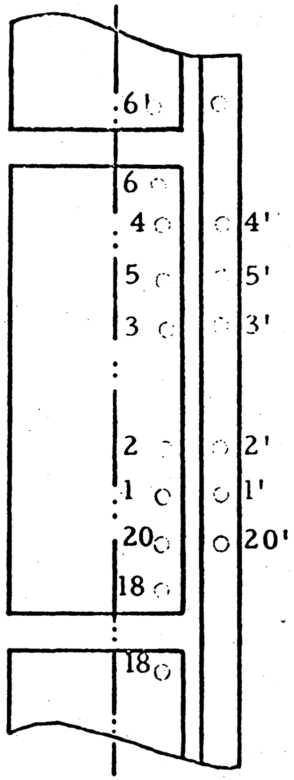
$A = 10.549 \times 10^{-4}$ cm^{-1}

K = 5.576×10^{-3} $\frac{watt}{cm\text{-}^{\circ}C}$

$T_{reference}$ = 25.60 °C

Date 3-8-67 PM	**Water**

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
24.0	20 ± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.027×10^{-1}	0.062
6' - ice	1.0231	25.84
6 - ice	1.0213	25.80
4 - 4'	0.0223	0.545
4 - ice		
5 - 5'	0.0223	0.552
5 - ice		
3 - 3'	0.0246	0.599
3 - ice		
2 - 2'	0.0254	0.625
2 - ice		
1 - 1'	0.0287	0.702
1 - ice		
20 - 20'	0.0296	0.724
20 - ice		
18 - 18'	0.0011	0.0135
18 - ice		
18' - ice	1.0180	25.70

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 25,8 °C

$R_{main\ heater} = R_m$ = 42.617 Ω

$emf_{std\ resistor} = V_{sr}$ = 26.541 mv

$r_{std\ resistor}$ = r = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r} =$ 278.3 ma

Power

$Q = I^2 R_m =$ 3.301 watt

Avg.$\Delta T = \overline{\Delta T} =$ 0.625 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

$A = 10.549 \times 10^{-4}\ cm^{-1}$

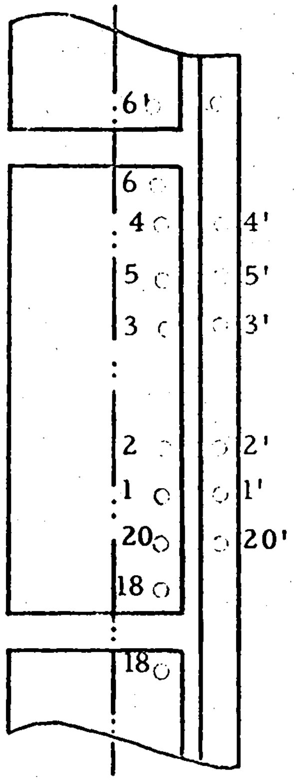
$K = 5.571 \times 10^{-3}\ \frac{watt}{cm\text{-}^{\circ}C}$

$T_{reference}$ = 25.47 °C

Date
5-8-67
AM

Water

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.010×10^{-1}	0.020
6' - ice	1.0004	25.25
6 - ice	0.0995	25.23
4 - 4'		
4 - ice	0.999 mv	25.21
5 - 5'	0.193×10^{-1}	0.479
5 - ice	0.9990 mv	25.21
3 - 3'	0.210×10^{-1}	0.511
3 - ice		
3'-ice	0.9785	24.70
2 - 2'	0.218×10^{-1}	0.536
2 - ice	0.9987 mv	25.21
1 - 1'	0.250×10^{-1}	0.61
1 - ice	0.9996	25.23
20 - 20'	0.256×10^{-1}	0.627
20 - ice	0.9972	25.18
18 - 18'	0.016×10^{-1}	0.04
18 - ice		
18' - ice	0.9945 mv	25.10
4'-ice	0.9805 mv	24.75
2'-ice	0.9761	24.65
20'-ice	0.9716	24.55

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 25.20 °C

$R_{\text{main heater}} = R_m =$ 42.617

$\text{emf}_{\text{std resistor}} = V_{sr} =$ 24.889 mv

$r_{\text{std resistor}} = r = 0.9538$

Current

$I = \dfrac{V_{sr}}{r} =$ 260.95 ma

Power

$Q = I^2 R_m =$ 2.902 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.552 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

$A = 10.549 \times 10^{-4}\ \text{cm}^{-1}$

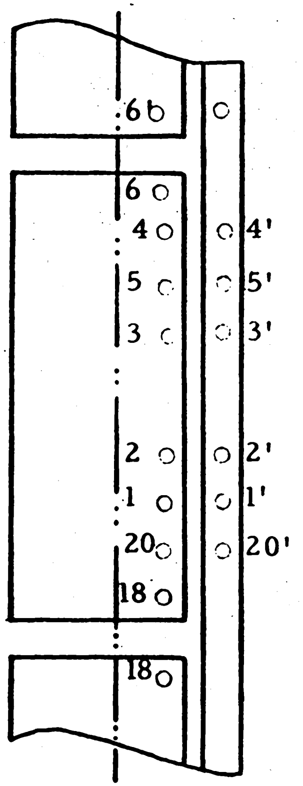
$K =$ 5.545×10^{-3} $\dfrac{\text{watt}}{\text{cm-}^{\circ}\text{C}}$

$T_{\text{reference}} =$ 24.92 °C

T_{bath} °C	$T_{\text{std cell}}$ °C
23.5	20 ± 1

Date 6-8-67 AM	Water

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	$0.003 x 10^{-1}$	0.032
6' - ice	1.0309	26.03
6 - ice	1.0293	25.98
4 - 4'	$0.215 x 10^{-1}$	0.525
4 - ice		
5 - 5'	$0.163 x 10^{-1}$	0.407
5 - ice		
3 - 3'	$0.226 x 10^{-1}$	0.5499
3 - ice		
2 -2'	$0.228 x 10^{-1}$	0.562
2 -ice		
1 -1'	$0.245 x 10^{-1}$	0.599
1 -ice		
20 -20'	$0.252 x 10^{-1}$	0.617
20 -ice		
18 -18'	$0.008 x 10^{-1}$	0.021
18 -ice	1.0265	25.92
18' -ice	1.0247	25.87

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 25.95°C

$R_{\text{main heater}} = R_m = 42.616\ \Omega$

$\text{emf}_{\text{std resistor}} = V_{sr} = 24.818$ mv

$r_{\text{std resistor}} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 260.2 ma

Power

$Q = I^2 R_m =$ 2.885 watt

$\text{Avg.}\Delta T = \overline{\Delta T} =$ 0.543 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

$A = 10.549 \times 10^{-4}\ \text{cm}^{-1}$

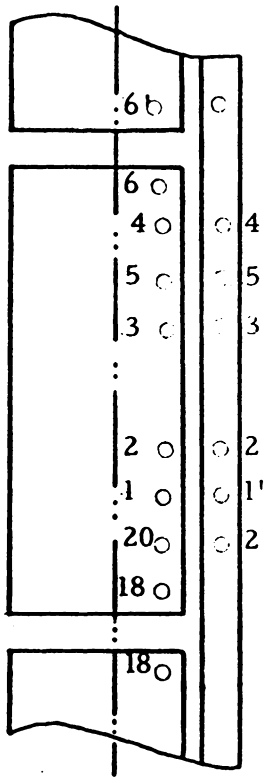
$K = 5.604 \times 10^{-3}\ \frac{\text{watt}}{\text{cm-}^{\circ}\text{C}}$

$T_{\text{reference}} =$ 25.68 °C

T_{bath} °C	$T_{\text{std cell}}$ °C
	20 ± 1

Date 8-8-67 AM	WATER	Thermo-couple Pair	emf mv	ΔT's, °C
		6 - 6'	0.009×10^{-1}	0.018
		6' - ice	0.9889	24.98
		6 - ice		
		4 - 4'	0.253×10^{-1}	0.618
		4 - ice		
		5 - 5'	0.275×10^{-1}	0.683
		5 - ice		
		3 - 3'	0.302×10^{-1}	0.736
		3 - ice		
		2 - 2'	0.287×10^{-1}	0.707
		2 - ice		
		1 - 1'	0.342×10^{-1}	0.833
		1 - ice		
		20 - 20'	0.348×10^{-1}	0.852
		20 - ice		
		18 - 18'	0.014×10^{-1}	0.035
		18 - ice		
		18' - ice	0.9817	24.80

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
	20 ± 1

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 24.89 °C

$R_{main\ heater} = R_m$ = 42.616 Ω

$emf_{std\ resistor} = V_{sr}$ = 28.867 mv

$r_{std\ resistor} = r = 0.9538$ Ω

Current

$I = \frac{V_{sr}}{r} =$ 302.6 ma

Power

$Q = I^2 R_m =$ 3.902 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.738 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

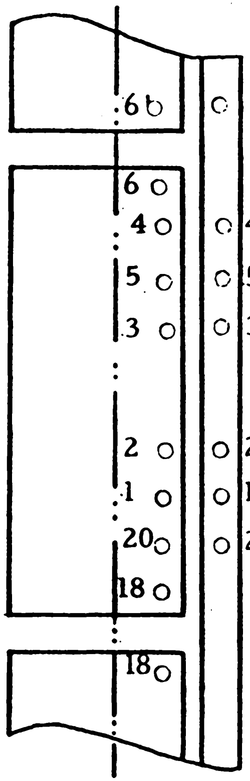
$A = 10.549 \times 10^{-4}$ cm^{-1}

$K = 55.77 \times 10^{-4} \frac{\text{watt}}{\text{cm-°C}}$

$T_{reference}$ = 24.52 °C

Date 11-8-67	Ethylene Glycol-1

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.5	20± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.007	0.02
6'- ice	1.1348	28.63
6 - ice	1.1340	28.60
4 - 4'	0.529	1.44
4 - ice	1.1357	28.65
5 - 5'	0.620	1.54
5 - ice		
3 - 3'	0.685	1.675
3 - ice	1.1351	28.63
2 -2'	0.677	1.665
2 -ice		
1 -1'	0.775	1.89
1 -ice		
20 -20'	0.786	1.93
20 -ice	1.1290	28.47
18 -18'	0.003	0.01
18 -ice	1.1145	28.11
18' -ice	1.1143	28.10
20'-ice	1.0506	26.51

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 28.46°C

$R_{main\ heater} = R_m$ = 42.613 Ω

$emf_{std\ resistor} = V_{sr}$ = 28.51 mv

$r_{std\ resistor}$ = r = 0.9538 Ω.

