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THE HEAT CONDUCTIVITY OF RUBBER AT LOW TEMPERATURES

by

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of the requirements for the degree of
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Approved

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I. INTRODUCTION

An elastomer is defined as a substance exhibiting long-range, reversible elasticity. The best known of these is, of course, rubber, the quality being so typical in its case that the rapidly expanding group of other elastomers is frequently called "synthetic rubber."

As a result of recent rubber shortages much theoretical and experimental work has been done on elastomers, but the study of their thermal conductivity is one which, to date, has received little attention. This has been due not so much to the greater usefulness of other fields of research in the understanding of the problem of elasticity as to the necessity of concentrating on production in quantity and development of the immediately-useful primary characteristics such as stretch, wear resistance and strength. It seems safe to assume, however, that with decreased stress on immediate production the study of further characteristics will play a much more prominent role.

A knowledge of thermal conductivity and the effect on it of change of temperature, amount of stretch and composition has an important bearing on many fields of both commercial and theoretical elastomer research. Examples of this are:

(a) Removal of the heat produced by constant flexing.

This is a major problem in the tire industry and in many other cases where elastomers act as shock absorbers.

(b) Obtaining homogeneous vulcanization of large masses. This requires a knowledge of temperature gradients within the mass in order to determine the distribution of sulphur required.

(c) Determination of equations of state of elastomers.

(d) Determination of the temperatures at which changes of state occur. (e.g. crystallization etc.) Changes of conductivity, coefficient of volume expansion, etc., often accompany these changes.

(e) Assistance in analyzing other long-chain hydrocarbons. The rubber molecule, because of its relatively simple structure, is easier to study than more complex molecules but behaves in a manner similar to many of them.

The theory of elasticity

Elastomers have certain properties in common, both in behaviour and molecular composition, which must be explained by any theory of elasticity. The most evident are:

(a) They exhibit long-range, reversible elasticity.

(b) They heat when stretched and cool if allowed to relax.

(c) Stress for any given degree of stretch is a linear function of temperature. For all but small stretch the stress increases with temperature.

(d) They exhibit both temporary and permanent plasticity.

(e) They harden when cold and tend to be thermoplastic at high temperature.

(f) They show crystalline characteristics at extreme stretches.

(g) They have characteristic molecular structure:

i. Very long chain molecules with many single bonds.

ii. More or less free rotation around the single bonds.

iii. Few cross bonds between molecules. The sections between cross bonds long and relatively free to move.

It is only recently that the first successful theory to explain these phenomena was put forward by Guth and Mark (1) and extended later by Guth (2), James and Guth (3) and Anthony, Caston and Guth (4). It was shown that the above characteristics could be qualitatively and quantitatively explained on the basis of a statistical model having the structure previously described. Their picture is as follows.

The elastomer molecules are long and have relatively few cross bonds. Consequently large numbers of the basic unit will be free of intermolecular ties. Since there are single bonds between the units rotation about these bonds will be possible, subject to the provision that the valence angle remain relatively constant. This quasi-freedom of

rotation means that the molecule can coil up in almost any configuration and that we might expect thermal agitation to keep the parts in constant motion.

Thus in the unstretched state the molecule would be curled up in a disordered configuration corresponding to its most probable position. If we are considering large numbers of molecules statistically it can be shown, for the case of a chain made up of successive molecules, that the probability of the ends of the chain being in a region dL at a distance L from one another is:

$$\text{Probability} = P(nN:b)\, L^2 dL = Ae^{-BL^2} L^2 dL$$

where n is the number of single bonds per molecule; N, the number of molecules in the chain; b, the length of the unit molecule (isoprene, for example, in the case of pure rubber); and $B = \frac{3}{2nN\,b^2}$. A is a normalizing constant.

By differentiation $\frac{dP}{dL} = 2AL(e^{-BL^2})(1 - BL^2)$.

This gives minima at $L = 0$ and ∞, and a maximum at $L = \sqrt{\frac{2nNb^2}{3}}$, this being the most probable length. Correcting for constant valence angle, a, we get the most probable length to be $\sqrt{\frac{2nNb_a^2}{3}}$ where $b_a = b \operatorname{Tan} \frac{a}{2}$. We note here that the straight line configuration and the case where the two ends are together are almost equally improbable.

From the above discussion we can assume that in the unstretched state the average separation of the ends is the most probable one. On stretching, the ends of the chains

would be moved from the most probable position to one less probable with the necessity of doing work. This work, in turn, is converted into increased energy of thermal agitation, with consequent increase in temperature (b)*. When the molecules are in any but the most probable state the Brownian movement tends to bring them to that state causing a constant pull on the ends and return to the original form if released (a), accompanied by cooling (b). If the substance is held in a stretched position and heated the increased Brownian movement should cause a greater pull on the ends.(c).

The plastic effects (d) are linked up with cross bonding of the molecules. If there are few bonds the molecules slip past one another easily and the substance can change form. If there are many bonds the units should hold their relative positions. Crystalization is explained on the basis of lining up of the molecules when almost straight (e).

In the statistical analysis of stress-strain characteristics the substance is compared with a gas at constant volume and the effects divided into the sum of two components; P_u, the internal energy contribution due to intermolecular forces, and P_s the kinetic energy contribution.

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* Properties explained are referred to by letter as listed on page 2.

By comparison with Van Der Waal's gas equation (4)

$$(p + \frac{a}{V^2})(V - b) = RT$$

or $$p = -\frac{a}{V^2} + \frac{RT}{V - b}$$

Compare $p = P_u + P_s$.

By analysis of this and other thermodynamic relations (3) explanations have been given for inversion points in the stress temperature curves (c) and the typical, S-shaped, stress-strain curve shown by all elastomers.

Thermal Conductivity

The theory of thermal conductivity of elastomers is practically an untouched field. Since they exhibit properties of solids, liquids, and even gases they could be expected to exhibit conductivity properties of all three. There would almost certainly be a high proportion of conduction by interbombardment of the Brownian type. In addition some conduction could be expected due to transfer of energy along the length of the molecule through the bonds. Cross conduction by means of intermolecular bonds would be expected to increase with vulcanization while thermal bombardment would decrease because of reduced freedom of motion. No statistical treatment of this problem has been made to date.

Methods of Measuring Conductivity

The principle of measurement of conductivity is the same for all methods, i.e. to measure the quantity of heat passing through given cross section of material with a given

temperature gradient across it. The definition of thermal conductivity (10) is - "The time rate of transfer of heat, by conduction, through unit thickness, across unit area for unit difference in temperature." In the calculation of the amount of heat transferred in any system of units the coefficient of thermal conductivity occurs as a proportionality factor, and can be defined by the equation

$$Q = Kt. \frac{A(T_2 - T_1)}{d}$$

or

$$K = \frac{Q}{t} \cdot \frac{d}{A} \cdot \frac{1}{T_2 - T_1}$$

where K is the coefficient of thermal conductivity; Q, the quantity of heat transferred; A, the cross-sectional area; T_1 and T_2, the temperatures on either side; d, the thickness; and t, the time. In c.g.s. units K has the dimensions (Cal. $Sec.^{-1}$ $Cm.^{-1}$ $Deg.^{-1}$).

