THE THERMAL CONDUCTIVITY OF BUTYL RUBBER
AT LOW TEMPERATURES.

by

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A thesis submitted in partial fulfilment of the requirements for the degree of Master of Arts in the Department of Physics.

The University of British Columbia
September - 1947

Approved
Sept. 27th, 1947.
ACKNOWLEDGMENT

The author is pleased to express his gratitude to Dr. Otto Bluh, under whose able supervision this work was completed.

He also wishes to acknowledge the contributions of the Research Division of the Polymer Corporation who provided the samples, of Messrs. F. Lang and D. S. Carter who assisted in building the apparatus, and of Mr. R.S. Codrington who did the photography for this thesis.

The research was carried out with the aid of a grant from the Associate Committee on Synthetic Rubber Research of the National Research Council of Canada.
# INDEX

## I. Introduction:
- Definition of thermal conductivity and fundamental equations. .................................................... 1
- Thermal conductivity of anisotropic media. ......................................................................................... 3
- Thermal conductivity as a function of temperature. ........................................................................... 3
- Methods of measuring thermal conductivity. ................................................................................. 8
- Previous measurement of the thermal conductivity of rubber. .................................................. 14

## II. Apparatus:
- Conductivity measuring unit. ............................................................................................................. 15
- The heating circuits. ............................................................................................................................ 17
- The cryostat and cooling system. ....................................................................................................... 18
- The temperature measuring circuits. .................................................................................................. 18
- The control circuits. ............................................................................................................................ 19

## III. Experimental Procedure:
- Thermocouple calibration. .................................................................................................................. 22
- Method of taking readings. ............................................................................................................... 23
- Method of analysing data. .................................................................................................................. 25
- Guard block erection. ........................................................................................................................ 26
- Measurement of power. ...................................................................................................................... 27
- Measurement of thickness. ................................................................................................................. 29
- Evaluation of Apparatus.
  1. Effect of temperature variation over the cold plate. .............................................................. 30
  2. Effect of variation of temperature with time. ............................................................................. 31

## IV. Results:
- The sample. ................................................................................................................................. 35
- Readings taken. ............................................................................................................................... 36
- Probable error. ............................................................................................................................... 36
- Discussion of results. ....................................................................................................................... 38
# PLATES

**Pictures**

<table>
<thead>
<tr>
<th>Plate</th>
<th>Description</th>
<th>Facing Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>A front view of the apparatus.</td>
<td>14</td>
</tr>
<tr>
<td>III.</td>
<td>A rear view of the apparatus.</td>
<td>14</td>
</tr>
<tr>
<td>III.</td>
<td>A close-up of the measuring unit.</td>
<td>15</td>
</tr>
</tbody>
</table>

**Diagrams**

<table>
<thead>
<tr>
<th>Diagram</th>
<th>Description</th>
<th>Facing Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV.</td>
<td>The measuring unit.</td>
<td>16</td>
</tr>
<tr>
<td>V.</td>
<td>The heater control circuit.</td>
<td>17</td>
</tr>
<tr>
<td>VI.</td>
<td>The Thermocouple circuit.</td>
<td>18</td>
</tr>
<tr>
<td>VII.</td>
<td>The A. C. automatic control.</td>
<td>19</td>
</tr>
<tr>
<td>VIII.</td>
<td>The D. C. automatic control.</td>
<td>20</td>
</tr>
<tr>
<td>IX.</td>
<td>The control circuit potentiometer.</td>
<td>21.</td>
</tr>
</tbody>
</table>

**Graphs**

<table>
<thead>
<tr>
<th>Graph</th>
<th>Description</th>
<th>Facing Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>X.</td>
<td>K versus T for GR - I with 2% Sulphur Unstretched.</td>
<td>36</td>
</tr>
<tr>
<td>XI.</td>
<td>K versus T for GR - I with 2% Sulphur at 100% Stretch.</td>
<td>36</td>
</tr>
<tr>
<td>XII.</td>
<td>K versus T for GR - I with 10% Sulphur Unstretched.</td>
<td>36</td>
</tr>
</tbody>
</table>
ABSTRACT

The thermal conductivity of GR-I gum stock was measured with an improved apparatus.

The thermal conductivity of butyl decreases with temperature showing a double value at temperatures between 0°C and -80°C. Stock containing 10% sulphur showed no hysteresis character, and the conductivity changed only slightly over the temperature range. For the stretched stock a hysteresis loop was found.
I. INTRODUCTION

This work has been done as part of a general program of rubber research now being carried out in the Physics Department of the University of British Columbia, with the aid of a grant from the Associate Committee on Synthetic Rubber Research of the National Research Council of Canada.

Definition of Thermal Conductivity and Fundamental Equation:

A simple and satisfactory definition of the thermal conductivity of an isotropic solid is based on the following experiment: One side of a thin slab of material of thickness \( d \) is held at a temperature \( T_1 \) and the other side at a lower temperature \( T_2 \) until the temperatures of all parts of the slab reach a constant value. When this state has been reached the heat near the centre of the wall will flow directly from one side to the other, so that all the heat entering through a small area on one side will leave through an equal area on the other. Then it will be found that the amount of heat \( Q \) passing in a time \( t \) through a small area \( A \) near the centre of the slab is given by:

\[
q = K A \frac{T_1 - T_2}{d} \cdot t
\]  

(1)

The constant \( K \) in this expression is defined as the thermal conductivity of the material.

For the mathematical theory of heat conduction this definition is generalized in the following way. It is
assumed that the existence of a temperature gradient in an isotropic medium causes a flow of heat in the direction of that temperature gradient and proportional to it. The temperature then becomes a scaler space function, and the vector flow of heat per unit area across an isothermal is given by:

$$\frac{dQ}{dt} = -K\nabla T$$  \hspace{1cm} (2)

If the temperature changes with time it is possible by well known means (1) to set up the continuity equation:

$$\nabla \cdot K\nabla T = C \frac{\partial T}{\partial t} \neq q$$  \hspace{1cm} (3)

Here $C$ is the volume specific heat, i.e. the product of density and specific heat, and $q$ represents the net source of heat per unit volume. It is standard practice to consider $q$ as everywhere zero, and $K$ as independent of the temperature. The equation then reduces to:

$$k\nabla^2 T = \frac{\partial T}{\partial t}$$  \hspace{1cm} (4)

where $k = \frac{K}{C}$ and is called the thermometric conductivity or thermal diffusivity. This is the fundamental differential equation of the mathematical theory of the conduction of heat in solids. If the temperature is independent of time this becomes

$$\nabla^2 T = 0$$  \hspace{1cm} (5)

which is Laplace's equation, and has known solutions for many boundary conditions.
Thermal Conductivity of anisotropic media.