Current

$I = \frac{V_{sr}}{r}$ = 298.9 ma

Power

$Q = I^2 R_m$ = 3.807 watt

Avg.$\Delta T = \overline{\Delta T}$ = 1.69 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

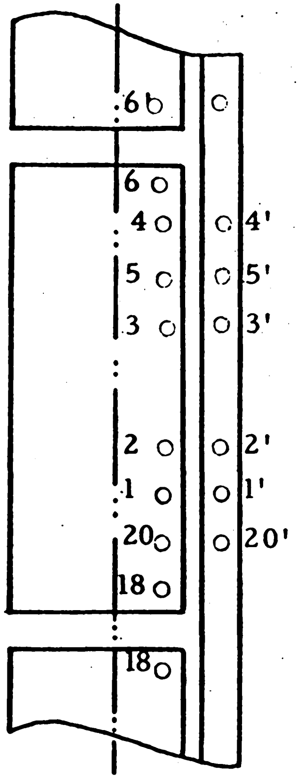
$A = 10.549 \times 10^{-4}$ cm^{-1}

K = 23.76×10^{-4} $\frac{watt}{cm-°C}$

$T_{reference}$ = 27.61 °C

Date 11-8-67 AM	Ethylene Glycol-2

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.008	0.015
6' - ice	1.0832	27.35
6 - ice	1.0825	27.32
4 - 4'	0.405	0.990
4 - ice	1.0822	27.30
5 - 5'	0.425	1.055
5 - ice	1.0827	27.34
3 - 3'	0.470	1.148
3 - ice	1.0822	27.30
2 -2'	0.466	1.145
2 -ice	1.0794	27.24
1 -1'	0.545	1.330
1 -ice	1.0808	27.27
20 -20'	0.551	1.350
20 -ice	1.0782	27.20
18 -18'	0.005	0.015(-)
18 -ice	1.0695	27.0
18' -ice	1.0697	27.0

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 27.23 °C

$R_{\text{main heater}} = R_m$ = 42.615 Ω

$\text{emf}_{\text{std resistor}} = V_{sr}$ = 23.646 mv

$r_{\text{std resistor}} = r = 0.9538$ Ω

Current

$I = \frac{V_{sr}}{r} =$ 247.9 ma

Power

$Q = I^2 R_m =$ 2.619 watt

Avg. $\Delta T = \overline{\Delta T} =$ 1.17 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

$A = 10.549 \times 10^{-4}$ cm^{-1}

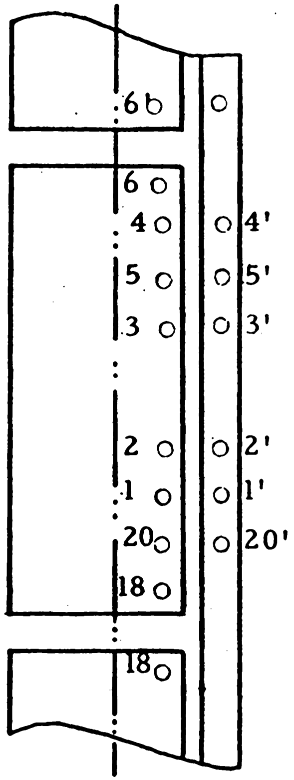
$K =$ 23.62×10^{-4} $\frac{\text{watt}}{\text{cm-°C}}$

$T_{\text{reference}}$ = 26.64 °C

T_{bath} °C	$T_{\text{std cell}}$ °C
23.5	20 ± 1

Date 11-8-67 AM	Ethylene Glycol-3

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.5	20± 1

Thermo-couple Pair	emf mv	ΔT's, °C
6 - 6'	0.000	0.000
6'- ice		
6 - ice	1.0200	25.75
4 - 4'	0.265	0.650
4 - ice		
5 - 5'	0.280	0.695
5 - ice	1.0208	25.77
3 - 3'	0.318	0.775
3 - ice	1.0211	25.80
2 -2'	0.315	0.775
2 -ice	1.0192	25.73
1 -1'	0.370	0.900
1 -ice		
20 -20'	0.374	0.915
20 -ice	1.0171	25.70
18 -18'	0.000	0.000
18 -ice	1.0108	25.55
18' -ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 25.78 °C

$R_{main\ heater} = R_m$ = 42.617 Ω

$emf_{std\ resistor} = V_{sr}$ = 19.344 mv

$r_{std\ resistor}$ = r = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r} =$ 202.8 ma

Power

$Q = I^2 R_m =$ 1.753 watt

Avg.ΔT = $\overline{\Delta T}$ = 0.785 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

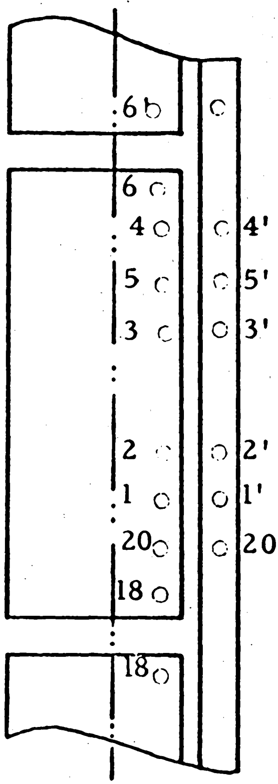
$A = 10.549 \times 10^{-4}\ cm^{-1}$

K = 23.55×10^{-4} $\frac{watt}{cm\text{-}°C}$

$T_{reference}$ = 25.37 °C

Date 24-8-67 PM	**Cyclohexanol**

Thermocouple Location



T bath °C	T std cell °C
22.5	20 ± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'		0.00
6' - ice	1.0583	26.72
6 - ice		
4 - 4'	0.0356	0.87
4 - ice	1.0507	26.52
5 - 5'		
5 - ice		
3 - 3'	0.032	1.055
3 - ice		
4' - ice	1.0151	25.62
2 -2'	0.0438	1.078
2 -ice		
1 -1'	0.0518	1.265
1 -ice		
20 -20'	0.0482	1.18
20 -ice	1.0476	26.45
18 -18'	0.0001	0.00
18 -ice		
18' -ice	1.0407	26.27
20' -ice	0.9999	25.25

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 26.49 °C

$R_{\text{main heater}} = R_m$ = 42.616 Ω

$\text{emf}_{\text{std resistor}} = V_{sr}$ = 16.758 mv

$r_{\text{std resistor}} = r$ = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r} =$ 175.7 ma

Power

$Q = I^2 R_m =$ 1.316 watt

Avg. $\Delta T = \overline{\Delta T} =$ 1.090 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

$A = 10.549 \times 10^{-4}\ \text{cm}^{-1}$

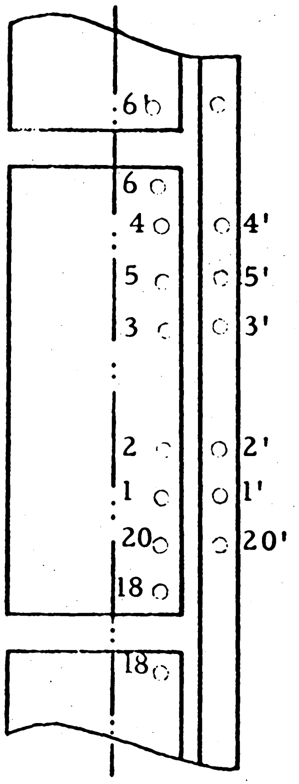
$K = 12.74 \times 10^{-4}\ \frac{\text{watt}}{\text{cm-}^{\circ}\text{C}}$

$T_{\text{reference}}$ = 25.94 °C

Date
24-8-67
PM

Cyclohexanol

Thermocouple Location



T_bath °C	T_std cell °C
23.5	20 ± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.0013	0.028
6' - ice	1.0542	26.61
6 - ice		
4 - 4'	0.0236	0.578
4 - ice	1.0492	2.649
5 - 5'		
5 - ice		
3 - 3'	0.0292	0.712
3 - ice		
4' - ice	1.0256	25.90
2 - 2'	0.0293	0.721
2 - ice		
1 - 1'	0.0351	0.858
1 - ice		
20 - 20'	0.0323	0.790
20 - ice	1.0474	26.45
18 - 18'	0.000	
18 - ice	1.0425	26.31
18' - ice		
20' - ice	1.0142	25.60

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 26.47 °C

$R_{\text{main heater}} = R_m$ = 42.616 Ω

$\text{emf}_{\text{std resistor}} = V_{sr}$ = 13.785 mv

$r_{\text{std resistor}} = r$ = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r}$ = 144.5 ma

Power

$Q = I^2 R_m$ = 0.890 watt

Avg. $\Delta T = \overline{\Delta T}$ = 0.732 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

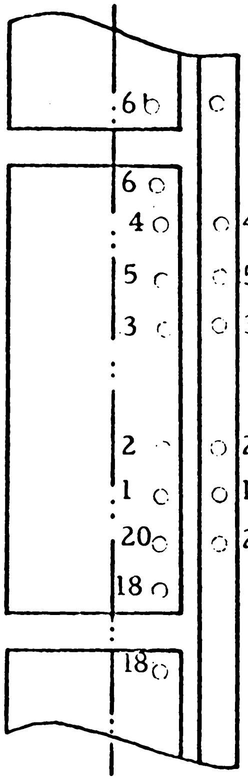
$A = 10.549 \times 10^{-4}\ \text{cm}^{-1}$

K = 12.83x10⁻⁴ $\frac{\text{watt}}{\text{cm-°C}}$

$T_{\text{reference}}$ = 26.11 °C

Date 24-8-67 PM	**Cyclohexanol**

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
22.48	20 ± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.0009	0.018
6' - ice	1.0902	27.50
6 - ice		
4 - 4'	0.0441	1.078
4 - ice	1.0799	27.25
5 - 5'		
5 - ice		
3 - 3'	0.0532	1.30
3 - ice		
4' -ice	1.0354	26.13
2 -2'	0.0540	1.328
2 -ice		
1 -1'	0.0634	1.548
1 -ice		
20 -20'	0.0595	1.458
20 -ice	1.0726	27.08
18 -18'	0.000	0.00
18 -ice		
18' -ice	1.0632	26.83
20'-ice	1.0163	25.67

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 27.17 °C

$R_{main\ heater} = R_m$ = 42.615 Ω

$emf_{std\ resistor} = V_{sr}$ = 18.715 mv

$r_{std\ resistor} = r$ = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r} =$ 196.2 ma

Power

$Q = I^2 R_m =$ 1.640 watt

Avg. $\Delta T = \overline{\Delta T} =$ 1.342 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

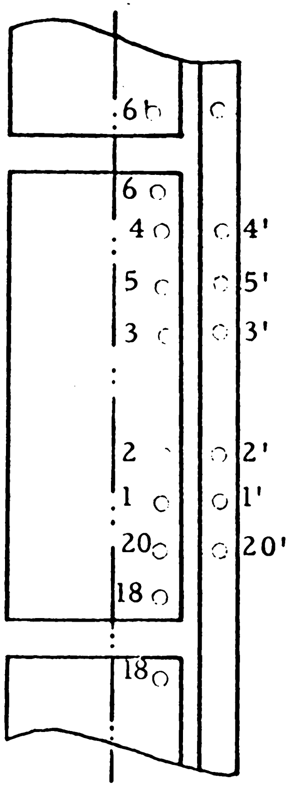
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K =$ $12.89 \times 10^{-4}\ \frac{watt}{cm\text{-}^\circ C}$

$T_{reference}$ = 26.49 °C

Date	
17-8-67 AM	**1.0% Polystyrene MW_1 in Benzene**

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.5	20 ± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.005×10^{-1}	0.0075
6' - ice		
6 - ice	0.9850	24.87
4 - 4'	0.150×10^{-1}	0.368
4 - ice	0.9847	24.87
5 - 5'	0.168×10^{-1}	0.418
5 - ice	0.9845	24.85
3 - 3'	0.190×10^{-1}	0.460
3 - ice		
2 - 2'	0.205×10^{-1}	0.505
2 - ice	0.9842	24.85
1 - 1'	0.240×10^{-1}	0.585
1 - ice	0.9844	24.85
20 - 20'	0.217×10^{-1}	0.53
20 - ice	0.9823	24.81
18 - 18'	0.005×10^{-1}	0.10
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 24.85°C

$R_{main\ heater} = R_m = 42.618\ \Omega$

$emf_{std\ resistor} = V_{sr} = 12.291$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 128.9 ma

Power

$Q = I^2 R_m =$ 0.7083 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.478 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

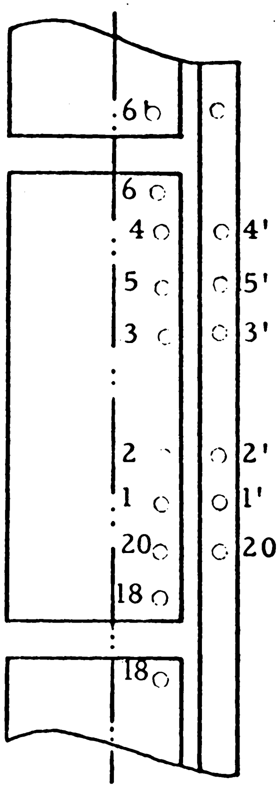
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K = 15.63 \times 10^{-4} \frac{watt}{cm\text{-}°C}$