Methods of measuring conductivity fall into three main classes.

(a) Measurement of rates of cooling. One such method (5) consisted of measuring the rates of cooling at the centre of large rubber spheres kept in a constant temperature chamber. It has the disadvantage that it actually measures the quotient $\frac{K}{Cd}$, where K is the thermal conductivity; C, the specific heat; and d, the density.

(b) Measurement of heat carried through to the low temperature side.

i. Measurement of the rise in temperature of a liquid or solid absorbing the heat transferred. This may be done by measuring the rise per unit time, or by measuring the rise in temperature when a constant flow of liquid passes through the apparatus.

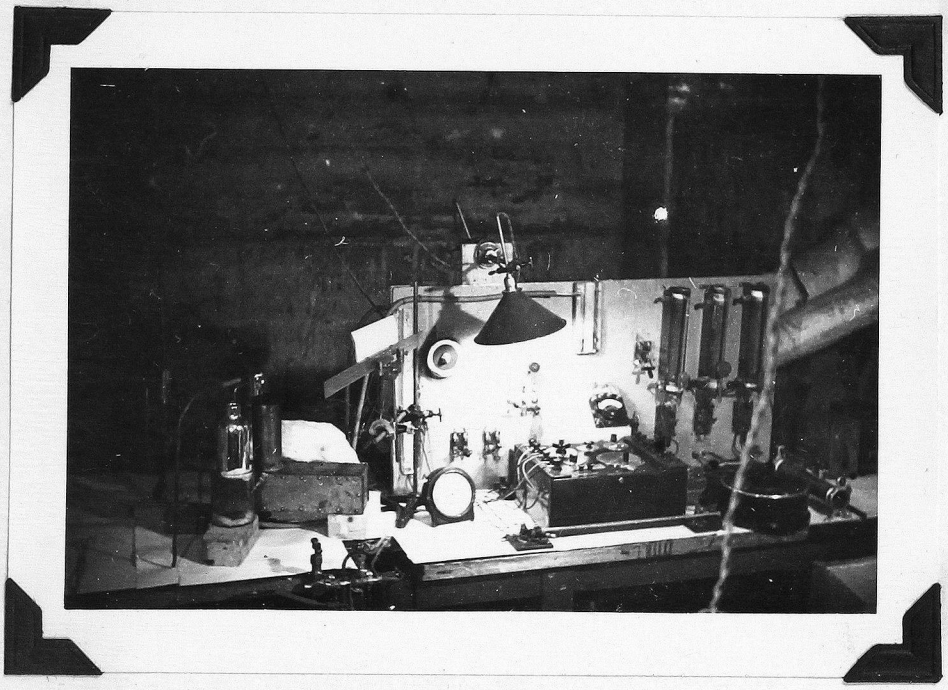
ii. Measurement of the rate of evaporation or melting caused by the heat transferred. One experiment of this type (6) consisted of measuring the quantity of nitrogen evaporating from a bag of the substance to be measured when the bag was immersed in liquid oxygen.

This method is most suitable for high conductivities or large surfaces, otherwise the amounts become unmeasurable.

(c) Measurement of the quantity of heat required to maintain a constant temperature gradient. (7), (8). This method is the one used in the experimental work herein described.

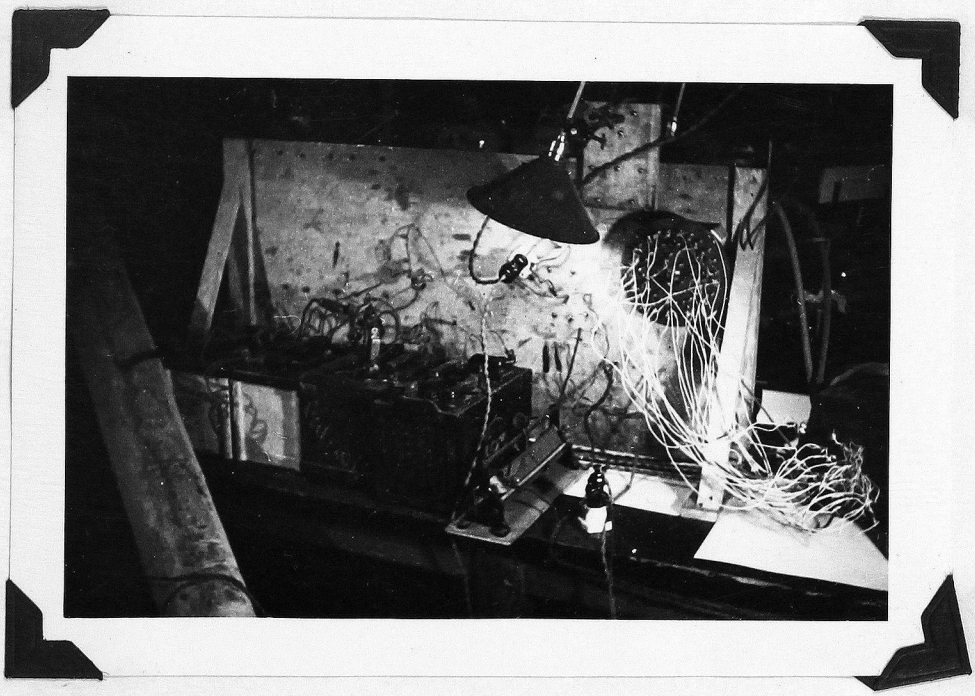
PLATE I

(a)



Front view of apparatus showing relative positions.

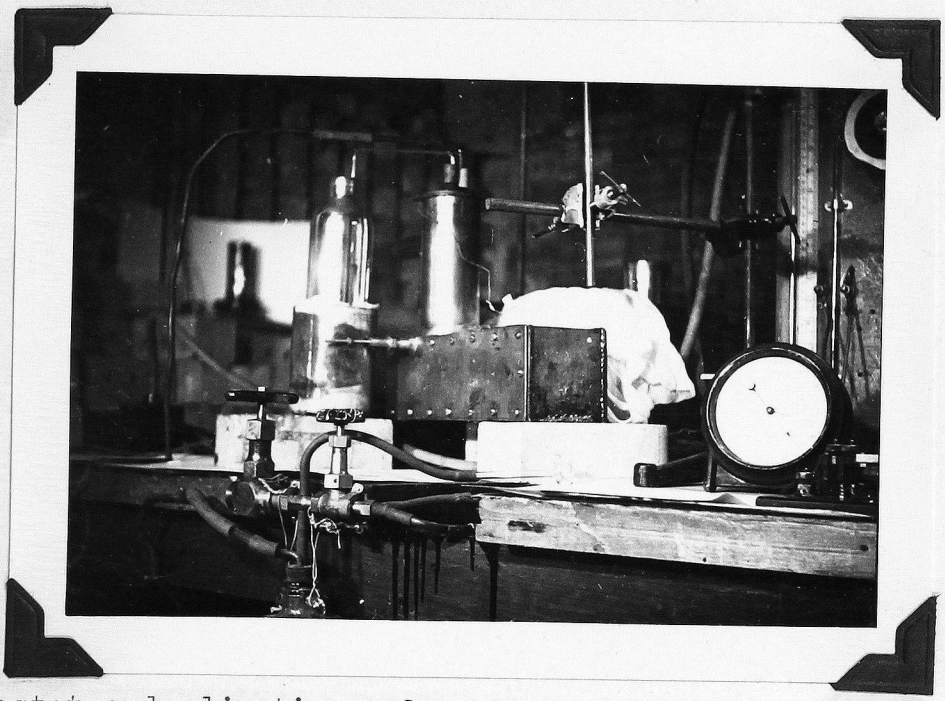
(b)



Back view of apparatus showing multiple switch.