Most mathematical work on heat conduction has been done for isotropic solids. However, there is a wide class of substances whose physical properties depend upon direction. In these substances, the flow of heat need not be parallel to the temperature gradient and equation (2) need not hold. In such media, the simplest assumption is that the component of the heat current in any direction depends linearly upon the three components of the temperature gradient, i.e.

\[
\left(\frac{\partial q}{\partial t}\right)_{q_i} = \lambda_{ij} \frac{\partial T}{\partial q_j}
\]

By a proper choice of coordinate axes, these equations may be reduced to

\[
\left(\frac{\partial q}{\partial t}\right)_{x_i} = K_i \frac{\partial T}{\partial x_i}
\]

and the number of constants needed to characterize the flow of heat reduced from nine to three (2). This set of axes, the principal axes of thermal conductivity, usually coincides with the optical axes, and the principal axes of elasticity.

Thermal conductivity as a function of temperature.

For many substances, and in particular for rubber, the thermal conductivity depends on the temperature, and since the mathematical theory of conduction has been based on the assumption that the conductivity is constant, it is of interest to see what effect such temperature variation has on the measurement of thermal conductivity. A first approximation
to the temperature dependence of the conductivity is given by

\[ K(T) = K_0 \left( 1 / \alpha T \right) \]  

(8)

The exact effect of this on the slab experiment used to define thermal conductivity is easily seen. Suppose that a slab of thickness \( d \) has one side kept at zero and the other side at a temperature \( T_0 \). When the steady state has been reached equation (3) yields

\[ \frac{\partial}{\partial x} K(T) \cdot \frac{\partial T}{\partial x} = 0 \]  

(9)

Since \( T \) depends only on \( x \) a first integral is immediately obtained.

\[ K(T) \frac{dT}{dx} = c \]  

(10)

and from the definition of \( K \), the constant \( c \) must equal the heat current across a unit area in the slab.

Using (8) we obtain

\[ K \left( 1 / \alpha T \right) \frac{dT}{dx} = \frac{dQ}{dt} \]

Separate the variables and integrate.

\[ K \int_0^T \left( 1 / \alpha T \right) dT = \frac{dQ}{dt} \int_0^l \, dx \]

\[ K \left[ \left( 1 / \alpha T \right) T_0 \right]_0^T = \frac{dQ}{dt} \left[ x \right]_0^l \]

\[ K \left( 1 / \alpha T \right) T_0 = \frac{dQ}{dt} l \]

or

\[ \frac{dQ}{dt} = K \left( 1 / \alpha T \right) T_0 \]

(11)

but

\[ K \left( 1 / \alpha T \right) = \frac{T_0}{K} \]
where \( \overline{K} \) represents the average thermal conductivity of the sample. Thus the defining experiment remains valid.

The effect of temperature dependent conductivity on the general equation for heat flow must now be investigated. Substitution of (8) into (3) gives

\[
\nabla \cdot \overline{K} \left( 1 - aT \right) \nabla T = C \frac{\partial T}{\partial t} \quad (12)
\]

which becomes, for the one-dimensional case

\[
K \frac{\partial^2 T}{\partial x^2} + a \left( \frac{\partial T}{\partial x} \right)^2 = C \frac{\partial T}{\partial t} \quad (13)
\]

In many experimental determinations of \( K \) a quantity measured is the temperature gradient \( \frac{\partial T}{\partial x} \), which must therefore be fairly large. To neglect this second term seems hardly justified unless \( a \) is extremely small. This difficulty may be overcome by the following argument. For many substances, and again for rubber, the volume specific heat as well as the thermal conductivity is temperature dependent, and we may assume that it too shows a linear dependence. Then equation (3) becomes for the one-dimensional case

\[
\frac{\partial}{\partial x} \cdot K \left( 1 - aT \right) \frac{\partial}{\partial x} T = - C \left( 1 - bT \right) \frac{\partial T}{\partial t} \quad (14)
\]

\[
= - C \left( 1 - aT \right) \frac{\partial T}{\partial t} + C \left( a - b \right) T \frac{\partial T}{\partial t}
\]

The last term in this expression may be kept small by keeping the time variation of temperatures and the temperature range small, and to get an approximate solution, may be omitted.
This is equivalent to assuming a constant thermometric conductivity. We may then write:

$$k \frac{\partial}{\partial x} (1 / aT) \frac{\partial T}{\partial x} = (1 / aT) \frac{\partial T}{\partial t}$$  \hspace{1cm} (15)$$

Make the substitution

$$U = (1 / aT)^2$$

Then

$$\frac{\partial U}{\partial x} = 2a \frac{\partial}{\partial x} (1 / aT) \frac{\partial T}{\partial x}$$

$$\frac{\partial U}{\partial t} = 2a \frac{\partial}{\partial t} (1 / aT) \frac{\partial T}{\partial t}$$

and (15) may be written as

$$k \frac{\partial^2 U}{\partial x^2} = \frac{\partial U}{\partial t}$$  \hspace{1cm} (16)$$

Compare this with the original one-dimensional heat flow equation:

$$k \frac{\partial^2 T}{\partial x^2} = \frac{\partial T}{\partial t}$$  \hspace{1cm} (17)$$

The formal identity of these two equations permits certain deductions. First, since a change in $U$ implies a change in $T$, the equations show that the rate of transmission of a slow change in temperature is independent of the temperature variation of $K$. Second, it is possible to show that the solutions to problems involving slow changes in temperature remain unchanged by variation of $K$ with temperatures. Consider the general solutions of (16) and (17). We may write

$$U = f (c \overline{x,t})$$  \hspace{1cm} (18)$$

where $c \overline{x,t}$ indicates some combination of the variables $x$ and
t and f some arbitrary function. The solution for (17) is similarly

$$T = f(c \overline{x,t})$$  \hspace{1cm} (19)

If we wish a solution to fit a certain set of boundary conditions a restriction on the form of f is implied. Suppose that we are given a boundary condition in terms of T, i.e.

$$T(o,t) = Q(o,t)$$  \hspace{1cm} (20)

To solve (16) this must first be written in terms of U, i.e.

$$U(T(o,t)) = P(o,t)$$  \hspace{1cm} (21)

This boundary condition on U will select a solution

$$U = f(c \overline{x,t})$$  \hspace{1cm} (22)

and as U is a function of T, we may determine T as

$$T(U) = g(c \overline{x,t})$$  \hspace{1cm} (23)

but this is a function $T(c \overline{x,t})$ determined from (16) and satisfying condition (20). At the same time it is of the form $g(c \overline{x,t})$ and satisfies (17). Thus the solution of (16) written in terms of T, which satisfies the boundary condition

$$T(o,t) = Q$$

is at the same time the solution of (17) satisfying the same boundary condition. This shows that, to the approximation considered in (15) temperature variation of the thermal conductivity produces no change in the solution to heat flow problems. (1)

(1) This argument is weakened by the fact that (16) and (17) are second order
differential equations, hence the most general solutions involve not one but two arbitrary functions. This restricts the discussion to those boundary conditions which involve only one of the functions in the solution.