$T_{reference} =$ 24.61 °C

Date		Thermocouple Pair	emf mv	ΔT's, °C
17-8-67 AM	**1.0% Polystyrene** **MW_1 in Benzene**			

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.5	20 ± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.005×10^{-1}	0.008
6' - ice		
6 - ice	0.9770	24.67
4 - 4'	0.115×10^{-1}	0.28
4 - ice		
5 - 5'	0.132×10^{-1}	0.33
5 - ice		
3 - 3'	0.150×10^{-1}	0.363
3 - ice		
2 - 2'	0.163×10^{-1}	0.408
2 - ice	0.9765	24.65
1 - 1'	0.195×10^{-1}	0.475
1 - ice	0.9765	24.65
20 - 20'	0.166×10^{-1}	0.405
20 - ice	0.9751	24.61
18 - 18'	0.005×10^{-1}	0.015
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 24.65 °C

$R_{main\ heater} = R_m = 42.618\ \Omega$

$emf_{std\ resistor} = V_{sr} = 11.035$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 115.7 ma

Power

$Q = I^2 R_m =$ 0.5707 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.377 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

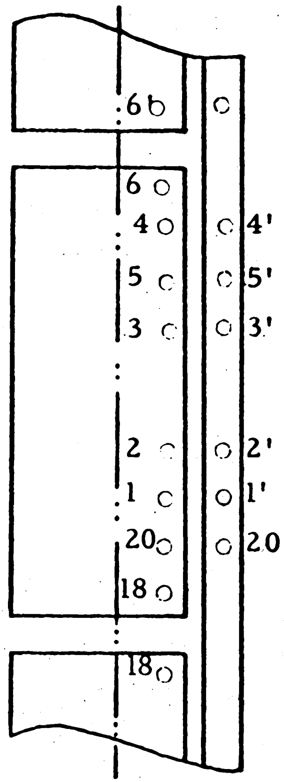
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K = 15.97 \times 10^{-4}\ \frac{watt}{cm\text{-}°C}$

$T_{reference} =$ 24.46 °C

Date			
18-8-67 AM	**10% Polystyrene MW$_1$ in Benzene**		

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.5	20 ± 1

Thermo-couple Pair	emf mv	ΔT's, °C
6 - 6'	0.011×10^{-1}	0.02
6' - ice	0.9835	24.84
6 - ice	0.9855	24.87
4 - 4'	0.130×10^{-1}	0.32
4 - ice	0.9850	24.87
5 - 5'	0.145×10^{-1}	0.36
5 - ice		
3 - 3'	0.163×10^{-1}	0.395
3 - ice		
2 - 2'	0.170×10^{-1}	0.42
2 - ice	0.9852	24.87
1 - 1'	0.198×10^{-1}	0.483
1 - ice	0.9850	24.87
20 - 20'	0.183×10^{-1}	0.448
20 - ice	0.9840	24.85
18 - 18'	0.001	0.003
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, $T_c = 24.86$ °C

$R_{main\ heater} = R_m = 42.618\ \Omega$

$emf_{std\ resistor} = V_{sr} = 11.025$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 115.6 ma

Power

$Q = I^2 R_m =$ 0.5694 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.404 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

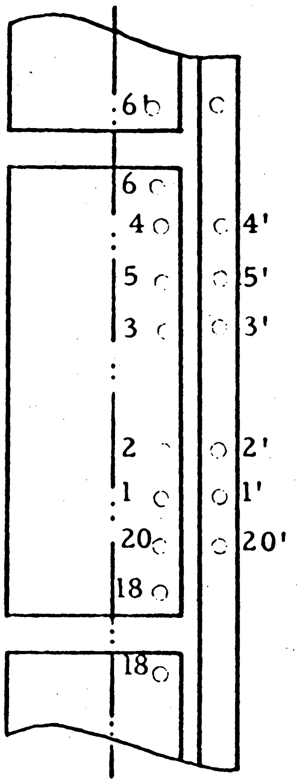
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K = 14.87 \times 10^{-4} \frac{watt}{cm\text{-}°C}$

$T_{reference} =$ 24.66 °C

Date 18-8-67 AM	**10% Polystyrene MW_1 in Benzene**

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.5	20 ± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.008×10^{-1}	0.015
6' - ice	1.0198	25.75
6 - ice	1.0208	25.77
4 - 4'	0.242×10^{-1}	0.59
4 - ice	1.0184	25.70
5 - 5'	0.273×10^{-1}	0.678
5 - ice		
3 - 3'	0.297×10^{-1}	0.725
3 - ice		
2 - 2'	0.313×10^{-1}	0.770
2 - ice	1.0184	25.70
1 - 1'	0.359×10^{-1}	0.878
1 - ice	1.0184	25.70
20 - 20'	0.1329×10^{-1}	0.805
20 - ice	1.0161	25.65
18 - 18'	0.005×10^{-1}	0.01
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, $T_c = 25.71$ °C

$R_{main\ heater} = R_m = 42.617\ \Omega$

$emf_{std\ resistor} = V_{sr} = 14.948$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 156.7 ma

Power

$Q = I^2 R_m =$ 1.046 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.741 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

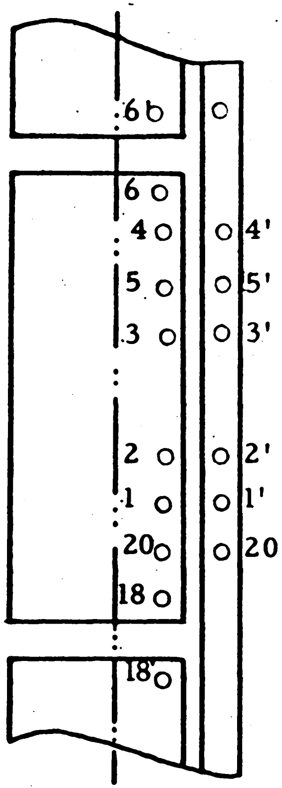
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K = 14.89 \times 10^{-4}\ \frac{watt}{cm\text{-}^{\circ}C}$

$T_{reference} = 25.34$ °C

Date	15% Polystyrene MW_1 in Benzene	Thermocouple Pair	emf mv	ΔT's, °C
		6 - 6'	0.003×10^{-1}	0.005
		6' - ice		
		6 - ice	1.0070	25.42
		4 - 4'	0.318×10^{-1}	.775
		4 - ice	1.0045	25.35
		5 - 5'	0.350×10^{-1}	0.87
		5 - ice		
		3 - 3'	0.370×10^{-1}	0.903
		3 - ice		
		2 - 2'	0.385×10^{-1}	0.948
		2 - ice		
		1 - 1'	0.438×10^{-1}	1.068
		1 - ice	1.0047	25.37
		20 - 20'	0.410×10^{-1}	1.005
		20 - ice	1.0030	25.32
		18 - 18'	0.000	0.000
		18 - ice		
		18' - ice		

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
22.8	20 ± 1

Heat Input to Measuring Cylinder

Avg. Copper Temp, $T_c = 25.37$ °C

$R_{main\ heater} = R_m = 42.617\ \Omega$

$emf_{std\ resistor} = V_{sr} = 16.640$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 174.5 ma

Power

$Q = I^2 R_m =$ 1.2977 watt

$\text{Avg.}\Delta T = \overline{\Delta T} =$ 0.928 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

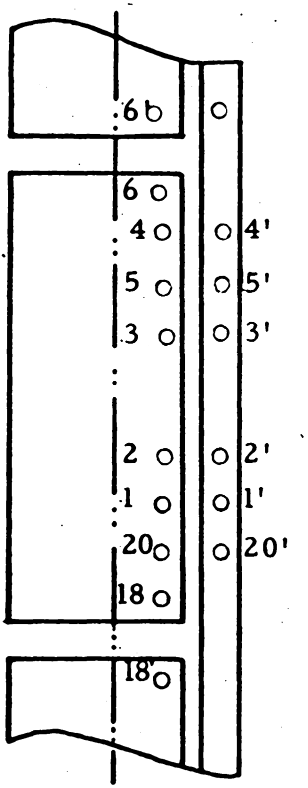
$A = 10.549 \times 10^{-4}\ \text{cm}^{-1}$

$K = 14.75 \times 10^{-4} \frac{\text{watt}}{\text{cm-°C}}$

$T_{reference} = 24.91$ °C

Date	15% Polystyrene MW_1 in Benzene

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
22.6	20 ± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.004×10^{-1}	0.05
6' - ice		
6 - ice	0.9573	24.18
4 - 4'	0.150×10^{-1}	0.368
4 - ice	0.9550	24.12
5 - 5'	0.167×10^{-1}	0.415
5 - ice		
3 - 3'	0.179×10^{-1}	0.435
3 - ice		
2 - 2'	0.190×10^{-1}	0.468
2 - ice	0.9548	24.12
1 - 1'	0.219×10^{-1}	0.535
1 - ice		
20 - 20'	0.209×10^{-1}	0.510
20 - ice	0.9545	24.10
18 - 18'	0.017×10^{-1}	0.04
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, $T_c = 24.13$ °C

$R_{main\ heater} = R_m = 42.619\ \Omega$

$emf_{std\ resistor} = V_{sr} = 11.734$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 123.0 ma

Power

$Q = I^2 R_m =$ 0.6448 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.455 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

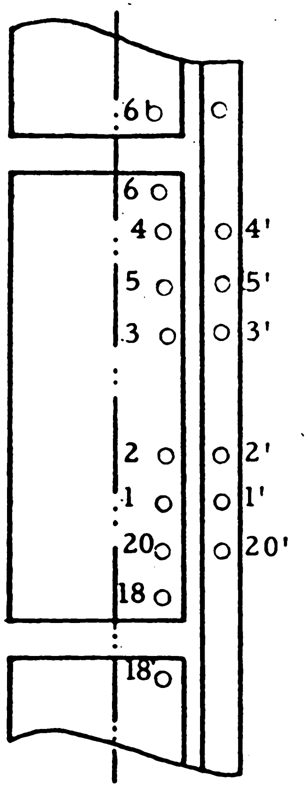
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K = 14.95 \times 10^{-4} \frac{watt}{cm\text{-}°C}$

$T_{reference} =$ 23.90 °C

Date	15.0% Polystyrene
24-8-67 AM	MW_1 in Benzene

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.010×10^{-1}	0.02
6' - ice		
6 - ice	0.9840	24.85
4 - 4'	0.233×10^{-1}	0.57
4 - ice	0.9825	24.80
5 - 5'	0.253×10^{-1}	0.628
5 - ice		
3 - 3'	0.275×10^{-1}	0.67
3 - ice		
2 - 2'	0.283×10^{-1}	0.698
2 - ice		
1 - 1'	0.329×10^{-1}	0.803
1 - ice	0.9820	24.80
20 - 20'	0.305×10^{-1}	0.748
20 - ice	0.9810	24.77
18 - 18'	0.013×10^{-1}	.033
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, $T_c = 24.81$ °C

$R_{\text{main heater}} = R_m = 42.618\ \Omega$

$\text{emf}_{\text{std resistor}} = V_{sr} = 14.266$ mv

$r_{\text{std resistor}} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 149.6 ma

Power

$Q = I^2 R_m =$ 0.9538 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.686 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

$A = 10.549 \times 10^{-4}\ \text{cm}^{-1}$

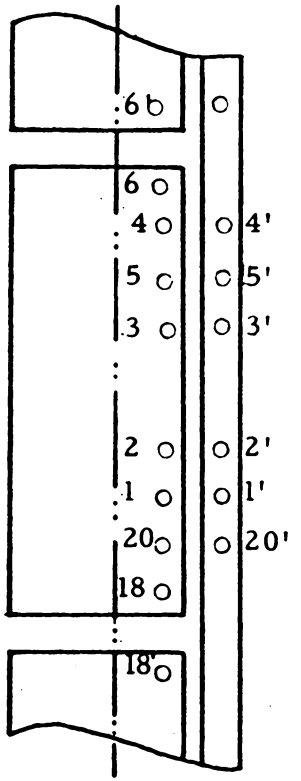
$K = 14.67 \times 10^{-4} \frac{\text{watt}}{\text{cm-}^\circ\text{C}}$