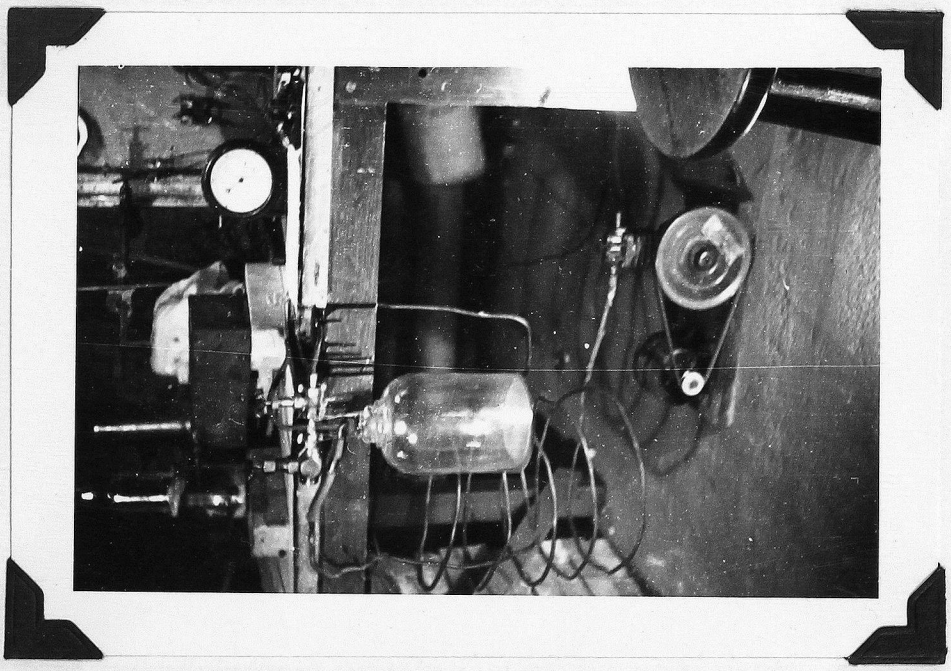
PLATE II

(a)



The cryostat and adjusting valves.

(b)



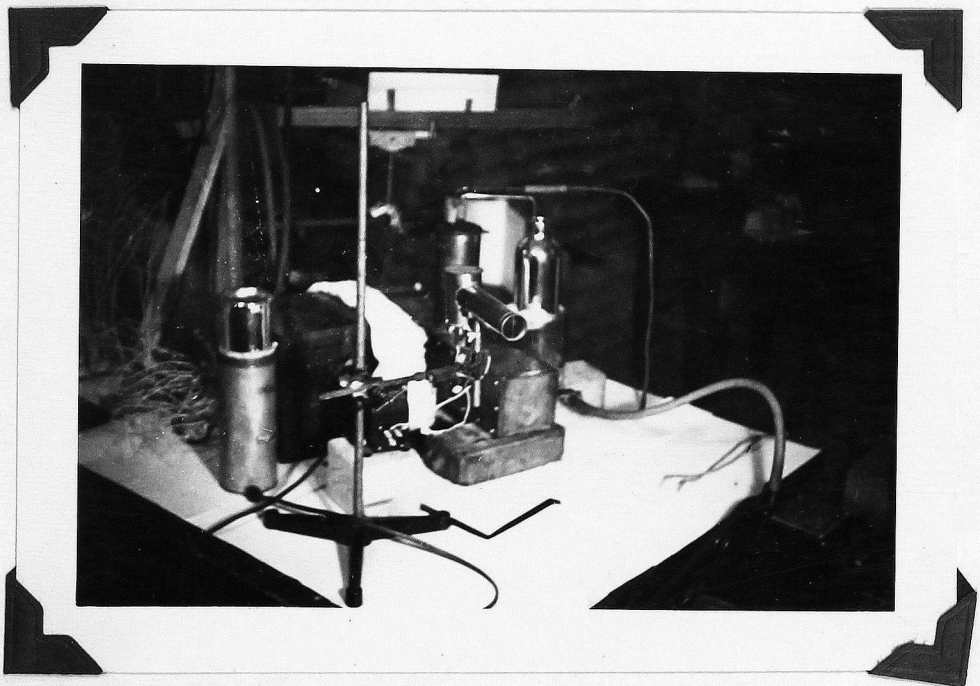
The cooling system showing valves, cooling coils and compressor.

PLATE III

(a)

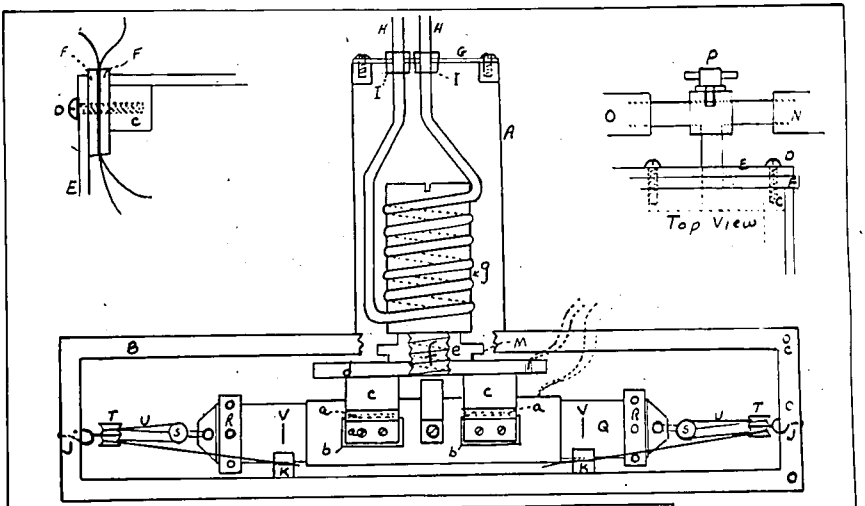
A close-up view of measuring circuits.

(b)



Cold junction, zone box and spotlight.