Methods of Measuring Thermal Conductivity.

We shall now consider a few methods of measuring thermal conductivity which may be applicable to rubber. These methods may be divided into three classes, depending upon the nature of the mathematical problem posed by each.

Type 1

Temperature constant, no radiation at surface.

Mathematically this calls for a solution of Laplace's equation subject to constant boundary conditions. Usually the temperature difference between two surfaces and the flow of heat across one of them are measured. This, with the geometrical constants of the apparatus and sample permit calculation of the temperature gradient, hence the thermal conductivity. The methods differ chiefly in the shape and disposition of the sample.

a. Wall or slab method.

A measured power passes through a slab of material from a hot to a cold plate, whose
temperatures are measured, direct flow being assured by a guard ring. The thermal conductivity is calculated from

\[ K = \frac{P}{A} \frac{d}{T_1 - T_2} \]

where \( P \) = power input to measuring plate
\( A \) = area of measuring plate
\( d \) = sample thickness
\( T_1 - T_2 \) = temperature differences between faces.

b. Cylindrical methods.

The sample is prepared in the form of a cylinder, power being supplied from the centre. If the sample is long enough in comparison to its radius the heat losses from the ends may be negligible and a guard ring unnecessary. This is the method used by Bridgman (3) with thin films of liquids. The conductivity is calculated from (4)

\[ K = \frac{P}{2\pi l} \ln \left( \frac{r_2}{r_1} \right) \frac{l}{(T_1 - T_2)} \]

where \( l \) = length of sample.
\( r_1, r_2 \) = outer and inner radii respectively.

c. Spherical shell methods.

The source of heat is located in the centre of a spherical shell of the
sample, thus making guarding precautions unnecessary. When the temperature is constant over the surfaces the conductivity may be calculated from:

\[ K = \frac{P}{T_1 - T_2} \frac{r_1 r_2}{2\pi(r_1 - r_2)} \]

**Type 2** Temperature constant, radiation from the surface.

These methods assume Newton's law of cooling; the loss of heat by "radiation" from a body to its environment is proportional to the difference between their temperatures. If the environment is at zero, the boundary conditions to the mathematical problem become

\[ \frac{\partial^2 T(s)}{\partial x^2} + h T(s) = 0 \]

since the heat flow across the boundary surface is proportional to both \( T \) and \( \frac{\partial T}{\partial x} \)

a. The method of Forbes (5)

One end of a long bar of the sample is heated, and all the heat lost by radiation so that the far end of the bar is at the temperature of the surroundings, which we take to be zero. The temperature is measured at a number of points and is plotted
of $x$, the distance along the bar. From this graph $\frac{\partial T}{\partial x}$ may be determined at any point $x$. Since all the heat is lost by radiation the power passing $x$ is given by

$$\frac{dQ}{dt} = a \int_{x_0}^{\infty} T(x) \, dx$$

where $a$ is the cooling constant of the bar, and may be determined by measuring the rate at which the bar cools. The integral may be evaluated from the graph and the thermal conductivity calculated directly from the defining equation

$$\frac{dQ}{dt} = KA \frac{\partial T}{\partial x}$$

b. The method of Lees (5)

A small sheet of the sample is sandwiched between two plates, one containing a heater, and the apparatus is varnished so that all parts will have the same emissivity. It is then suspended in an enclosure and allowed to cool, so that the emissivity
may be determined. A measured quantity of power is then supplied to the heater until thermal equilibrium has been established. Temperatures of the plates are then measured and the loss of heat from each calculated from the known emissivity. This determines the flow of heat across the sample and $K$ is calculated as in the slab method.

**Type 3** Temperature varying with time.

This group may be sub-divided into those experiments in which the sample is allowed to cool subject to constant boundary conditions, and those in which the steady state temperature is measured with varying boundary conditions.

a. The cooling sphere method.

A sphere of radius $a$ initially at a uniform temperature $T_0$ is allowed to cool in a medium at constant temperature. It may be shown (6) that the temperature at the centre at a time $t$ is approximately

$$T = A_1 \exp(-k a_1 t)$$

where

$$A_1 = \frac{2T_0}{a_1} \sin a_1 a - a_1 a \cos a_1 a$$
anda_1 is the first positive root of
ax \cos ax \neq (ah - 1) \sin ax = 0
h being the emissivity. The values
of ka_1 and A_1 are determined from two
observations of the temperature and the
value of the thermal diffusivity
calculated.

b. The method of King (7).

One end of a long rod of material
was heated by a periodic current obey­
ing a sine law. The velocity v with
which the corresponding variation in
temperature was transmitted down the
sample was measured by use of two
thermocouples. Experiments were made
with waves of two different periods
t_1 and t_2 and the velocities, which
depended on the periods, determined as
v_1 and v_2. Then the thermal diffusiv­
ity k is given by

\[ k = \frac{t_1 t_2 v_1 v_2}{A \sqrt{\frac{(v_1^2 - v_2^2)}{t_2 v_2^2 - t_1 v_1^2}}} \]

Dr Blúh has suggested that this method
might be applied to rubber by heating
one side of a thin sheet by radiation
and measuring the temperature of the
other side by a sensitive bolometric
method. This enables temperatures to be measured at points approximately half a wave length apart. The wave length is given (5) by

$$\lambda = \sqrt{\frac{k}{2w}}$$

hence, for reasonable frequencies, is low for rubber.

Previous measurements of the Thermal Conductivity of Rubber.

In spite of the practical importance of this property in such processes as the increase in temperature in flexed samples, and in vulcanization only relatively few measurements of the thermal conductivity of rubber have been made. Lees (4) in 1848 measured the conductivity of ebonite. Later, in 1923, Griffith and Kaye at the National Physical Laboratories made measurements of the thermal conductivities of a great many substances, including both hard and gum rubber of unidentified composition using a two plate method with a guard ring. They determined the effect of filler on thermal conductivity, but specify the filler as "mineral matter". (8) Frumkin and Dubinker have determined the diffusivity by measuring the change in temperature with time in the centre of a sphere which is allowed to cool in an enclosure by radiation. (9) Recently a similar measurement has been made by J. Rehner, Jr. (10) who immersed spheres of a uniform temperature in boiling water, and measured the diffusivity of a wide variety of natural and
PLATE I

A front view of the apparatus showing the switch panels, control panels, measuring instruments and automatic controls.
PLATE II

A rear view of the apparatus showing the automatic controls, the cryostat zone box and selector switch.
synthetic stocks, all clearly identified. Schallamach measured the conductivity of natural rubber at low temperatures using the hot plate method. (11)

The project at the Physics Department of University of British Columbia was begun in 1944 by Dauphinee, who measured the conductivity of natural rubber, stretched and unstretched, at temperatures between 20°C and -160°C. (12) The work was continued by Ivey (13) who redesigned the apparatus and made measurements on GR-S. The measurements described in the present thesis were made on an improved form of the apparatus used by Ivey.