$T_{\text{reference}} =$ 24.47 °C

T_{bath} °C	$T_{std\ cell}$ °C
22.6	20 ± 1

Date 23-8-67 PM	1.0% Polystyrene MW_2 in Benzene

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.0002	0.00
6'- ice	0.9483	23.95
6 - ice		
4 - 4'	0.0162	0.396
4 - ice	0.9466	23.90
5 - 5'	0.0172	0.427
5 - ice		
3 - 3'	0.0193	0.470
3 - ice		
4'- ice	0.9297	23.50
2 -2'	0.0200	0.492
2 -ice		
1 -1'	0.0228	0.556
1 -ice		
20 -20'	0.0218	0.533
20 -ice	0.9442	23.85
18 -18'	0.0004	.01
18 -ice		
18' -ice	0.9390	23.73
20'-ice	0.9218	23.30

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 23.86°C

$R_{\text{main heater}} = R_m$ = 42.619 Ω

$\text{emf}_{\text{std resistor}} = V_{sr}$ = 12.285mv

$r_{\text{std resistor}} = r$ = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r}$ = 128.8 ma

Power

$Q = I^2 R_m$ = 0.707 watt

Avg.$\Delta T = \overline{\Delta T}$ = 0.479 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

$A = 10.549 \times 10^{-4}\ \text{cm}^{-1}$

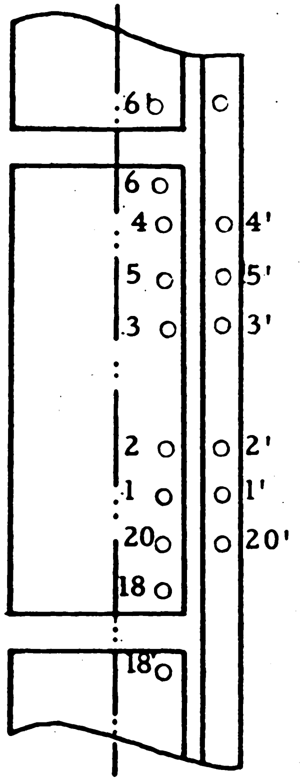
K = 15.6×10^{-4} $\frac{\text{watt}}{\text{cm-°C}}$

$T_{\text{reference}}$ = 23.62 °C

T_{bath} °C	$T_{\text{std cell}}$ °C
22.5	20 ± 1

Date 23-8-67 PM	1.0% Polystyrene MW_2 in Benzene

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
22.5	20 ± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.00	0.0
6' - ice	0.9394	23.72
6 - ice		
4 - 4'	0.0135	0.330
4 - ice	0.9386	23.70
5 - 5'	0.0141	0.350
5 - ice		
3 - 3'	0.0157	0.380
3 - ice		
4'-ice	0.9248	23.37
2 - 2'	0.0166	0.410
2 - ice		
1 - 1'	0.0191	0.465
1 - ice		
20 - 20'	0.0178	0.435
20 - ice	0.9371	23.65
18 - 18'	0.0005	0.01
18 - ice		
18' - ice	0.9327	23.56
20'-ice	0.9188	23.23

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 23.68 °C

$R_{main\ heater} = R_m$ = 42.620 Ω

$emf_{std\ resistor} = V_{sr}$ = 11.230 mv

$r_{std\ resistor}$ = r = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r}$ = 117.8 ma

Power

$Q = I^2 R_m$ = 0.591 watt

Avg. $\Delta T = \overline{\Delta T}$ = 0.395 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

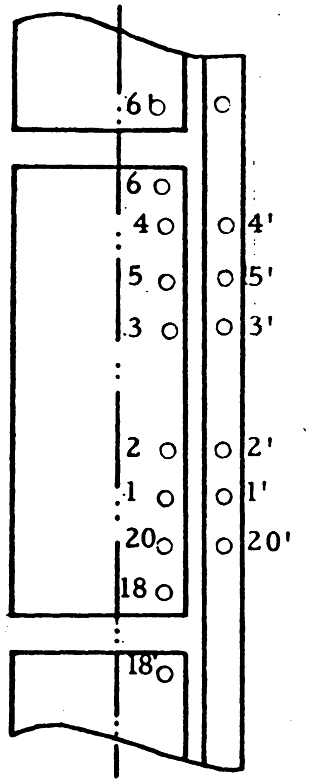
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K = 15.8 \times 10^{-4}\ \frac{watt}{cm\text{-}°C}$

$T_{reference}$ = 23.46 °C

Date 23-8-67 PM	1.0% Polystyrene MW_2 in Benzene

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
22.5	20± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.0013	0.028
6' - ice	0.9603	24.25
6 - ice		
4 - 4'	0.0204	0.499
4 - ice	0.9568	24.16
5 - 5'	0.0226	0.560
5 - ice		
3 - 3'	0.0242	0.590
3 - ice		
4'-ice	0.9360	23.65
2 -2'	0.0251	0.618
2 -ice		
1 -1'	0.0289	0.705
1 -ice		
20 -20'	0.0267	0.654
20 -ice	0.9548	24.11
18 -18'	0.0014	.036
18 -ice		
18' -ice	0.9477	23.93
20'-ice	0.9272	23.42

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 24.11 °C

$R_{main\ heater} = R_m = 42.619\ \Omega$

$emf_{std\ resistor} = V_{sr} = 13.771$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 144.3 ma

Power

$Q = I^2 R_m =$ 0.887 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.604 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

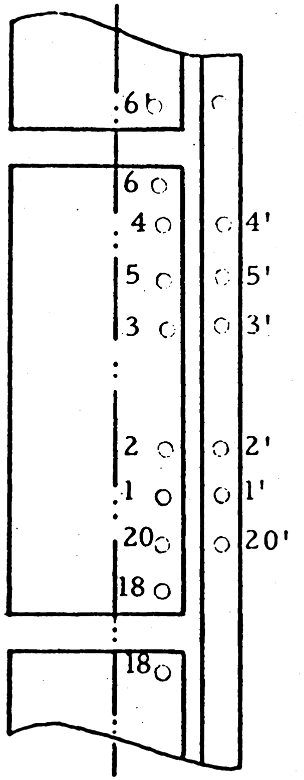
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K =$ 15.5×10^{-4} $\frac{watt}{cm\text{-}^{\circ}C}$

$T_{reference} =$ 23.81 °C

Date 11-8-67 PM	1.0% Polystyrens MW_2 in Benzene

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.0	20 ± 1

Thermo- couple Pair	emf mv	ΔT's, °C
6 - 6'	0.025×10^{-1}	0.053
6' - ice		
6 - ice		
4 - 4'	0.630×10^{-1}	1.54
4 - ice		
5 - 5'	0.666×10^{-1}	1.652
5 - ice	1.0662	26.90
3 - 3'	0.727×10^{-1}	1.78
3 - ice	1.0672	26.95
2 - 2'	0.735×10^{-1}	1.81
2 - ice	1.0654	26.87
1 - 1'	0.806×10^{-1}	1.97
1 - ice	1.0656	26.89
20 - 20'	0.796×10^{-1}	1.95
20 - ice		
18 - 18'	0.003×10^{-1}	0.009
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 26.90 °C

$R_{main\ heater} = R_m$ = 42.615 Ω

$emf_{std\ resistor} = V_{sr}$ = 23.737 mv

$r_{std\ resistor}$ = r = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r} =$ 248.9 ma

Power

$Q = I^2 R_m =$ 2.640 watt

$Avg.\Delta T = \overline{\Delta T} =$ 1.784 °C

Thermal Conductivity

$K = QA / T$

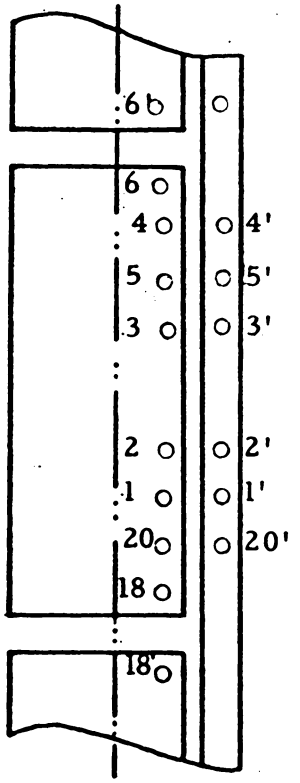
$A = 10.549 \times 10^{-4}$ cm^{-1}

$K = 1.561 \times 10^{-3} \frac{watt}{cm\text{-}°C}$

$T_{reference}$ = 26.0 °C

Date 20-8-67 PM	2.5% Polystyrene MW_2 in Benzene

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.0007	0.013
6' - ice	0.9800	24.75
6 - ice		
4 - 4'	0.0123	0.300
4 - ice	0.9779	24.70
5 - 5'	0.0139	0.345
5 - ice		
3 - 3'	0.0148	0.360
3 - ice		
4' - ice	0.9653	24.38
2 - 2'	0.0151	0.373
2 - ice		
1 - 1'	0.0177	0.430
1 - ice		
20 - 20'	0.0166	0.405
20 - ice	0.9772	24.68
18 - 18'	0.0010	0.026
18 - ice		
18' - ice	0.9737	24.60
20' - ice	0.9600	24.25

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 24.68 °C
$R_{\text{main heater}} = R_m$ = 42.618 Ω
$\text{emf}_{\text{std resistor}} = V_{sr}$ = 10.656 mv
$r_{\text{std resistor}} = r$ = 0.9538 Ω

Current
$I = \frac{V_{sr}}{r}$ = 111.8 ma

Power
$Q = I^2 R_m$ = 0.533 watt
Avg. $\Delta T = \overline{\Delta T}$ = 0.369 °C

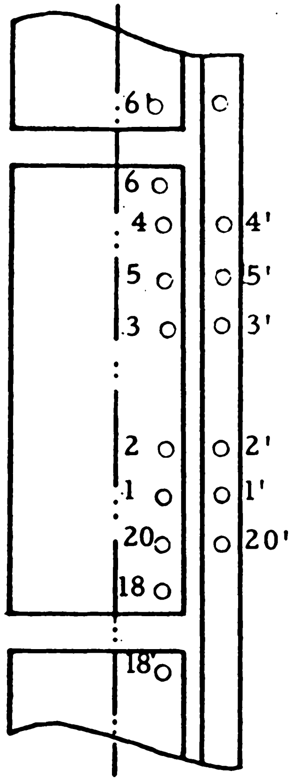
Thermal Conductivity
$K = QA / \overline{\Delta T}$
$A = 10.549 \times 10^{-4}$ cm^{-1}
K = 15.2×10^{-4} $\frac{\text{watt}}{\text{cm-}^{\circ}\text{C}}$

$T_{\text{reference}}$ = 24.50 °C

T_{bath} °C	$T_{\text{std cell}}$ °C
23.0	20 ± 1

Date 21-8-67 AM	2.5% Polystyrene MW_2 in Benzene	Thermocouple Pair	emf mv	ΔT's, °C	Heat Input to Measuring Cylinder

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.0015	0.033
6' - ice	1.0037	25.32
6 - ice		
4 - 4'	0.0224	0.548
4 - ice	0.9999	25.25
5 - 5'	0.0248	0.615
5 - ice		
3 - 3'	0.0264	0.643
3 - ice		
4'-ice	0.9781	24.70
2 -2'	0.0272	0.670
2 -ice		
1 -1'	0.0312	0.760
1 -ice		
20 -20'	0.0292	0.715
20 -ice	0.9991	25.22
18 -18'	0.00	0.00
18 -ice		
18' -ice	0.9945	25.11
20'-ice	0.9698	24.50