PLATE IV



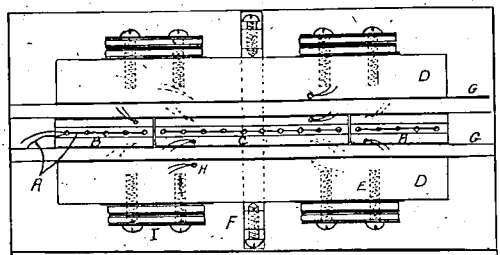
THE CRYOSTAT AND ITS CONTENTS

II. EXPERIMENTAL

The cryostat and evacuation circuit (Plate IV)

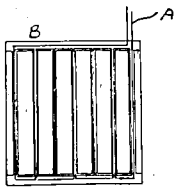
In order to properly insulate the apparatus at the low temperatures at which the experiments were conducted it was necessary to construct a cryostat that could be evacuated, to provide inlets and outlets for cooling tubes, thermocouples and evacuation apparatus, and at the same time provide reasonable facilities for adjustment of the degree of stretch. This was accomplished by the unit shown on Plate IV. The sides of the cryostat were made of 1/8 in. brass plate, as was the cylindrical tower, A, containing the cooling unit. The top of the tower and the sides of the cryostat were faced with 1/2 in. wide brass flanges, B, with tapped holes, C, part way through for studs, D, which held the side plates, E, (also constructed of 1/8 in. brass) in place. Between these pieces and the flanges where rubber gaskets, F, held in place on one side by glyptol and sealed on the other with stopcock lubricant. The thermocouples were led into the cryostat through a double gasket (see small diagram) on one side which insulated them from the metal. The cover plate, G, of the tower had two holes for cooling tube outlets, H; the seal around them being accomplished by means of rubber stoppers, I, and stopcock lubricant. At each end of the cryostat was a

PLATE V

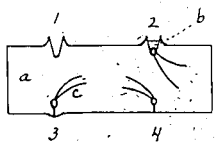


THE CONDUCTIVITY MEASURING UNIT

Bottom view. Thermocouples leading away from the bottom are shown by solid lines, those on top are shown by dotted lines.



Method of wiring central heating blocks.



Installation of thermocouples

a. Copper block.
b. Glyptol.
c. Thermocouple.

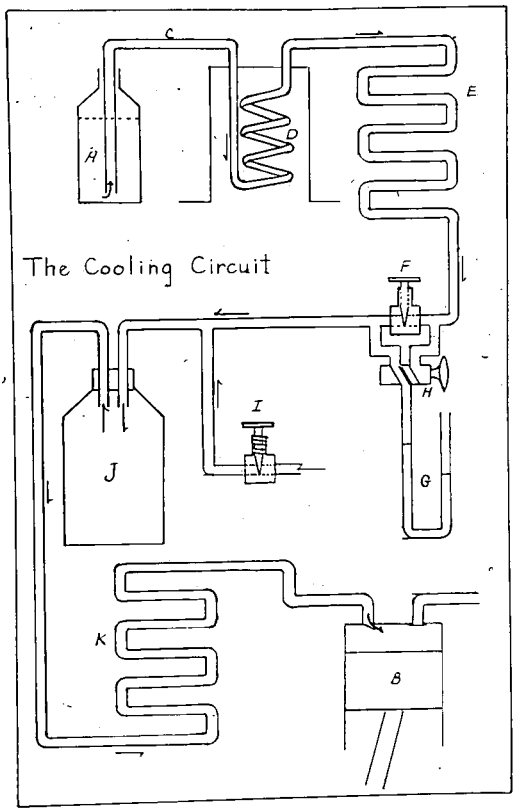
hook, J, to which the stretchers were attached, and at the front (inside) were thumbscrew clamps, K, to hold the stretcher cords. Suspension of the main apparatus was accomplished by bakelite supports (not shown in the diagram) which fitted under the lip, M, of the cooling unit. The cryostat was evacuated by means of a Cenco Hyvac pump through the outlet, N, and pressure was measured by a small manometer attached to tube, O. The small screw, P, was used to let air into the cryostat when necessary.

The conductivity measuring apparatus (Plates IV, V, VI - 5)

This apparatus was modelled after Schallamach's (8) apparatus for measuring conductivity at low temperatures, with very considerable revision to allow for stretching experiments and the consequent increase in the amount of heat to be absorbed. The heat was generated in resistance wire, A, (Plate V) which was threaded through holes in the copper heating blocks, B and C. The central block, C, was 4 cm. long, 3.2 cm. wide and .6 cm. thick while the blocks, B, were each 2 cm. long and the same width and thickness. The outside copper blocks, D, were tapped for studs, E, (to hold the heat leads, I, securely in place). Clamp, F, pressed the whole unit tightly against the two rubber pieces, G, to ensure good contact. A total of twelve thermocouples were attached to the blocks as shown in the diagram at H. The method of installing is also shown on Plate V (bottom).

The method by which the thermal conductivity was

PLATE VI



measured can readily be seen. Electrical energy was converted into heat in the heating blocks and the only path for the heat to follow was through the rubber strips. Heat would flow only when there was a temperature drop across the rubber. The temperature drop was measured by means of the thermocouples and this, along with the amount of heat produced and the dimensions of the rubber, was sufficient to determine the conductivity. The inner heating block, C, was the one used for actual measurements; the outside heating blocks, B, served the purpose of a guard ring to prevent conduction laterally along the rubber.

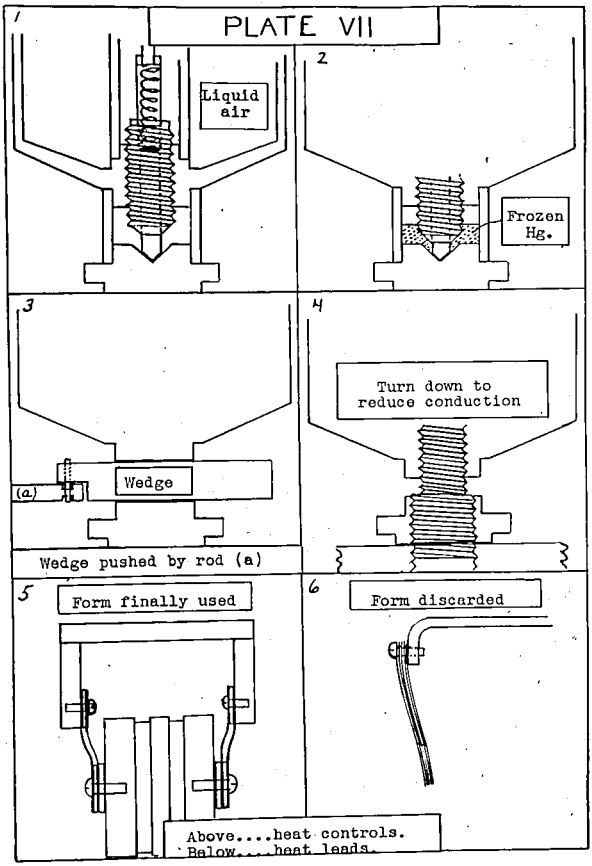
The stretchers (Plate IV)

The rubber strips, Q, were clamped securely at each end by means of clamps, R (Plate IV), to which were attached small pulleys, S. Other pulleys, T, were attached to the hooks, J, at each end of the cryostat. The pulley arrangement was threaded with strong cord, U, giving a mechanical advantage of three. When stretching was completed the ends of the cords were held by thumbscrews, K. Two lines, V, marked on the rubber, served as markers and stretch was calculated by measuring between them.