IIAPPARATUS.

The apparatus used by Ivey and Dauphinee had been located in a storage basement in the Science Building, which had become untenable. For this reason, and since the apparatus would have to be moved to the new Physics Building, it was decided that it should be rebuilt in a more portable form in one of the ground floor laboratories. While being rebuilt two important improvements were made; a heat shunt was made between the guard blocks and the cold block to overcome the great overheating of the guards, mentioned by Ivey, (13) and semi-automatic controls were put on the cold side and the guard blocks.

Conductivity measuring unit.

The actual measuring unit (plate IV) had three parts, one cold block and two heating assemblies. The cold block was
PLATE III

A close-up of the measuring unit.
was a piece of copper, 1 cm thick shaped in the form of a rectangle 10 cm by 4 cm on top of a triangle, which led down to a large tapped copper plug. Into this plug fitted a copper cylinder, threaded at the top, and having a copper spiral soldered about it, through which was drawn the cold vapour from a flask of liquid nitrogen, and at extreme temperatures, the liquid itself. Around the block, immediately above the cold cylinder were wound two heaters, one of 20 ohms, supplied from a 12 volt source, the current being manually controlled, and the other of 700 ohms, supplied by current at 110 volts from the automatic control.

In each heating assembly was a measuring block and a guard block. The measuring block was a piece of copper 1 cm thick and machined to exactly 4 cm by 6 cm. A 20 ohm heater supplied by power at 12 volts was wound in this block, near the side not in contact with the sample. Around the measuring block fitted the guard block. A plate of half inch brass 10 cm by 6 cm was machined down to one quarter inch, leaving two ridges half an inch apart and one quarter inch wide. This was intended to combine strength with a low heat capacity and high thermal conductivity. At either end of this were fitted two copper blocks, each 2 cm by 6 cm, containing heaters, one of 20 ohms, supplied by manually controlled current at 12 volts, and one of 300 ohms supplied by power at 110 volts from the automatic guard block control. The centre section of the brass plate was recessed slightly, and four tapped holes were made in it. Fibre plugs
Plate IV The Conductivity measuring unit

Top elevation

- a thermocouple
- b 20 ohm heater
- c 500 ohm heater
- d difference thermocouple
- e cooling coil
- f bakelite block

Side elevation

End elevation
held in recesses in the back of the measuring block fitted into these holes. The measuring block was adjusted flush with the face of the cold block by four screws which pressed against the fibre plugs. Two thermocouples were located near the tops of the measuring block, two near the tops of the guards, and two near the top of the cold block, and one at a point just below the bottom of the sample. A difference thermocouple was put between one of the measuring blocks and its guard block.

Two closely fitting copper bars were sweated between the ridges on the back of each guard block and a plate of eighth inch copper of the same shape as the cold block was screwed to these. The lower end of the plate was connected to the cold block by a piece of flexible copper sheeting which passed between the cylinder and the tapped plug. This was the heat shunt, which was intended to provide a low resistance path to heat picked up by the guards. A heater was wound around the plates to control the heat loss through them.

The heating circuits. (Plate V)

Power was provided by a set of twelve heavy duty storage batteries. The current to each of the low resistance heaters was controlled by a set of slide wire rheostats. Small milliammeters were put in series with the guard block heaters \((G_1G_2)\) and the cold block auxiliary heater \((A_1)\). A switching arrangement enabled a Weston Model 1 milliammeter to be put in series with the heater in either of the measuring blocks, or a Weston Model 1 voltmeter across it.
The cryostat and cooling circuit.

The measuring unit was placed in a large brass box, the thermocouples and heater leads passing between rubber gaskets, so that the box could be evacuated. This was done by means of a Cenco Megavac pump, and readings were taken at pressures of less than 1 cm of mercury, as shown by a closed tube manometer on the control panel.

The cooling fluid was drawn by a pump from a large Dewar flask through the cooling coils. The rate of flow was controlled by two valves, one a needle valve between the cooling coil and the pump, and the second opening to the atmosphere between the first valve and the pump. The rate of flow was estimated by measuring the pressure in the cooling coils with an open tube manometer. This manometer was provided with a two position stop cock so that it could be used to measure the difference in pressure across the needle valve. Between these valves and the cooling coil, and again between the valves and the pump, the coolant passed through a large copper coil which warmed it. Immediately in front of the pump was a five gallon tank which served to steady the intermittent action of the pump.

The temperature measuring circuit. (Plate VI)

Temperature was measured by means of a set of twelve copper-copel thermocouples. The copel used was especially made for thermocouple use and proved completely satisfactory.
Plate VI  Thermocouple Circuit

Selector switch

Zone box

Measuring junction

Reversing switches

TCP TCQ

Potentiometer

Reference junction
The thermal e.m.f. was measured by means of a White Double Potentiometer designed for thermocouple pyrometry used with a Leeds and Northrup H.S. galvonometer. The thermojunctions in the measuring unit were connected through a twenty-four position selector switch in series with the reference junction and the potentiometer. The potentiometer could be read to a tenth of a microvolt, and had an arrangement whereby internal contact e.m.f.'s could be compensated. To do this the power was taken off the circuit and a small resistance put in series with the galvonometer. The position of the galvonometer when this circuit was closed was used as the null point for balancing the instrument. The White Double Potentiometer has a further advantage in that the bridge current is provided from two separate sources, one giving 100 ma. for the coarse adjustment and the other giving 10 ma. for the fine adjustment. This relieved the drain on the batteries and made the bridge current more stable.

The control circuits.