Avg. Copper Temp, T_c = 25.23 °C

$R_{\text{main heater}} = R_m$ = 42.618 Ω

$\text{emf}_{\text{std resistor}} = V_{sr}$ = 14.234 mv

$r_{\text{std resistor}} = r$ = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r} =$ 149.2 ma

Power

$Q = I^2 R_m =$ 0.949 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.659 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

$A = 10.549 \times 10^{-4}\ \text{cm}^{-1}$

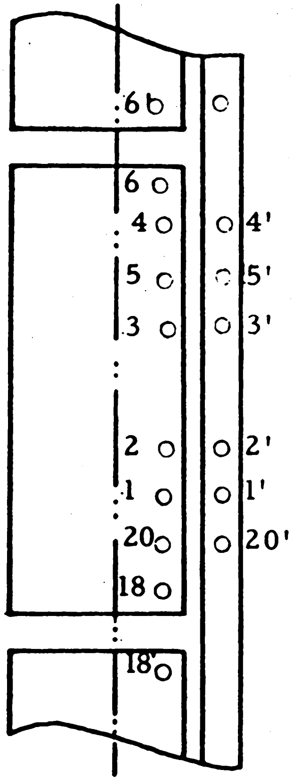
$K =$ 15.2×10^{-4} $\frac{\text{watt}}{\text{cm-°C}}$

$T_{\text{reference}}$ = 24.90 °C

T_{bath} °C	$T_{\text{std cell}}$ °C
23.5	20 ± 1

Date 21-8-67 AM	2.5% Polystyrene MW_2 in Benzene

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.0002	0.00
6' - ice		
6 - ice	1.0187	25.70
4 - 4'	0.0293	0.715
4 - ice	1.0156	25.63
5 - 5'	0.0321	0.798
5 - ice		
3 - 3'	0.0332	0.810
3 - ice		
4'-ice	0.9884	24.95
2 -2'	0.0345	0.850
2 -ice		
1 -1'	0.0394	0.960
1 -ice		
20 -20'	0.0370	0.907
20 -ice	1.0132	25.60
18 -18'	0.0015	0.038
18 -ice		
18' -ice	1.0051	25.38
20'-ice	0.9762	24.66

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 25.58 °C

$R_{\text{main heater}} = R_m = 42.617\ \Omega$

$\text{emf}_{\text{std resistor}} = V_{sr} = 16.188$ mv

$r_{\text{std resistor}} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 169.7 ma

Power

$Q = I^2 R_m =$ 1.227 watt

$\text{Avg.}\Delta T = \overline{\Delta T} =$ 0.840 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

$A = 10.549 \times 10^{-4}\ \text{cm}^{-1}$

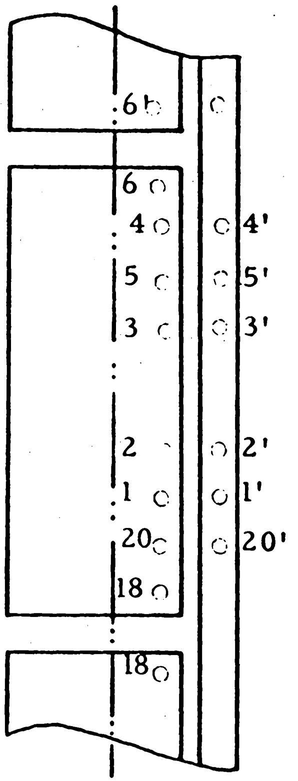
$K = 15.4 \times 10^{-4}\ \frac{\text{watt}}{\text{cm-°C}}$

$T_{\text{reference}} =$ 25.16 °C

T_{bath} °C	$T_{\text{std cell}}$ °C
23.5	20 ± 1

Date 14-8-67 **AM**	**10% Polystyrene** **MW_2 in Benzene**

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.004	0.005
6' - ice		
6 - ice	0.9958	25.15
4 - 4'	0.162×10^{-1}	0.395
4 - ice	0.9949	25.12
5 - 5'	0.190×10^{-1}	0.470
5 - ice	0.9960	25.15
3 - 3'	0.214×10^{-1}	0.52
3 - ice		
2 - 2'	0.220×10^{-1}	0.54
2 - ice	0.9944	25.10
1 - 1'	0.260×10^{-1}	0.634
1 - ice	0.9946	25.10
20 - 20'	0.244×10^{-1}	0.598
20 - ice	0.9932	25.07
18 - 18'	0.006	0.015
18 - ice	0.9895	25.0
18' - ice		

T_{bath} °C	$T_{std\ cell}$ °C
23.0	20 ± 1

Heat Input to Measuring Cylinder

Avg. Copper Temp, $T_c = 25.10$ °C

$R_{main\ heater} = R_m = 42.618\ \Omega$

$emf_{std\ resistor} = V_{sr} = 12.515$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 131.2 ma

Power

$Q = I^2 R_m =$ 0.7336 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.526 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

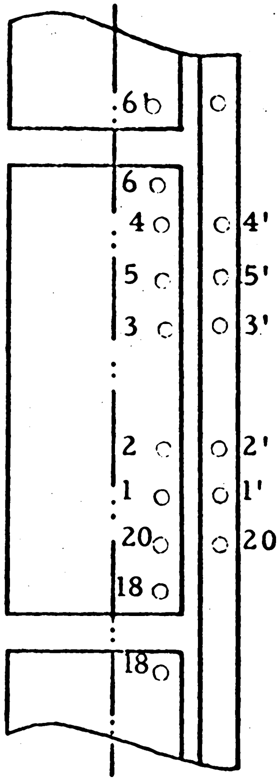
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K = 14.71 \times 10^{-4}\ \frac{watt}{cm\text{-}^{\circ}C}$

$T_{reference} = 24.84$ °C

Date 13-8-67 AM	10% Polystyrene MW_2 in Benzene

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.003×10^{-1}	0.003
6' - ice		
6 - ice	1.0134	25.6
4 - 4'	0.220×10^{-1}	0.54
4 - ice	1.0130	25.6
5 - 5'	0.260×10^{-1}	0.645
5 - ice	1.0132	25.6
3 - 3'	0.283×10^{-1}	0.69
3 - ice		
2 - 2'	0.295×10^{-1}	0.725
2 - ice	1.0120	25.55
1 - 1'	0.344×10^{-1}	0.84
1 - ice	1.0221	25.55
20 - 20'	0.320×10^{-1}	0.78
20 - ice	1.0120	25.55
18 - 18'	0.006×10^{-1}	0.015
18 - ice	1.0068	25.45
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, $T_c = 25.56^\circ C$

$R_{\text{main heater}} = R_m = 42.617\ \Omega$

$\text{emf}_{\text{std resistor}} = V_{sr} = 14.447$ mv

$r_{\text{std resistor}} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 151.5 ma

Power

$Q = I^2 R_m =$ 0.9782 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.703 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

$A = 10.549 \times 10^{-4}\ \text{cm}^{-1}$

$K = 14.68 \times 10^{-4} \frac{\text{watt}}{\text{cm-}^\circ C}$

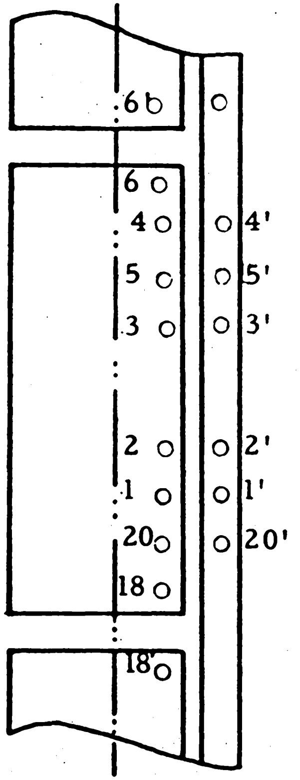
$T_{\text{reference}} = 25.21\ ^\circ C$

T_{bath} °C	$T_{\text{std cell}}$ °C
23.0	20 ± 1

Date 16-8-67 AM

15% Polystyrene MW_2 in Benzene

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.025×10^{-1}	0.06
6' - ice		
6 - ice	1.0639	26.85
4 - 4'	0.230×10^{-1}	0.56
4 - ice	1.0550	26.87
5 - 5'	0.271×10^{-1}	0.67
5 - ice		
3 - 3'	0.301×10^{-1}	0.735
3 - ice		
2 - 2'	0.310×10^{-1}	0.765
2 - ice		
1 - 1'	0.355×10^{-1}	0.865
1 - ice	1.0650	26.87
20 - 20'	0.340×10^{-1}	0.833
20 - ice	1.0630	26.82
18 - 18'	0.003×10^{-1}	0.008
18 - ice		
18' - ice		

T_{bath} °C	$T_{std\ cell}$ °C
23.0	20 ± 1

Heat Input to Measuring Cylinder

Avg. Copper Temp, $T_c = 26.85$°C

$R_{main\ heater} = R_m = 42.615\ \Omega$

$emf_{std\ resistor} = V_{sr} = 14.767$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 154.8 ma

Power

$Q = I^2 R_m =$ 1.0212 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.738 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

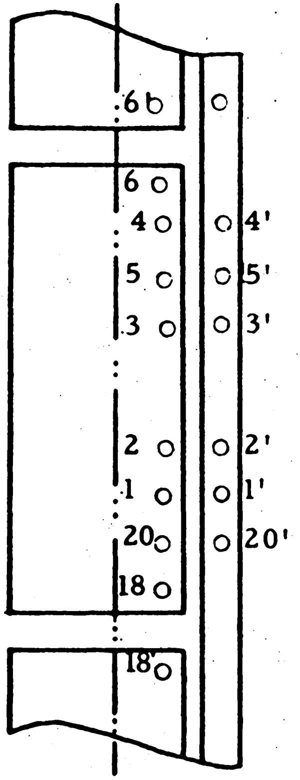
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K = 14.59 \times 10^{-4}\ \frac{watt}{cm\text{-}°C}$

$T_{reference} =$ 26.48 °C

Date 15-8-67 PM	15% Polystyrene MW_2 in Benzene

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.0	20 ± 1

Thermo-couple Pair	emf mv	ΔT's, °C
6 - 6'	0.020	0.04
6' - ice		
6 - ice	1.1006	27.76
4 - 4'	0.331x10^{-1}	0.81
4 - ice	1.1009	27.77
5 - 5'	0.380x10^{-1}	0.94
5 - ice		
3 - 3'	0.415x10^{-1}	1.015
3 - ice		
2 - 2'	0.425x10^{-1}	1.045
2 - ice	1.1008	27.76
1 - 1'	0.497x10^{-1}	1.21
1 - ice	1.1003	27.75
20 - 20'	0.460x10^{-1}	1.128
20 - ice	1.0982	27.72
18 - 18'	0.004x10^{-1}	0.013
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 27.75°C

$R_{\text{main heater}} = R_m$ = 42.614 Ω

$\text{emf}_{\text{std resistor}} = V_{sr}$ = 17.390 mv

$r_{\text{std resistor}} = r$ = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r}$ = 182.3 ma

Power

$Q = I^2 R_m$ = 1.416 watt

Avg.ΔT = $\overline{\Delta T}$ = 1.025 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

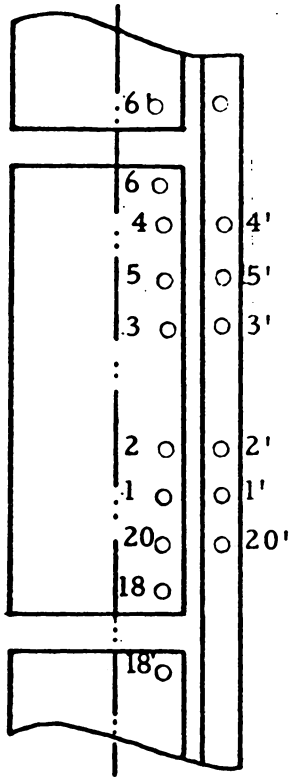
$A = 10.549 \times 10^{-4}\ \text{cm}^{-1}$