Heat Leads and cooling circuit (Plates IV, V, VII)

The heat that passed through the rubber strips, as well as any heat that was carried to the apparatus by the strips and by radiation from the side walls, was carried away through thin flexible double strips of 1/32 in. copper, 1 in. wide, a (Plate IV). Pieces of aluminum foil, b, between these

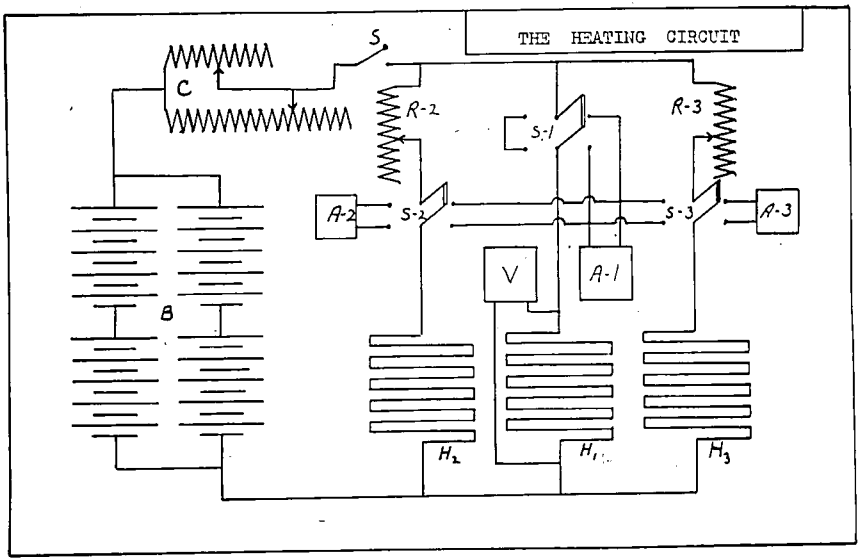
PLATE VII


1
Liquid air
2
Frozen Hg.
3
Wedge
(a)
Wedge pushed by rod (a)
4
Turn down to reduce conduction
5
Form finally used
6
Form discarded
Above....heat controls.
Below....heat leads.

and the main blocks ensured good heat contact. The thin strips were soldered and bolted to rigid 1/4 in. copper leads, c, which carried the heat to the top piece, d, also of 1/4 in. copper. At the centre of the top piece was a raised part, e, with a lip, M, to support the unit, and an internal thread into which the threaded end, f, of the solid copper core of the cooling coil, g, was screwed. The outer part of the core had a spiral groove turned in it, and after the cooling coil was wound into the groove it was soldered in place. An end view of the heat lead system is shown in Plate VII-5.

Cooling was accomplished by the circuit shown in Plate VI. The vacuum flask, A, was filled with liquid oxygen which was drawn through the circuit by a small compressor, B, operated as a suction pump. From the vacuum flask, a mixture of gaseous and liquid oxygen was drawn through a thin, insulated, glass tube, C, to one end of the cooling coil, D, in the cryostat. Here the remaining liquid oxygen was evaporated by the heat carried up from the main unit. From the coil the gaseous oxygen was drawn through a warming coil, E, and thence to a needle valve, F, which regulated the amount of oxygen drawn through. The manometer, G, was equipped with a two-way stopcock, H, and could be used to indicate the amount of vacuum on either side of the valve, F. In close proximity to valve, F, was a second needle valve, I, used to permit air to enter the circuit. This valve served the double purpose of decreasing the vacuum against which the compressor worked and

PLATE VIII



of reducing the concentration of oxygen, and consequently the danger of explosion. (The compressor was oil-lubricated). From this valve, I, the mixture was drawn into a carboy, J, which served to cut down fluctuations caused by the compressor, thence to a second warming coil, K, on to the compressor, B, and out into the air.

The method described above is by no means the first one that was employed. The original method of heat control used by Schallamach (8) was tried but found inadequate to carry the greater amounts of energy required for this apparatus. Diagrams of this and three other methods tried, as well as the original type of heat lead, are shown in Plate VII. All of these methods had the disadvantage of requiring a liquid air container within the apparatus. The method shown in fig. 4 was the most successful of all as far as control was concerned, but failed to reach sufficiently low temperatures.

The heating circuit (Plate VII)

Power for the three central heating coils of the main unit, H-1, H-2, H-3. (Plate VII) was supplied by four 6-volt storage batteries, B, arranged to give 12 volts across the unit as shown in the diagram. Control of the whole was provided by a master switch, S, and a 40 ohm variable rheostat, C, with a 380 ohm rheostat in parallel for fine adjustment. The circuit was then divided into three parts. Part 1 led directly to a double-pole, double-throw switch, S-1, connected

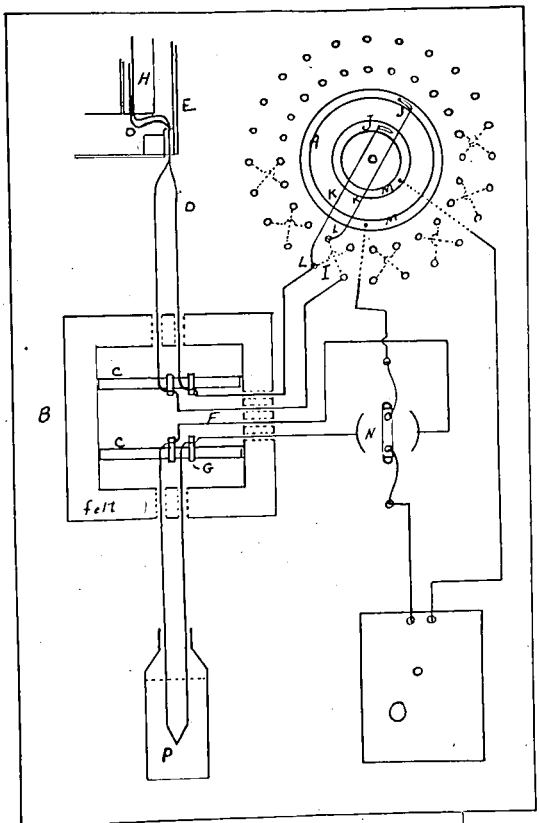
to make it possible to shut off the circuit, get a direct connection through, or put a 0 - 600 m.a. milliammeter A- 1 in series. From the switch the circuit went directly to the cryostat and the central heating coil, H-1, and then back to the batteries. The potential difference across the heating coil was measured by means of a 0 - 5 volt voltmeter, V, graduated to 1/30 volt. Branches 2 and 3 of the heating circuit were identical. Each had a 40 ohm rheostat, R - 2, R - 3, to give individual control, followed by a double-pole, double-throw switch, S -2, S - 3, which made it possible to put in series a small milliammeter, A - 2, A - 3, or, for accurate readings, ammeter A - 1. From the switch each circuit ran to one of the other heating blocks, H - 2, H - 3, and back to the batteries.

The thermocouple circuit (Plate IX)

Considerable difficulty was encountered in setting up a satisfactory thermocouple circuit. The thermocouple pyrometer is by far the best instrument for this type of work because of its negligible heat capacity, small size, small time lag and flexibility, but its operation requires great care if accurate results are to be attained.