The apparatus as used by Ivey was operated by two experimenters, one controlling the cold block by means of the auxiliary heater, while the other made the actual measurement. This year a system of automatic controls was designed and built which permitted data to be taken by a single experimenter. A photo cell control circuit was used in conjunction with a galvonometer and a constant impedance potentiometer. Experiments were made with a phase-control thyatron circuit which proved unsatisfactory. Two types of bias control circuits were used,
one with an A.C. source and a single thyratron, and the other with D.C. current and a pair of thyratrons. The A.C. control was based on the ability of a thyratron to act as an amplifier when supplied with A.C. plate voltage. The tube was biased to cut-off by a cathode resistor, and the grid tied to a photocell that was grounded through a one megohm resistor. When light reflected from the galvonometer mirror fell on the photocell it conducted current, and drove the grid positive, allowing the tube to conduct on each positive half cycle. (Plate VII). This control had the very desirable property of self-damping, and brought the system to static equilibrium. However it was unsatisfactory since a sudden variation in temperature would make it lose control, by throwing the galvonometer spot right across the photocell before enough heat had been added. For this reason a D.C. control was used. In this control a thyratron was fixed when the grid went positive in response to a stimulus on the photocell. Since the thyratron plate was held at a constant D.C. voltage it carried current until the voltage was removed. To shut it off a second photocell and thyratron assembly was used. In the plate of this thyratron was a 10,000 ohm resistor, so that a considerable drop in voltage occurred when the tube fired. Between the plates of the thyratron was a 400 μμfd. condenser, which was charged when the first thyratron was fired. When the second one conducted this condenser discharged and drove the plate of the first one negative, thus shutting off the
Plate VII  Photocell control circuit D.C. type

R 10 000 ohm
R2, R3, R5, R6 1 megohm
R4 1000 ohm 10w
R7 225 ohm 75w
R8 500 ohm 10w
R9 1000 ohm 10w
R10 500 ohm heater
T1, T2 2050 thyristors
T3, T4 918 photocell
C 200 u ufd. cond.
current. (Plate VIII) Under operating conditions the galvonometer spot moved between the two photocells, so that the system made small oscillations about its equilibrium temperature. When complete equilibrium was desired these oscillations were removed manually by decreasing the current under control of the automatic system, and increasing the power under manual control. Two such control circuits were built, one having as plate load a 300 ohm heater in the guard block, and the other either a 700 ohm heater in the cold block, or, since the circuit itself could provide only 100 ma. and more power was frequently needed, a telephone relay, which when closed permitted 240 ma. to flow through the 700 ohm heater.

To act as a detector some sort of a potentiometer arrangement was necessary, which would present to the galvonometer an approximation to its critical damping resistance. To cancel out the e.m.f. of the thermocouple used as a detector and still detect variations in temperature, the thermocouple was connected in series with the galvonometer and a small resistor through which flowed a small very sensitively controlled current, giving rise to a voltage drop which opposed the thermal e.m.f. Thus the galvonometer faced a constant resistance which was made equal to its critical damping resistor. In order to have control over sensitivity a potentiometer was put in series with the galvonometer, so that the current could be reduced and galvonometer overdamped at will. (Plate IX)
Plate IX  Control Circuit Potentiometer

Thermocouple

R1 1 megohm
R2 20000 ohm
R3 20000 ohm 1/2 turn slide wire pot.
R4, R6 100 ohm
R5 10000 ohm
III EXPERIMENTAL PROCEDURE.

Thermocouple calibration.

The thermocouple had been calibrated by Ivey at five fixed points:

1. The freezing point of water
2. The boiling point of water
3. The freezing point of mercury
4. The sublimation point of carbon dioxide
5. The boiling point of oxygen

It was considered sufficient this year to check the calibration at the freezing point of water, the sublimation point of carbon dioxide and the boiling point of oxygen. Close agreement was found between the data obtained now and that obtained by Ivey, the difference in the average of the readings being less than two microvolts at any point. Therefore it was considered that the original calibration charts could still be used. The difference between individual thermocouples was determined at three fixed points, and a comparison with the existing deviation charts showed a negligible variation. Approximate confirmation of this was obtained as follows: The apparatus was assembled with no smaple in place, good thermal contact between the polished copper faces being provided by strips of foil, and held in equilibrium at various temperatures. The thermocouples were then read and differences noted. This method was found satisfactory only at relatively high temperatures where radiation from the walls was negligible.
When the apparatus was re-assembled in the new laboratory, a new zone box was made and the calibration again checked at the ice point and the liquid oxygen point. A variation of less than two microvolts was found, and re-calibration considered unnecessary. Since the thermo-electric power varied between 20 and 40 microvolts per degree over the range used, the temperature measurements were considered accurate to at least one-tenth of a degree.

Method of taking readings.

Readings were taken in two different ways to obtain the change in conductivity occurring as the sample cooled, and as it warmed up. For the first type, the heaters were turned off and the system cooled as rapidly as possible until the cold block was two or three degrees below the temperature desired. The auxiliary heater in the cold block was then turned on and the cold side heated as rapidly as possible to the desired temperature. The control circuit potentiometer was then balanced, and the automatic control circuit adjusted to hold the cold side at constant temperature. In the meantime the measuring blocks and guards had been cooling. When they reached a temperature some ten degrees above that of the cold side, the heaters were turned on and adjusted manually to stop the temperature drop. A galvonometer was put in series with the difference thermo-couple between one measuring block and its guard, and the guard temperature put under control of the automatic circuit,
the other guard block being adjusted by hand. The apparatus was then left for ten minutes to reach equilibrium, and readings were taken for the next ten minutes. When the temperature drift remained less than one microvolt per minute for five minutes, temperatures of all blocks were recorded, and the current and voltage in the measuring heaters read.

To find the changes produced on warming the sample, the apparatus was first cooled as rapidly as possible to the lowest obtainable temperature (about -160°C), an operation which took at least an hour. The above procedure was then reversed, the apparatus being first heated as rapidly as possible, then the cold side stopped and the warm side balanced. These readings were obtained in much less time than the others, since the hot blocks could be warmed much more rapidly than they could be cooled.

For most of the readings the cold side was adjusted to complete static equilibrium, but many were taken while its temperature was oscillating about the equilibrium position. None of these temperature oscillations seemed to be transferred to the heating blocks, and the mean temperature of the cold side was used in calculations. This will be justified in a later paragraph. All temperature readings were made while the automatic control heater was off, since some of the thermocouples showed a disturbing tendency to respond to the closing of the 110 volt circuits, in spite of the fact that when tested for electrical pick up no effect was found. This test was made when use of an alternating
current control circuit was contemplated. One thermojunction was placed in the center of a large induction coil, and held at constant temperature by a stream of air. No change was observed in the e.m.f. registered by the balancing potentiometer when a 60 cycle current of two amperes was passed through the coil.