$K = 14.58\text{x}10^{-4} \frac{\text{watt}}{\text{cm-}^\circ\text{C}}$

$T_{\text{reference}}$ = 27.24 °C

Date 16-8-67 AM	15% Polystyrene MW₂ in Benzene

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.010×10^{-1}	0.02
6' - ice		
6 - ice	1.1460	28.90
4 - 4'	0.413×10^{-1}	1.008
4 - ice		
5 - 5'	0.463×10^{-1}	1.165
5 - ice		
3 - 3'	0.527×10^{-1}	1.288
3 - ice		
2 - 2'	0.545×10^{-1}	1.34
2 - ice	1.1410	28.77
1 - 1'	0.635×10^{-1}	1.55
1 - ice	1.1410	28.77
20 - 20'	0.590×10^{-1}	1.447
20 - ice	1.13788	28.70
18 - 18'	0.019×10^{-1}	0.045
18 - ice		
18' - ice		

T_{bath} °C	$T_{std\ cell}$ °C
23.5	20 ± 1

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 28.79 °C

$R_{main\ heater} = R_m = 42.613\ \Omega$

$emf_{std\ resistor} = V_{sr} = 19.410$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 203.5 ma

Power

$Q = I^2 R_m =$ 1.765 watt

Avg. $\Delta T = \overline{\Delta T} =$ 1.30 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

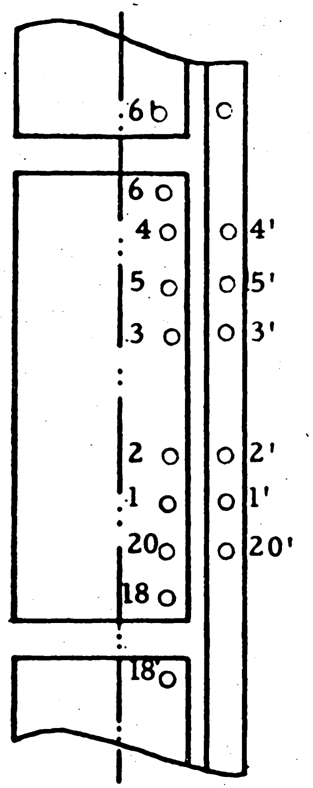
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K = 14.32 \times 10^{-4}\ \frac{watt}{cm\text{-}°C}$

$T_{reference} = 28.14$ °C

Date	0.1% Polystyrene
21-8-67	MW_3 in Benzene

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.5	20 ± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.020×10^{-1}	0.040
6' - ice		
6 - ice	0.9650	24.27
4 - 4'	0.117×10^{-1}	0.285
4 - ice	0.9634	24.32
5 - 5'	0.132×10^{-1}	0.328
5 - ice		
3 - 3'	0.136×10^{-1}	0.33
3 - ice		
2 - 2'	0.145×10^{-1}	0.358
2 - ice	0.9636	24.32
1 - 1'	0.164×10^{-1}	0.40
1 - ice		
20 - 20'	0.155×10^{-1}	0.38
20 - ice	0.9618	24.30
18 - 18'	0.012×10^{-1}	0.03
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, $T_c = 24.33\ ^{\circ}C$

$R_{main\ heater} = R_m = 42.619\ \Omega$

$emf_{std\ resistor} = V_{sr} = 10.458$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 109.6 ma

Power

$Q = I^2 R_m =$ 0.5119 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.347 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

$A = 10.549 \times 10^{-4}\ cm^{-1}$

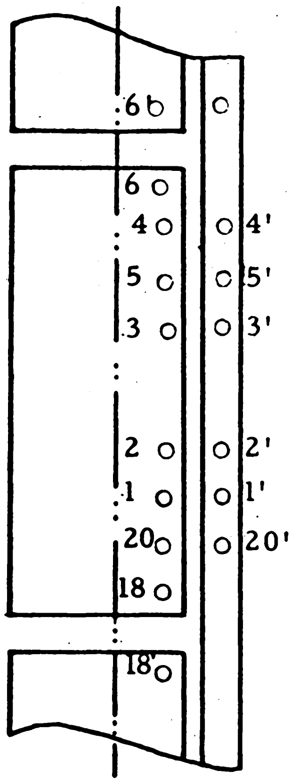
$K = 15.56 \times 10^{-4}\ \frac{watt}{cm\text{-}^{\circ}C}$

$T_{reference} = 24.16\ ^{\circ}C$

Date
21-8-67
PM

0.1% Polystyrene
MW_3 in Benzene

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.010×10^{-1}	0.02
6' - ice		
6 - ice	0.9608	24.27
4 - 4'	0.135×10^{-1}	0.33
4 - ice	0.9609	24.27
5 - 5'	0.145×10^{-1}	0.36
5 - ice		
3 - 3'	0.148×10^{-1}	0.36
3 - ice		
2 - 2'	0.155×10^{-1}	0.383
2 - ice		
1 - 1'	0.177×10^{-1}	0.433
1 - ice	0.9605	20.27
20 - 20'	0.9600	24.25
20 - ice	0.165×10^{-1}	0.403
18 - 18'	0.008×10^{-1}	0.02
18 - ice		
18' - ice		

T_{bath} °C	$T_{std\ cell}$ °C
23.5	20 ± 1

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 24.27°C

$R_{main\ heater} = R_m$ = 42.619 Ω

$emf_{std\ resistor} = V_{sr}$ = 10.970 mv

$r_{std\ resistor} = r$ = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r} =$ 115.0 ma

Power

$Q = I^2 R_m =$ 0.5638 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.378 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

$A = 10.549 \times 10^{-4}$ cm^{-1}

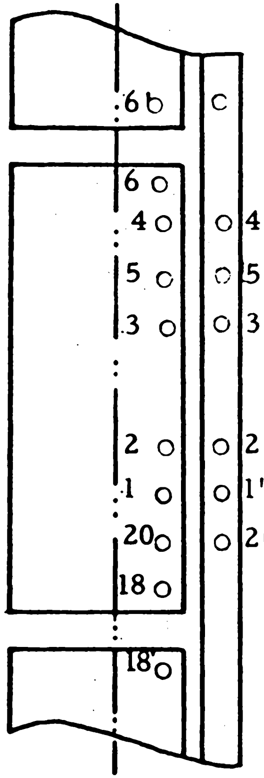
$K = 15.74 \times 10^{-4} \frac{watt}{cm\text{-}°C}$

$T_{reference}$ = 24.08 °C

Date 21-8-67 PM

0.1% Polystyrene MW_3 in Benzene

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.5	20± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.005×10^{-1}	0.008
6' - ice		
6 - ice	0.9690	24.47
4 - 4'	0.151×10^{-1}	0.37
4 - ice	0.9685	24.46
5 - 5'	0.168×10^{-1}	0.418
5 - ice		
3 - 3'	0.176×10^{-1}	0.428
3 - ice		
2 - 2'	0.182×10^{-1}	0.448
2 - ice	0.9680	24.45
1 - 1'	0.207×10^{-1}	0.505
1 - ice		
20 - 20'	0.194×10^{-1}	0.475
20 - ice	0.9665	24.40
18 - 18'	0.015×10^{-1}	0.04
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, $T_c = 24.45$°C

$R_{main\ heater} = R_m = 42.619\ \Omega$

$emf_{std\ resistor} = V_{sr} = 11.915$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 124.9 ma

Power

$Q = I^2 R_m =$ 0.6649 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.441 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

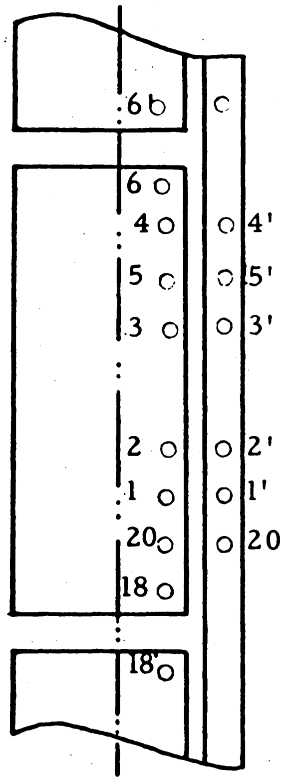
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K = 15.90 \times 10^{-4}\ \frac{watt}{cm\text{-}^{\circ}C}$

$T_{reference} =$ 24.23 °C

Date	
22-8-67 PM	1.0% Polystyrene MW3 in Benzene

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.5	20 ± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.004×10^{-1}	0.005
6' - ice		
6 - ice	0.9865	24.92
4 - 4'	0.147×10^{-1}	0.36
4 - ice	0.9855	24.90
5 - 5'	0.165×10^{-1}	0.41
5 - ice		
3 - 3'	0.181×10^{-1}	0.44
3 - ice		
2 - 2'	0.192×10^{-1}	0.475
2 - ice	0.9847	24.87
1 - 1'	0.224×10^{-1}	0.535
1 - ice		
20 - 20'	0.209×10^{-1}	0.510
20 - ice	0.9840	24.84
18 - 18'	0.006×10^{-1}	0.017
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 24.88°C

$R_{main\ heater} = R_m$ = 42.618 Ω

$emf_{std\ resistor} = V_{sr}$ = 11.784 mv

$r_{std\ resistor}$ = r = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r} =$ 123.5 ma

Power

$Q = I^2 R_m =$ 0.6499 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.455 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

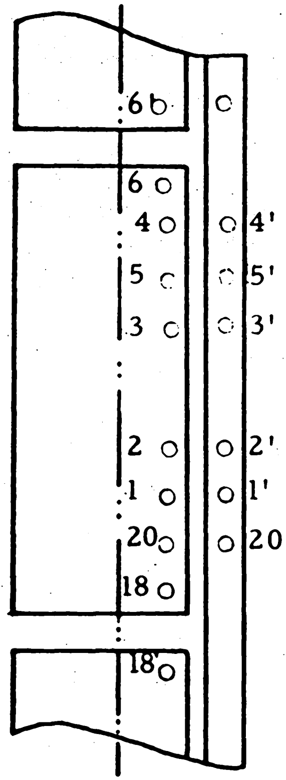
$A = 10.549 \times 10^{-4}$ cm^{-1}

$K = 15.07 \times 10^{-4}$ $\frac{watt}{cm\text{-}°C}$

$T_{reference} =$ 24.65 °C

Date	
22-8-67 PM	1.0% Polystyrene MW_3 in Benzene

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.5	20± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.015×10^{-1}	0.03
6'- ice		
6 - ice	0.9810	24.77
4 - 4'	0.126×10^{-1}	0.308
4 - ice	0.9795	24.72
5 - 5'	0.142×10^{-1}	0.353
5 - ice		
3 - 3'	0.155×10^{-1}	0.375
3 - ice		
2 -2'	0.164×10^{-1}	0.405
2 -ice	0.9790	24.72
1 -1'	0.190×10^{-1}	0.465
1 -ice		
20 -20'	0.176×10^{-1}	0.43
20 -ice	0.9784	24.70
18 -18'	0.002×10^{-1}	0.008
18 -ice		
18' -ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, $T_c = 24.73°C$

$R_{main\ heater} = R_m = 42.618\ \Omega$

$emf_{std\ resistor} = V_{sr} = 10.897$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 114.2 ma

Power

$Q = I^2 R_m =$ 0.5557 watt

Avg.$\Delta T = \overline{\Delta T} =$ 0.389 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

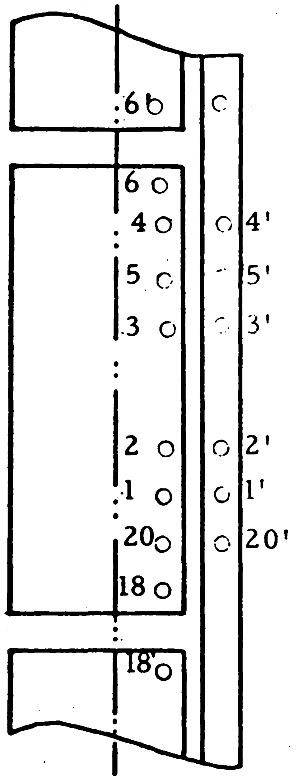
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K =$ 15.07×10^{-4} $\frac{watt}{cm\text{-}°C}$