Contact potentials made it necessary to design a circuit completely of copper except for the copel element of the copper-copel thermocouple and the potentiometer terminals which could not be changed. Copper strips were placed over all contacts, thumbscrews, etc., to make a complete cir-

PLATE IX



THE THERMOCOUPLE CIRCUIT

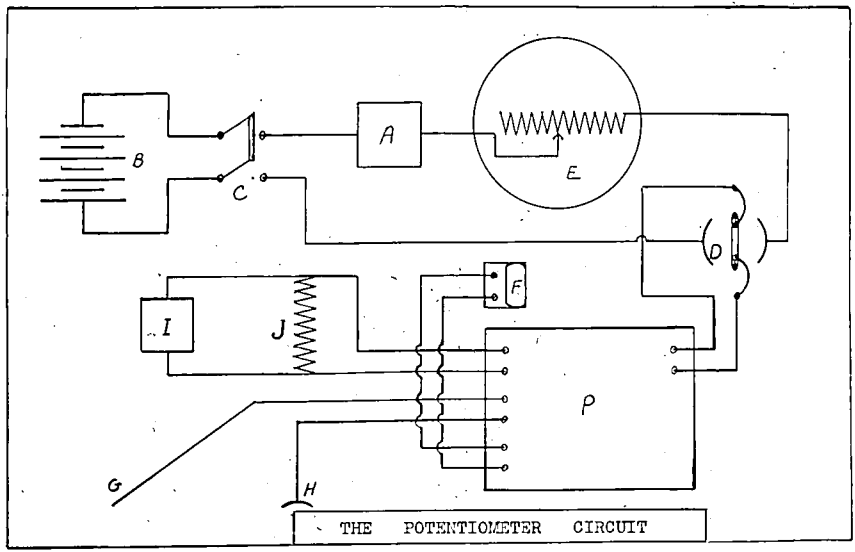
cuit and an all-copper multiple switch, A, was made to replace the radio switch first used.

To check for stray e.m.f's. in the switches and potentiometer the circuit was made completely reversible, even to the current in the potentiometer. This was accomplished by placing ordinary reversing switches with copper strips over the brass parts in the cold junction and the potentiometer power circuit, and connecting the two by means of a rod to make them move as one. In addition the multiple switch, A, (Plate IX) had a double set of contacts to reverse the hot junctions.

The circuit ends of the thermocouples and cold junction were kept at the same temperature by running them into a felt-lined zone box, B, with free space inside about 6 in. each way. There, the ends were wound around copper leads and clamped tight with thumbscrews on two vertical panel boards, C.

The hot junctions of the twelve thermocouples were fastened in grooves in the heating blocks, H, the leads, D, taken out between the gaskets of the cryostat, E, and into the zone box, B. The ends of the thermocouples were wound around the copper leads, F, and clamped tight on the panels, C, by means of thumbscrews, G. The copper leads were taken directly to the large multiple reversing switch, A. By wiring the two rings of contacts in pairs, as shown in the diagram at I, the reversing of the thermocouples was secured. Spring contacts, L, covered

PLATE X



with copper, were connected by means of copper strips, K, and other spring contacts, J, to copper rings, M, from which one lead went directly to the reversing switch, N, and the other went to the potentiometer, O, and thence to the other contact of the reversing switch. From the reversing switch leads were taken back to the zone box where the ends of the cold junction were attached. The cold junction, P, was immersed in an ice bath.

The potentiometer circuit (Plate X)

Power was supplied for the potentiometer by a 2 - volt storage battery, B (Plate X). One side of the circuit was taken direct from the double pole switch, C, to a reversing switch, D. The other side was taken first to an ammeter, A, then to an oil-immersion, slide-wire rheostat, E, with a fine adjustment and on to the other side of the reversing switch. The other terminals of the switch were connected directly to the potentiometer, P. An Eppley standard cell, F, (P.D. = 1.01890 volts) was used to set the potentiometer. The e.m.f. terminals were connected as described in the thermocouple circuit to the multiple switch, G, and the cold junction reversing switch, H. A Leeds and Northrup mirror galvanometer, I, sensitive to less than 10^{-7} volts was used with a 600 ohm damping resistance, J, in parallel. Light for the mirror was supplied by a small spotlight and reflected to a translucent scale near the instrument panel.

The potentiometer itself was a Weston model having three ranges with sensitivities of 10^{-5}, 10^{-6} and

10^{-7} volts, respectively. Since the 10^{-6} volt range was sufficient for this work it was used throughout.

Calibration and installation of thermocouples

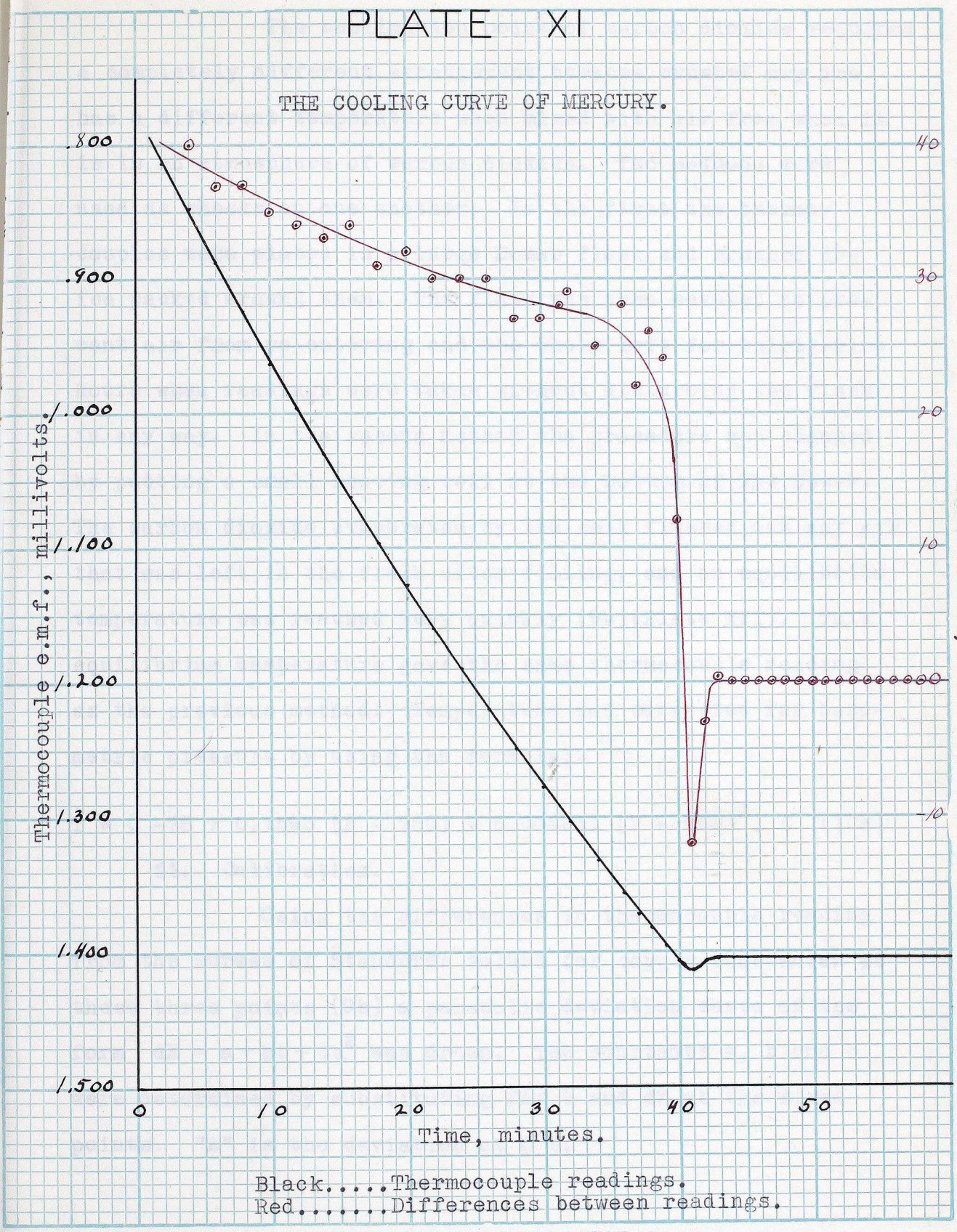
i. Fixed Points.