**Method of analysing data.**

Consider a hot block of heat capacity C at a temperature $T_0$ surrounded by a guard ring at a temperature $T_1$ resting on a sheet of rubber of conductivity $K$. If the block is provided with a supply of power $P$, the rate at which it heats up will be given by

$$ C \frac{dT_0}{dt} = P \neq a(T_1 - T_0) - KA \frac{T}{d} \frac{dT}{dx} \tag{24} $$

If the rubber sheet is of thickness $d$, and rests on a plate kept at a temperature $T_2$, the equilibrium condition will be

$$ 0 = P \neq a(T_1 - T_0) - KA \frac{T_0 - T_2}{d} \tag{25} $$

If at the same time the guard has been adjusted to the same temperature as the heating block, we have

$$ P = KA \frac{T_1 - T_2}{d} $$

from which

$$ K = \frac{Pd}{A(T_1 - T_2)} $$
Guard block correction.

Not all readings could be taken under the ideal circumstances described above, since it was found impossible, particularly for the stretched sample, to get the guards down to a low enough temperature, even with the heat shunt. There are two probable reasons for this:

1. At lowest temperature it was found that the blocks became covered with frost, thus increasing their emissivity.

2. A large part of the stretched sample extended beyond the measuring unit and picked up a great deal of radiation.

When the guards and the measuring blocks were at different temperatures a correction had to be made, taking into account the power transmitted to the heater block from the guard block. It was assumed that to a first approximation the heat transfer depended linearly on the temperature difference (v. equation 25). On this assumption the transfer coefficient $a$ could be determined at any temperature by making two readings employing the same value of $T_o$ and $T_2$ and different readings of $T_1$. Such readings were taken, and the average value of $a$ at various temperatures determined as shown in Table 1. The product of $a$ and the temperature difference between guards and heater (which was kept small) was added to the measured power to give the time rate of transfer of heat.
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<th>Temperature degrees centigrade</th>
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Measurement of power.

The power supplied to the heaters was determined by reading the voltage across them and the current flowing. It was necessary to correct these readings for two effects. First, the voltage read was developed not across the heater alone, but across the heater and the leads in series. Second, the voltmeter and ammeter were not in the circuit under operating conditions, hence their effect on the circuit had to be taken into account. An analysis of the circuit leads to the following approximate formula:

$$ P_t = \frac{P_m \cdot R}{R + r} \cdot \left[ 1 - \left( \frac{R}{R_v} \right)^2 \left( 1 - \frac{R_a}{R_c} \right) \right] $$

(26)

where $P_t$ = true power

$P_m$ = measured power = E.I.

$R$ = heater resistance

$r$ = lead resistance
Rv = resistance of voltmeter
Ra = resistance of ammeter

When numerical values are substituted we obtain for the two heaters:

\[(Pt)_1 = 0.995 E_1 l_1\]
\[(Pt)_2 = 0.997 E_2 l_2\]

This enables the conductivity \(K\) to be calculated from the general formula.

\[K = \frac{(Pt \not a \cdot dT) \cdot d}{A \cdot DT}\]

Where \(dT\) = difference in temperature between measuring block and guard
\(DT\) = difference in temperature between measuring block and cold block.
\(A\) = area of measuring block
\(d\) = thickness of sample

Since the area of both blocks was exactly 24 cms\(^2\) numerical values may be substituted, giving for \(K\) as determined from the two blocks

\[K_1 = 9.88 \times 10^{-3} \cdot d_1 \cdot \frac{E_1 l_1}{DT} \neq 9.92 \times 10^{-3} \cdot d_1 \cdot \frac{adT}{DT}\]
\[K_2 = 9.90 \times 10^{-3} \cdot d_2 \cdot \frac{E_2 l_2}{DT} \neq 9.93 \times 10^{-3} \cdot d_2 \cdot \frac{adT}{DT}\]

If \(d_1\) and \(d_2\) are measured in centimeters these formulae give \(K\) in calories per second per degree per centimeter.
Measurement of thickness.

Thickness was measured in three ways.

(1) A micrometer for soft materials was used to measure the sample before it was clamped in place.

(2) A travelling microscope was removed from a comparator and mounted on a stand that fitted over the cryostat. Parallel bench marks were carefully made along the top of the blocks, and the separation of these marks was measured, with and without the sample in place. The difference in these measurements gave the thickness of the sample.

(3) A large micrometer was used to measure the distance between the backs of the guards, with and without the sample in place. Fair agreement was obtained between these measurements. e.g. for one sample:

- Soft materials micrometer .154 cm.
- Travelling microscope .152 cm.
- Large micrometer .150 cm.

Any value used in calculation was the mean of about ten readings. These readings showed a spread of about .04 millimeters with the micrometer, and rather more than that with the microscope. For this reason the thickness measurements are considered accurate to within only about 5%.

When the unit was in place the microscopic measurement could be made only at the top of the blocks, therefore the apparatus was removed and two bench marks
put on the ends of the guards and the cold block. Using these, microscopic determinations of the separation of the plates was made. This agreed to within 5% with the measurements at the top. Measurements made with the large calipers at a number of points confirmed this agreement.

To determine the effect of linear expansion a Plexiglas window was put into the top of the cryostat, and measurements of separation between bench marks made at various temperatures. These measurements were rather uncertain, but when corrected for the expansion of the copper indicated that the average value of the linear expansion coefficient for the sample, over the temperature range used, could be taken as about $1 \times 10^{-4}$. This is of the order expected from the values for the specific volume obtained by Bekkedahl (14) for natural rubber. The relative variation in plate separation over the temperature range used was thus about 2%, hence could be neglected.

Evaluation of the apparatus.

Temperature variation over the cold plate.

Since the cold side was cooled from the lower end, there was some variation in temperature over the surface of the plate. This variation is certainly less than the temperature variation that would be produced between the top and the bottom of the block if all the power passing through it entered at the top. The part of the cold block warmed by the measuring heaters was 4 cms. high, 6 cms. long and
l cm. thick, and the maximum power passing through it was about 1.5 watts. Since the thermal conductivity of copper is about 1 cal./deg.-sec.-cm. over the whole temperature range used, we have for the difference in temperature over the block

\[
\frac{1.5 \times 4}{1 \times 6 \times 4.18} = .25 \text{ degrees}
\]

The actual measured temperature difference between the thermocouples at the top and at the bottom was never as great as one-tenth degree, and was therefore neglected.