$T_{reference} =$ 24.54 °C

Date 22-8-67 PM	1.0% Polystyrene MW_3 in Benzene

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.5	20± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.017×10^{-1}	0.038
6' - ice		
6 - ice	0.9976	25.17
4 - 4'	0.189×10^{-1}	0.463
4 - ice	0.9965	25.15
5 - 5'	0.210×10^{-1}	0.523
5 - ice		
3 - 3'	0.230×10^{-1}	0.56
3 - ice		
2' - ice	0.9706	24.54
2 - 2'	0.242×10^{-1}	0.598
2 - ice		
1 - 1'	0.279×10^{-1}	0.680
1 - ice		
20 - 20'	0.261×10^{-1}	0.640
20 - ice	0.9935	25.10
18 - 18'	0.006×10^{-1}	0.017
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, $T_c = 25.12$ °C

$R_{main\ heater} = R_m = 42.618\ \Omega$

$emf_{std\ resistor} = V_{sr} = 13.310$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 139.5 ma

Power

$Q = I^2 R_m =$ 0.8293 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.577 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

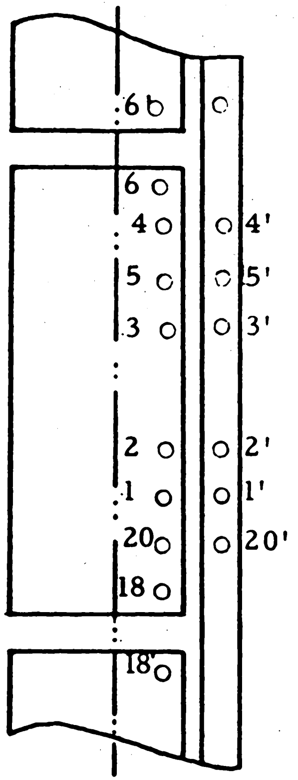
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K = 15.16 \times 10^{-4} \frac{watt}{cm\text{-}°C}$

$T_{reference} = 24.83$ °C

Date 25-8-67 PM	5% Polystyrene MW_3 in Benzene

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.010	0.02
6' - ice		
6 - ice	0.9820	24.80
4 - 4'	0.153	0.375
4 - ice	0.9850	24.90
5 - 5'		
5 - ice		
3 - 3'	0.190	0.463
3 - ice		
2 - 2'	0.196	0.483
2 - ice	0.9850	24.90
1 - 1'	0.235	0.573
1 - ice		
20 - 20'	0.216	0.528
20 - ice	0.9781	24.70
18 - 18'	0.009	0.003
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 24.83°C

$R_{\text{main heater}} = R_m$ = 42.618 Ω

$\text{emf}_{\text{std resistor}} = V_{sr}$ = 11.78 mv

$r_{\text{std resistor}} = r$ = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r} =$ 123.5 ma

Power

$Q = I^2 R_m =$ 0.6499 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.484 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

$A = 10.549 \times 10^{-4}\ \text{cm}^{-1}$

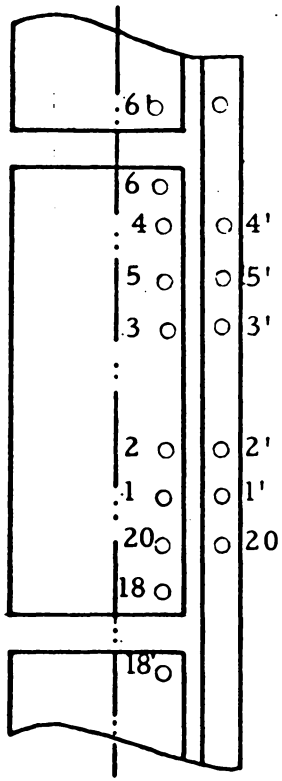
$K = 14.17 \times 10^{-4} \frac{\text{watt}}{\text{cm-°C}}$

$T_{\text{reference}}$ = 24.6 °C

T_{bath} °C	$T_{\text{std cell}}$ °C
23.0	20 ± 1

Date 25-8-67 PM	5% Polystyrene MW_3 in Benzene

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.0	20± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.007×10^{-1}	0.015
6' - ice	0.10195	25.75
6 - ice	0.10180	25.70
4 - 4'	0.264×10^{-1}	0.645
4 - ice	0.10142	25.60
5 - 5'		
5 - ice	0.10145	25.62
3 - 3'	0.310×10^{-1}	0.755
3 - ice		
2 - 2'	0.324×10^{-1}	0.798
2 - ice	1.0134	25.58
1 - 1'	0.370×10^{-1}	0.903
1 - ice		
20 - 20'	0.346×10^{-1}	0.848
20 - ice	1.0120	25.55
18 - 18'	0.005×10^{-1}	0.015
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 25.63°C

$R_{main\ heater} = R_m$ = 42.617 Ω

$emf_{std\ resistor} = V_{sr}$ = 15.080 mv

$r_{std\ resistor}$ = r = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r} =$ 0.1581 ma

Power

$Q = I^2 R_m =$ 1.0653 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.790 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

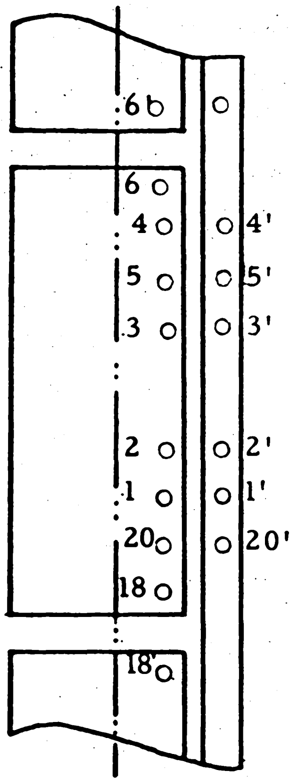
$A = 10.549 \times 10^{-4}$ cm^{-1}

$K = 14.23 \times 10^{-4} \frac{watt}{cm\text{-}^{\circ}C}$

$T_{reference}$ = 25.23 °C

Date	5% Polystyrene MW_3 in Benzene

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
23.0	20± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.000	0.000
6' - ice		
6 - ice	0.10465	26.40
4 - 4'	0.355×10^{-1}	0.868
4 - ice	0.10415	26.27
5 - 5'		
5 - ice	0.10415	26.27
3 - 3'	0.416×10^{-1}	1.015
3 - ice		
2 - 2'	0.428×10^{-1}	1.053
2 - ice	0.10405	26.25
1 - 1'	0.493×10^{-1}	1.203
1 - ice		
20 - 20'	0.460×10^{-1}	1.128
20 - ice	0.10390	26.21
18 - 18'	0.006×10^{-1}	0.017
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 26.28°C

$R_{main\ heater} = R_m = 42.616\ \Omega$

$emf_{std\ resistor} = V_{sr} = 17.51$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 183.6 ma

Power

$Q = I^2 R_m =$ 1.4366 watt

Avg.$\Delta T = \overline{\Delta T} =$ 1.053 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

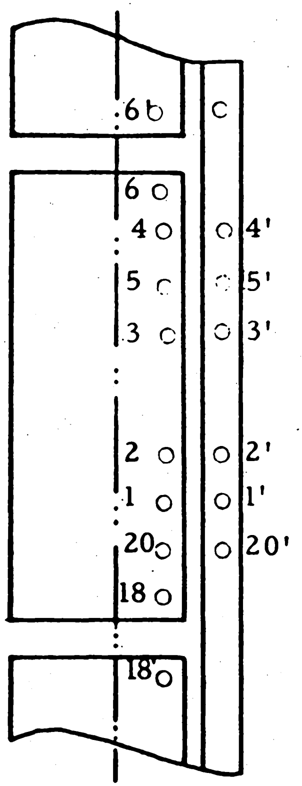
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K = 14.39 \times 10^{-4} \frac{watt}{cm\text{-}°C}$

$T_{reference} =$ 25.75 °C

Date 23-8-67 AM	10.0% Polystyrene MW_3 in Benzene

Thermocouple Location



T_{bath} °C	$T_{std\ cell}$ °C
	20 ± 1

Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.012×10^{-1}	0.025
6' - ice		
6 - ice	1.0620	26.80
4 - 4'	0.230×10^{-1}	0.563
4 - ice	1.0560	26.65
5 - 5'	0.263×10^{-1}	0.653
5 - ice		
3 - 3'	0.290×10^{-1}	0.708
3 - ice		
2 - 2'	0.290×10^{-1}	0.715
2 - ice	1.0555	26.63
1 - 1'	0.345×10^{-1}	0.843
1 - ice	1.0553	26.63
20 - 20'	0.320×10^{-1}	0.783
20 - ice	1.0537	26.60
18 - 18'	0.005×10^{-1}	0.015
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, $T_c = 26.67$ °C

$R_{main\ heater} = R_m = 42.616\ \Omega$

$emf_{std\ resistor} = V_{sr} = 14.220$ mv

$r_{std\ resistor} = r = 0.9538\ \Omega$

Current

$I = \dfrac{V_{sr}}{r} =$ 149.1 ma

Power

$Q = I^2 R_m =$ 0.9474 watt

Avg. $\Delta T = \overline{\Delta T} =$ 0.711 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

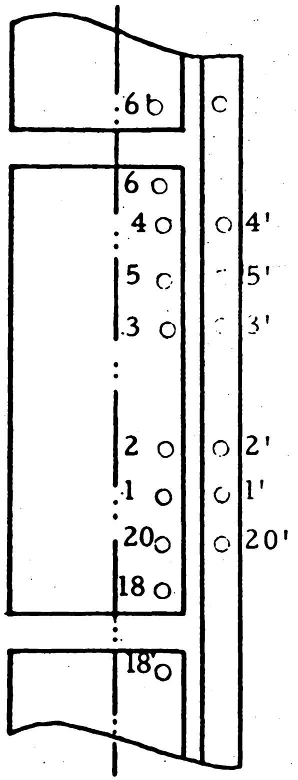
$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K = 14.06 \times 10^{-4}\ \dfrac{watt}{cm\text{-}^{\circ}C}$

$T_{reference} = 26.32$ °C

Date 23-8-67 AM	10.0% Polystyrene MW_3 in Benzene

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.025×10^{-1}	0.058
6' - ice		
6 - ice	1.0950	27.63
4 - 4'	0.315×10^{-1}	0.77
4 - ice	1.0870	27.45
5 - 5'	0.357×10^{-1}	0.888
5 - ice		
3 - 3'	0.393×10^{-1}	0.96
3 - ice		
2 - 2'	0.398×10^{-1}	0.98
2 - ice	1.0868	27.45
1 - 1'	0.468×10^{-1}	1.143
1 - ice		
20 - 20'	0.432×10^{-1}	1.058
20 - ice	1.0845	27.37
18 - 18'	0.008×10^{-1}	0.02
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, $T_c = 27.48\,^\circ C$

$R_{\text{main heater}} = R_m = 42.615\ \Omega$

$\text{emf}_{\text{std resistor}} = V_{sr} = 16.555\ mv$

$r_{\text{std resistor}} = r = 0.9538\ \Omega$

Current

$I = \frac{V_{sr}}{r} =$ 173.6 ma

Power

$Q = I^2 R_m =$ 1.2844 watt

$\text{Avg.}\Delta T = \overline{\Delta T} =$ 0.966 °C

Thermal Conductivity

$K = QA \,/\, \overline{\Delta T}$

$A = 10.549 \times 10^{-4}\ cm^{-1}$

$K = 14.03 \times 10^{-4}\ \frac{watt}{cm\text{-}^\circ C}$

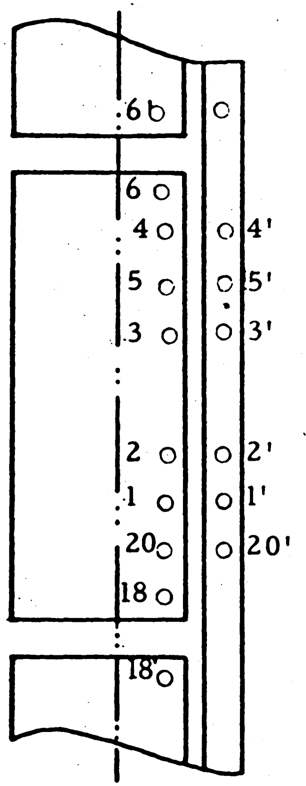
$T_{\text{reference}} = 27.00\,^\circ C$