Three fixed points were used in calibration, the freezing point of water, the freezing point of mercury and the sublimation point of CO_2. The ice point was obtained was obtained by immersing the thermocouples in a bath of crushed ice and water in a vacuum flask. At no time was any measurable change in the ice point noticed. This is to be expected, as the ice point is easily reproducible to 1/1000 °C. (9a)

The mercury used for the mercury freezing point had been redistilled by the Chemical Engineering department of the University of British Columbia and seemed to be of good purity. When a cooling test was made the freezing point proved to be very sharply defined, and could be maintained constant to the nearest microvolt (1/30 °C.) for over an hour. (Plate XI)

When calibrating in mercury the blocks and the thermocouples were coated with Duco Cement to prevent amalgamation, and held well below the surface of the mercury. The mercury container was placed in dry ice. Readings were taken as the mercury cooled and the freezing point was considered reached when there had been no difference in thermocouple readings for fifteen minutes. When the freezing point was reached the remaining thermocouples were checked repeatedly.

PLATE XI



NO. S 36 GRAPH PAPER. SMITH DAVIDSON & WRIGHT, LTD.

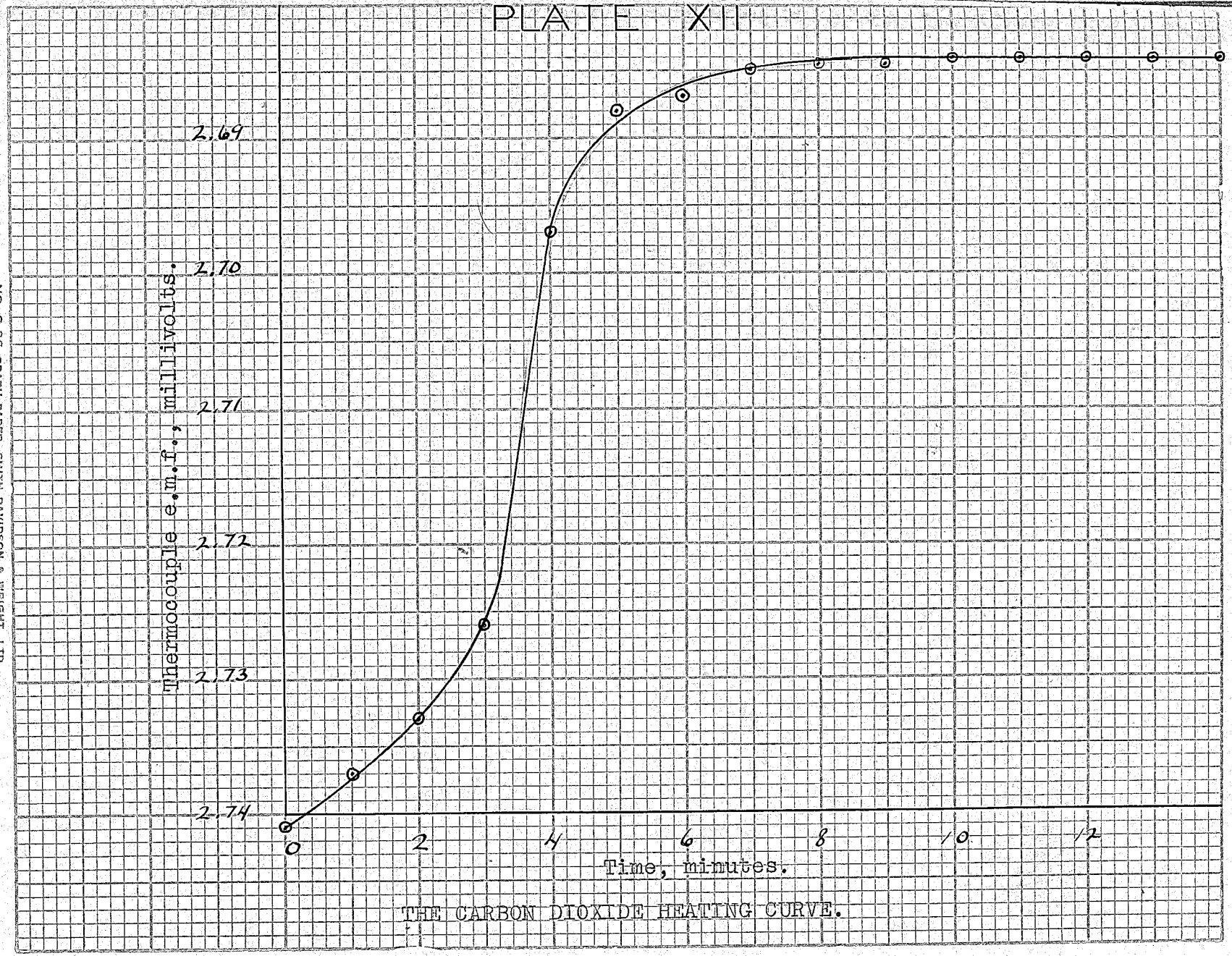
The sublimation point of carbon dioxide required a completely different arrangement because crushed dry ice has a different temperature when mixed with air from when it is in an atmosphere of carbon dioxide. Two methods were used as checks on one another. In the first the thermocouples were placed in a large Dewar flask and crushed dry ice packed around them. The flask was then covered to prevent air from re-entering and the whole left for thirty-nine hours when readings were taken without disturbing the flask in any way. In the second method the procedure was changed by putting a small heating coil at the bottom of the Dewar. The carbon dioxide evaporated by the coil flushed out any air that was left in the flask after filling, and an equilibrium temperature was reached very quickly (9b)(Plate XII). This equilibrium temperature gave the same thermocouple reading as the previous method. Temperature was corrected for barometric pressure by using the formula:-

$$T = (-78 + 0.1595 (P - 760) - 0.000011 (P - 760)^2) \ C \quad (10a)$$

ii. Calibration.

Using the differences in thermocouple reading from the Bureau of Standards values for copper-constantan at these three points (9b) a parabolic deviation curve of the form $dE = a + bt + ct^2$ was drawn. The constants a, b and c were determined by substituting for t and dE at the fixed points. "A" is the deviation at 0°C.