**Variation of Temperature with time.**

The condition of equilibrium was considered as obtained when the rate of change of the boundary temperature remained less than one-twentieth degree per minute for ten minutes. An approximation to the true temperature gradient in the sample may be obtained from a consideration of the mathematical solutions to the temperature distribution problem. The temperature at any point in the sample is given by the sum of a term depending on the initial condition and one depending on the boundary state. Physically this means that to the stationary temperature must be added a quantity depending on the rate of cooling inside the sample. Carslaw (6) gives for the temperature in rod of length initially at zero, with one end suddenly raised to a temperature \( T_1 \) a condition approximating that of the sample

\[
T = T_1 \frac{X}{\lambda} \sum_{n=1}^{\infty} \frac{T_1}{n} \frac{\cos n\pi}{\pi} \sin \frac{n\pi x}{\ell} e^{-k \frac{n^2 \pi^2}{\ell^2} t}
\]
If we write $T_0$ for the stationary temperature and consider the temperature at the centre for large values of $t$ we get

$$\frac{T_0 - T}{T_0} = \frac{1}{\nu} \exp \left( -k \frac{L^2}{l^2} t \right)$$

hence, the time required for the centre of the sample to reach within 1% of its final value is

$$t = \frac{L^2}{\nu} n \left( 0.01 \times \frac{1}{\nu} \right)$$

Substitution of numerical values gives

$$t = 15 \text{ seconds}.$$  From this it is clear that the principal factor involved in reaching equilibrium is the time needed for heat to flow from the copper blocks. The influence of the slow change in boundary temperature can also be approximate. Carslaw (6) gives in the case of one boundary at a varying temperature C.t

$$T = \frac{C x}{k l} \left( k t - \frac{l^2 - x^2}{3 t} \right)$$

which is a very rough approximation to the condition in our experiment.

Differentiating this partially with respect to $x$ at the boundary, and changing notation, we get

$$\frac{\partial T}{\partial x} (l,t) = \frac{T}{l} \neq \frac{1}{3} \frac{l}{k} \frac{dT}{dt}$$

Substituting numerical values, we find the correction due to a temperature drift of one microvolt per minute as .03 degrees per centimeter. Since the temperature gradient used was on the order of 50 degrees per centimeter this term is clearly negligible.
Many of the readings were taken while the cold block temperature executed small oscillations about its equilibrium position. When such was the case, the temperature of the hot block was found to be unaltered, and the average value of the cold face temperature was used in calculations. An approximation to the conditions under this type of equilibrium is: one side at a constant temperature $T$, the other side at a temperature $a \cos \omega t$. The effect of this sinusoidal variation on the temperature gradient can be obtained from Cardlaw's solution (6) for the temperature in a rod of length $l$, one side being held at zero while the other is at a temperature $a \cos \omega t$. The stationary part of the solution is

$$T = \frac{a}{2} \left( \frac{\sin u (l \neq i) x e^{-\frac{1}{2} \omega t}}{\sin u (l \neq i) l} - \frac{\sin u (l - i) x e^{\frac{1}{2} \omega t}}{\sin u (l - i) l} \right)$$

where $u = \sqrt{\frac{\omega}{2k}}$

Partial differentiation with respect to $x$ at $x = 0$ gives, after a little manipulation

$$\frac{T(0,t)}{x} = \frac{a}{2} \left( \frac{(\cos u (l \neq i) l e^{\frac{1}{2} \omega t} - \cos u (l - i) l e^{-\frac{1}{2} \omega t})}{(\sin u l \cosh u l)^2 + (\cos u l \sinh u l)^2} \right)$$

$$= a \frac{\partial}{\partial l} \left( \frac{(\sin u l \cosh u l \sin \omega t - \cos u l \sinh u l \cos \omega t)}{(\sin u l \cosh u l)^2 + (\cos u l \sinh u l)^2} \right)$$

Carrying out the differentiation indicated, and substituting numerical values gives for the maximum value of this contribution to the temperature gradient, something close to 10. a. per cm. Since the maximum range of the oscillations was 14 microvolts, the value of $a$ was less than .25 degrees,
per centimeter, less than $\frac{1}{2}$. The average contribution was, of course, zero.

This discussion of the accountable errors in the apparatus would lead to an expected error in the readings of about 2%. Actually, the readings taken showed a much greater range of error than this. Some improvements are still to be made, chiefly in the cooling circuit and in the measuring unit.

1. The use of a flowing liquid as a coolant has two disadvantages. First, it is wasteful of the liquid nitrogen, and second, it is not sufficiently dependable to be left for long periods of time, even with the temperature control circuits. A better cooling system would employ a heat bridge to a flask of the liquid coolant.

2. The geometry of the measuring unit could be improved. As it is, the guard block surrounds the measuring blocks on only three sides, two faces being left exposed. A better arrangement would employ a guard block completely surrounding the measuring heater. The block should also be of much greater area. At present the greatest part of the heated surface is used for making measurements. This was done to eliminate errors in the measurement area, and to minimize the effect of surface defects. However the low thermal conductivity of rubber reduces the importance of contact resistance, and samples have been supplied that are fairly free of surface flaws. The exact measurement of area presents no difficulty. If the guard block has a large area
the conditions in the region of measurement will be
closer to those called for by the theory, and at the same
time any effect of large temperature gradients on the state of
the sample will be reduced. Another flaw in the apparatus
lies in the poor arrangements for measuring thickness. An
instrument has been designed which embodies some of these
improvements, and its construction was laid aside in
order to investigate the effect of the modifications made
this year to the old equipment.

IV RESULTS

1. The Samples

The rubber samples used were prepared from
GR-I gum stocks by the Research Division of Polymer
Corporation at Sarnia. They had been carefully molded
to ensure plane parallel surfaces, as free as possible
from defects. The formulae used were:

Sample 1 - GR-I / 2% S

- Butyl rubber - 100 pts.
- Sulphur - 2 pts.
- Zinc Oxide - 1.0 pts.
- Tetramethyl thuiran disulfide - 1.0 pts.

Sample 11 - GR-I / 10% S

- Butyl rubber - 100 pts.
- Sulphur - 10 pts.
- Zinc Oxide - 1.0 pts.
- Tetramethyl thuiran disulfide - 1.0 pts.

Cure 60' at 307° F.
Readings taken.

Measurements were made on sample 1 at zero and 100% stretch, and on sample 2 unstretched, at temperatures between 20°C and -170°C. It was found that the apparatus was unsatisfactory for readings beyond this range; at higher temperatures it seemed impossible to get consistent readings, and at low temperatures the guard block correction became unduly great. The results are tabulated in the following three tables, and for comparison the duplicable readings are plotted. In the tables, $E_1$, $E_g$ and $E_2$ indicate the thermal e.m.f. produced by the thermocouples in the measuring blocks, the guard blocks and the cold side, respectively. $V$, $I$ indicate the power readings, $D_T$ the temperature difference across the sample, $d_T$ the difference in temperature between the guards and the measuring blocks, $\bar{T}$ the average temperature in the sample, and $K$ the value of the thermal conductivity.

Probable error.