T_{bath} °C	$T_{\text{std cell}}$ °C
23.5	20 ± 1

Date 23-8-67 AM

10.0% Polystyrene MW_3 in Benzene

Thermocouple Location



Thermocouple Pair	emf mv	ΔT's, °C
6 - 6'	0.006×10^{-1}	0.01
6' - ice		
6 - ice	1.2415	31.5
4 - 4'	0.770×10^{-1}	1.881
4 - ice	1.2190	30.6
5 - 5'	0.883×10^{-1}	2.192
5 - ice		
3 - 3'	0.955×10^{-1}	2.337
3 - ice		
2 - 2'	0.974×10^{-1}	2.395
2 - ice	1.2190	30.6
1 - 1'	1.134×10^{-1}	2.767
1 - ice	1.2177	30.6
20 - 20'	1.048×10^{-1}	2.570
20 - ice	1.2150	30.4
18 - 18'	0.005×10^{-1}	.013
18 - ice		
18' - ice		

Heat Input to Measuring Cylinder

Avg. Copper Temp, T_c = 30.8°C

$R_{\text{main heater}} = R_m$ = 42.610 Ω

$\text{emf}_{\text{std resistor}} = V_{sr}$ = 25.804 mv

$r_{\text{std resistor}} = r$ = 0.9538 Ω

Current

$I = \frac{V_{sr}}{r}$ = 270.5 ma

Power

$Q = I^2 R_m$ = 3.1178 watt

Avg. $\Delta T = \overline{\Delta T}$ = 2.357 °C

Thermal Conductivity

$K = QA / \overline{\Delta T}$

$A = 10.549 \times 10^{-4}\ \text{cm}^{-1}$

$K = 13.95 \times 10^{-4} \frac{\text{watt}}{\text{cm-°C}}$

$T_{\text{reference}}$ = 29.6 °C

T_{bath} °C	$T_{\text{std cell}}$ °C
22.6	20 ± 1

APPENDIX H

MATERIALS AND APPARATUS

MATERIALS

This section contains the uses and specifications for the various materials used in this investigation.

Acetone.- Technical grade. Used as washing and cleaning solution for glassware and thermal conductivity cell.

Benzene.- Reagent grade. Used to prepare solutions for thermal conductivity measurements.

Benzene.- Purified grade. Used to rinse thermal conductivity cell, viscometers, and so forth.

Cleaning solution.- Chromic acid in sulfuric acid. Constituents used to clean glassware.

Distilled water.- Used as bath water and to check performance of thermal conductivity cell.

Ethylene glycol.- Purified grade. Used to check performance of thermal conductivity cell.

Methanol.- Certified grade. Used to prepare viscosity solutions in so-called theta-solvent.

Polystyrene.- Industrial (styron) samples at three molecular weights. Obtained from Dow Chemical Co., Midland, Mich. Used to prepare solutions for thermal conductivity measurements.

Thermocouple wire.- Iron, copper, and Constantan 30-guage thermocouple wire. Used to make thermocouples and as resistance wire for heaters.

Toluene.- Certified grade. Used in the cleaning of thermal conductivity cell.

Wiring insulation.- Thermofit RNF, a type of heat-shrink polyolefin tubing. Obtained from Polyscientific Company, Division of Litton Industries, Blacksburg, Virginia. Used as outer sheathing for thermocouples and heater wires.

APPARATUS

The following section is a listing of the apparatus used in this investigation.

Balance.- Analytical, 100-gram capacity, 0.0001-gram increment. Model No. 220-D, Serial No. M-13860. Obtained from Voland and Sons, Inc., New Rochelle, New York. Used for weighing polystyrene for thermal conductivity solutions and for density and viscosity weighings.

Beckman thermometers.- Graduated in 1/100° C, range approximately 0 to 200° C. No. 2936, distributed by Eimes and Amend, New York. Used to calibrate differential thermocouples for thermal conductivity cell.

Beckman-type thermometer.- Graduated in 1/100° C, range approximately 0 to 100° C. Distributed by Fisher Scientific Company, Pittsburgh, Pennsylvania. Used to calibrate differential thermocouples for thermal conductivity cell.

Bridge.- Kelvin-type bridge, range 0 to 10.1 ohms in five ranges with overall limit of error 0.1 percent. Serial No. 5706, obtained from the Rubicon Division of Minneapolis-Honeywell Regulator Company, Philadelphia, Pennsylvania. Used to calibrate standard resistor for current measurement.

Bridge.- Wheatstone-type portable bridge, range 1 ohm to 10.0 megohm in seven ranges with overall limit of error 0.1 percent. Catalog No. 1071, obtained from the Rubicon Division of Minneapolis-Honeywell Regulator Company, Philadelphia, Pennsylvania. Used to calibrate heater resistor over temperature range, 20 to 30° C.

Cooling system.- Consisting of water cooling bath, agitators, pumps, auxiliary bath with thermo regulator capable of maintaining ± 0.01° C. Model M-1, modified to include cooling coil. Obtained from Cannon Instrument Company, Boalsburg, Pennsylvania. Used for temperature control during thermocouple calibration, viscosity measurements, and thermal conductivity measurements.

Electrical support equipment.- Various fixed and variable resistors, switches, ohmeters, voltmeters, appropriate for controlling and indicating power input to thermal conductivity cell heaters.

Galvanometer.- Spotlight, Series 3400 D.C., Serial No. 117034, sensitivity 0.001 μamp per millimeter, dual 100 mm scale, subdivided 0-100 and 50 - 0 -50. Obtained from the Rubicon Division of Minneapolis-Honeywell Regulator Company, Philadelphia, Pennsylvania. Used in conjunction with potentiometer and the two bridges as a null detector.

Glass thermometers.- Several T range -2 to 51° C by 0.1° C increments. Used to indicate bath temperatures for thermal conductivity and viscosity measurements.

Glassware.- Various beakers, vials, Dewars, bottles, flasks, pipettes, burettes, and so forth. Used to prepare viscosity and thermal conductivity samples, and so forth.

Magnetic stirrer.- Two, Catalog No. 14-411-2, 115 volts, 50 to 60 cycle, 0.2 amp., manufactured by Fisher Scientific Company. Used to stir solutions for thermal conductivity tests.

Osmometer.- High-speed membrane osmometer, manufactured by Mechrolab Division of Hewlett-packard, Inc. Measurements made at NASA Langley Research Center, Hampton, Virginia. Used to measure number average molecular weights of polystyrene samples.

Potentiometer.- Range 0 to 1.6 volts in three ranges with overall limit of error of 0.015 percent of reading, Serial No. 52218. Obtained from the Rubicon Division of Minneapolis-Honeywell Regulator Company, Philadelphia, Pennsylvania. Used for all thermocouple readings and to measure potential drop across the standard resistor.

Power supply.- D.C., Sorenson, Model QM21.0 - 0.71, input 115 volts, 0.5 amps at 50/400 cycles; output 21 D.C. volts, 0.71 amps. Serial No. 7107. Used as power supply to main heater of thermal conductivity cell.

Power supply.- D.C., Sorenson, Model QM3.0 - 0.64, input 115 volts, 0.5 volt, 0.5 amp at 50/400 cycles; output 0.3 D.C. volt at 0.71 amp, Serial No. 5248. Used as a power supply to bottom guard heater of thermal conductivity cell.

Power supply.- D.C., Sorenson, Model QM3.0 - 1.3, input 115 volts, 0.5 amp at 500 cycles; output 3.0 D.C. volts at 1.3 amps, Serial No. 5237. Used as power supply to bottom guard heater of thermal conductivity cell.

Power supply.- D.C. Model 850, Programmable Power Supply; input 115 volts, output 0-15 volts, 0-1 amp, manufactured by Harrison Laboratories, Inc. Used as power supply to top guard heater of thermal conductivity cell.

Pyconometer.- Nominal 10.0 ml, Kimax Pyconometer, side arm with cap. Used to measure density of solvents for thermal conductivity tests.

Resistor.- Copper wire wound resistor, nominal 0.1 ohm, calibrated. Used to measure current to thermal conductivity cell main heater.

Shunt.- 0.1000 ohm, Leeds and Northrup Shunt, 0.04 percent accuracy. Used to check Kelvin Bridge when calibrating standard resistor.

Thermocouples.- Made of 30-guage Copper-Constantan wire, Catalog No. 9B188, insulated with silicone-impregnated asbestos on each conductor and silicone-impregnated fiber glass overall, manufactured by Honeywell, Inc. Calibrated and used as differential thermocouples in thermal conductivity cell.

Standard cell.- Eppley Model No. 2776, calibrated as 1.01923 volts. Used in conjunction with potentiometers.

Thermocouple selector switch.- Lewis Engineering Company, low emf, silver contact thermocouple selector switch, 20-position. Used to select thermocouples read with potentiometer.

Thermal conductivity cell.- Designed and constructed at VPI for this experiment (see detailed drawings and description elsewhere in text).

Timers.- Precision time-it timers, in seconds and tenths, 115 volts, 60 cycles, 5 watts. Used to time viscosity tests.

Transformers.- Sola constant voltage transformer, Catalog No. 30806, single phase, 120-volt, 60-cycle input; 115-volt, 1.04-amp output, produced by Sola Electric Company, Chicago, Illinois. Used to stabilize input to power supplies.

Viscometers.- Cannon-Fenske routine-type visconnectors, various calibrated by Epps (7). Used to determine limiting viscosity number of polystyrene in solvents and the apparent viscosity of polymer solutions.

Voltage stabilizer.- Serial No. 6,487, input 95-130 volts, 1.25 amps, 60 cycles, single phase, output 115 volts, 60 watts, produced by Raytheon Manufacturing Company, Waltham, Massachusetts. Used to stabilize input to power supplies.

MOLECULAR WEIGHT AND CONCENTRATION DEPENDENCE OF THE THERMAL CONDUCTIVITY OF POLYSTYRENE IN BENZENE

By

Lionel B. Epps, Jr.

ABSTRACT

The thermal conductivities of polystyrene in benzene solutions at concentrations of 0.1 to 15 weight percent were measured at 25° C and atmospheric pressure. Osmotic pressure measurements and information supplied by the manufacturer indicated number average molecular weights $\left(\overline{M}_N\right)$ of 21,000, 264,000, and 660,000 for the three polystyrene polymers studied. The following equation was obtained by regression analysis of the results and predicts the measured thermal conductivity within ± 2 percent in the range of variables studied.

$$K = 0.1088 - 0.1311\ C + 0.57629\ C^2 - 6.40 \times 10^{-5} \left(\overline{M}_N \times 10^{-5}\right)^2$$
$$- 4.2 \times 10^{-3}\ C\left(\overline{M}_N \times 10^{-5}\right)$$

where: K = thermal conductivity of solution, Btu/hr-ft-°F

C = weight fraction polymer

$\overline{M}_N$ = number average molecular weight

The conductivities were measured in a steady-state concentric cylinder apparatus developed for measuring the thermal conductivity of viscous liquids. The annular gap was 0.052 inches and guard heaters were employed to minimize end losses and distortion of the steady-state

temperature distribution at the ends. The apparatus was calibrated with three liquids of known thermal conductivity, water, cyclohexanol and ethylene glycol. The calibration factor was found to be constant to within experimental error (± 3 percent) over the range of measurements.