The error in the measurement of area and thickness, of power and of absolute temperature could affect only the absolute value of the conductivity. The measuring blocks had been carefully machined and their dimensions determined to within .2%. Before the sample was clamped in place the surface was cleaned and inspected for flaws. The presence of small scratches is insignificant because of the small area they occupy, and because of the plastic nature of butyl rubber. Contact resistance is an unimportant source of
PLATE X
K vs T for GR - 1 with 2% S - Unstretched

10^4
K x 10

-180 -140 -100 -60 -20
T degrees C
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PLATE XL

K vs T for GR - I with 10% S Unstratched

K x 10^4

T degrees C
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TABLE IV

GR - I (2% Sulphur) - 100% Stretch

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error in measurements of low thermal conductivity. The thickness was more difficult to measure, and the accuracy of its measurement cannot be considered to be more exact than within 5%, a major source of error. The change in thickness introduced by thermal expansion was negligible, as is the change in area. The measurement of power depended upon the accuracy of the current and voltage readings, which were made on meters whose scales were calibrated to milliamps, and to .05 volts respectively. Since the needles passed over mirrors in order to eliminate errors due to parallax, the meters could be read to the nearest milliamp, and the nearest .01 volt. Therefore the error in measurements of current and voltage is everywhere less than 1%. The lead resistance was about 1% of the heater resistance, and the change in resistance with temperature, as determined by the electrical measurements, was small, therefore negligible error is introduced by this effect. Measurement of absolute temperature was good to the nearest degree, and since the conductivity measurements involved a range of ten degrees over the sample, this may be considered sufficiently accurate.

A more serious difficulty lay in the measurement of temperature difference. The thermocouples had been calibrated to the nearest 2 μV, which is equivalent to the nearest tenth degree at lowest temperatures, and to about one twentieth at room temperature. This indicates an accuracy of about 2% in this measurement. The guard block error had been calibrated using a set of preliminary readings
and was negligible throughout most of the work, except at temperatures below -150. In all, the expected error was on the order of 5%; however the grouping of the readings taken indicated a greater error than this, and probably the readings cannot be trusted to be more accurate than 8%.

Discussion of Results.

The results plotted for the unstretched sample with low sulphur content show similarity to those obtained by Dauphinee and Ivey. The hysteresis loop was found to extend over a wider temperature range, and to start at higher temperatures. In this respect it shows a similarity to that found for the old samples of GR-S by Ivey. (13) Some points in the range above 40° show signs of a double value for the thermal conductivity as found by Dauphinee (12) for natural rubber. The numerical value of the thermal conductivity, it will be noticed, is very close to that found for natural rubber. These similarities are to be expected, since butyl shows similarities to both G.R.S. and Hevea in its other physical properties. Like G.R.S. it has many weak secondary linkages, and hence shows a considerable non-reversible elasticity. Like natural rubber it is capable of great elongations and crystallizes readily on stretching.

The values of the thermal conductivity for the stretched samples are about 20% lower than those for the same sample unstretched, and show the same general dependence on temperature, however the hysteresis loop has either disappeared completely, or been greatly reduced in magnitude.
This again shows agreement with the results of natural rubber and G.R.S. in which the hysteresis loop is reduced by stretching.

These measurements were made only in the direction perpendicular to the stretch, hence for the anisotropic stretched sample only one of the components of the conductivity tensor was measured. On the basis of the kinetic theory of rubber as developed by Guth (15) this decrease is to be expected. This theory uses as a model of rubber, a set of chains connected into a network by links of varying strength. Along the chain are strong molecular bonds, on the order of magnitude of those in solids, while between the chains act weak Van der Waal's forces, similar to those acting between the molecules of a liquid. The peculiar properties of rubber arise from the freedom of the molecular units in the chains to rotate about the bonds, hence the freedom of the chains to adopt various configurations in the material. When the sample is stretched these chains are lined up in the direction of strain, and the elastic forces are produced as a result of the tendency of Brownian motion to bring them back to a state of higher entropy. It seems reasonable to expect that the rate of transfer of energy down the chain would be on the order of that in crystalline solids, while that across the chains would be lower like that of organic liquids.

When the sample is stretched then, the conductivity in the direction of stretch should increase, and that
perpendicular to stress should decrease. An attempt was made to use Forbes' method to get an approximation to the conductivity in direction of stretch. Results were uncertain but indicated an increase.

The results for the sample with 10% sulphur were more difficult to explain. The hysteresis loop did not occur, and the conductivity charged much more slowly with temperature. A few points were obtained, giving twice the average value. There were too many of these to consider as accidental, but an explanation is rather difficult. The thermal conductivity of sulphur has been measured by Kaye and Higgins (16) but using the additive assumption for the effect of fillers on the conductivity does not explain the reduction in thermal conductivity at room temperature. If the results are significant, the change must be due to some modification in the structure of the polymer, and it would be interesting to find the effect of increased sulphur content on the thermal conductivity of other rubbers.

Using the value of the volume specific heat of GR - I, found by Hamil, Mrowca and Anthony (17), the value of the thermometric conductivity at room temperature is found as about $7.5 \times 10^{-4}$ cm/sec. which is in fair agreement with that found by Rehner (15).

Using the Bridgman formula (3) with values for the size of the unit cell of Butyl given by Bunn (1) and values for the sound velocity determined by the author, gives a value for the thermal conductivity of $4.3 \times 10^{-4}$ cal/deg-sec-cm.
which is about 20% too high, but is in the proper range.

In summary we may say that,

1. The thermal conductivity of Butyl decreases with temperature showing a double value at temperatures between 0°C. and -80°, that is, down to the second order transition point. The principal curve may be roughly represented by three straight lines. From -180° to -120° the thermal conductivity is roughly given by \( K = (0.5 - 0.01T) \times 10^{-4} \) from -120 to -50 it has the constant value of 2.1, and from -50 to room temperature is approximately \( 0.017 (T - 100) \times 10^{-4} \), where \( T \) is in degrees absolute. The variation of thermal conductivity with temperature does not exactly follow that of the specific heat as determined for polyisobutylene by Ferry and Parks. (19)

This is shown by the accompanying table of thermal diffusivity.

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2. The stock containing 10% sulphur showed a different variation, the conductivity changing only slightly over the temperature range. This is surprising considering the known variation in the specific heat.
3. For the stretched stock, an indefinite hysteresis loop was found, and the flat part of the curve associated with the hysteresis effect in the unstretched sample vanished.

Before too many conclusions are drawn, a more thorough study of thermal conductivity of polymers must be undertaken. This work, it is hoped, is only a small part of the experimental studies of thermal conductivity to be made at the University of British Columbia, which studies should lead to a clearer understanding of the somewhat obscure mechanism involved in heat transfer through solids.
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