PLATE XII



THE CARBON DIOXIDE HEATING CURVE.

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$$b = \frac{(dE_1 - a)t_2^2 - (dE_2 - a)t_1^2}{t_1 t_2 (t_2 - t_1)}$$

$$c = \frac{(dE_2 - a)t_1 - (dE_1 - a)t_2}{t_1 t_2 (t_1 - t_2)}$$

With this graph and the standard copper-constantan tables (9b) any temperature could be calculated.

When two thermocouples had been calibrated in this manner the remaining ones were compared with them at various temperatures using a mixture of alcohol and dry ice in a vacuum flask. Dry ice was packed around the outside of the flask to prevent any rise in temperature, and rock wool around the whole to insulate it. By this means graphs of deviation from the previously calibrated thermocouples were drawn for each of the remaining ones. It was found that because of the fact that all thermocouples were made from the same piece of Copel wire most deviations were very small and almost independent of temperature, apparently being chiefly due to individual contact potentials in the zone box or leads.

iii. Installation.

The thermocouples were set into the blocks by making a groove from the edge of the block with a fine cold chisel. (Plate V) This groove was filled with glyptol and the thermocouple inserted in it. The raised edges of the groove were then pounded down over the wires and the surface filed and sandpapered smooth again. In this manner it was possible to get the thermocouples very close to the surface

and yet keep the surface perfectly smooth and so ensure good contact.

The method of taking readings

The procedure in taking readings was as follows. (using the case where the desired temperature is lower as an example).

1. The oxygen valve was turned on full to make the apparatus cool quickly.
2. When the required temperature was almost reached the oxygen was turned off and heat turned on full to stop the cooling.
3. As soon as the temperature drift was slowed down the oxygen valves were manipulated until an almost stationary state was reached.
4. By adjusting the current in the heater coils the temperature drift in the outside blocks was completely stopped.
5. As soon as the outer blocks were stationary the current in the heater blocks was adjusted to give constant temperature in them as well.
6. The temperatures of the two small heater blocks (guard blocks) were compared with the temperature of the centre one and adjusted until very nearly the same.
7. Both outer and inner blocks were checked for drift of temperature, and if there was any it was stopped.

8. When the temperature was stationary everywhere readings were taken of the current and voltage of the centre block.

9. Two complete sets of readings were taken of the thermocouples. If, during the course of a set of readings, there was a drift of more than one microvolt the system was readjusted and all readings repeated.

10. Current and voltage were again read. In any appreciable change occurred all readings were repeated.

This process required on the average around forty minutes to complete, provided that the apparatus was running well. The fastest time for any reading was twenty minutes. Because the heating coils could only carry a limited current the readings taken for rising temperature required an hour or more.

Readings taken

Many preliminary readings and test runs were made before the actual final readings were taken. Almost at once it became obvious that the apparatus was not reaching sufficiently low temperatures. The original design was intended for use down to about -100 °C, but because of the much larger size and heat capacity of the main unit considerable changes had to be made before the heat removing system would

reach that temperature.

After more readings were taken it became apparent that much lower temperatures would be needed to overcome supercooling effects and the cooling unit was redesigned to the form finally used. (Plate IV, V, VI) It is with this form that all the final readings were taken.

Readings were taken for increasing and decreasing temperatures in the range from -170° C. to +40° C. and for 0%, 50% and 100% stretch. After the 0% and 50% stretch readings were completed it became apparent from 100% stretch results that more readings would have to be taken to check parts of the results. This was done for both 0% and 50% stretch with the result that readings formerly thought to represent experimental errors were shown to fit into the general pattern.

For each degree of stretch measurements of the rubber were taken using a pair of thin calipers for width. Thickness was determined by measuring with a micrometer the total thickness of the blocks with no rubber between and again when the strips were stretched in place.

In all cases the actual measurement of conductivity was based on the centre heating block. The outer blocks were used only to prevent lateral conduction. In this way edge effects were eliminated. Since the only surface of the inner block that was exposed to radiation from a warmer surface was the bottom edge extraneous heat sources were neglected.

III. RESULTS

The equation and method of calculation

The equation of thermal conductivity, as shown previously, can be put into the form:-

$$K = \frac{Q}{t} \cdot \frac{d}{A} \cdot \frac{1}{T_2 - T_1}$$

where Q is the amount of heat transferred; t, the time; A, the area of the conducting surface (assuming here that opposite faces are parallel); d, the thickness; and $T_2 - T_1$, the temperature difference between the two faces.

We may think of K as consisting of three factors, namely: a power factor, $\frac{Q}{t}$; a dimension factor, $\frac{A}{d}$; and a temperature factor, $\frac{1}{T_2 - T_1}$ or $\frac{1}{dT}$. The determination of each factor required a separate set of readings.

i. Power factor.

To determine the power factor it was necessary to find what proportion of the electrical energy was used up in the heating coil itself. Using subscripts C, v, a, l to represent coil, voltmeter, ammeter and leads respectively we have;-

$$I_c = I_a - I_v = I_a - \frac{V_v}{R_v}$$

$$V_c = V_v - I_c R_1$$

$$\text{Power} = P = I_c V_c = (I_a - \frac{V_v}{R_v})(V_v - I_c R_1) \quad \text{watts.}$$

$$= I_a V_a - \frac{V_v}{R_v} - I_a I_c R_1 + \frac{V_v I_c R_1}{R_v} \quad \text{watts.}$$

Ignoring the slight difference between I_c and I_a for small corrections, and using the relations

$$V_v = V_v I_a (R_c + R_1) \quad \text{and} \quad I_a = \frac{I_a V_v}{(R_c + R_1)},$$

$$P = I_a V_v \left(1 + \frac{R_1}{R_v} - \frac{R_c + R_1}{R_v} - \frac{R_1}{R_c + R_1}\right) \quad \text{watts.}$$

where $R_1 = 0.14$ ohms; $R_v = 300$ ohms; $R_c R_1 = 5$ ohms.

$$\text{Thus} \quad \frac{Q}{t} = 0.954 \; I_a V_a \quad \text{watts.}$$

$$= 0.228 \; I_a V_a \quad \text{Calories/second.}$$

ii. Dimension factor

The dimension factor is easily obtained from the measurements taken. Calling the width of the strip of rubber, w; the total thickness of rubber as measured, 2d; and putting in the length of the central heating block, 4.01 cm., the dimension factor becomes $\frac{d}{A} = \frac{d}{2 \times 4.01 \times w}$.

This factor varied slightly each time the rubber was put in, but was always between 0.0073 and 0.0079.

iii. Temperature factor.

The readings of all the thermocouples on the inside block were corrected to correspond to the one used as the original standard, and then averaged. The deviation graph was then used to convert it to the Bureau of Standards copper-constantan tables (9b) and the temperature calculated by interpolation.

Substituting F for the dimension factor and correcting for lead resistance the following expression for conductivity is obtained.

$$K = \frac{0.228\ IV \cdot F}{T_2 - T_1} \qquad \frac{Cal.}{Sec.\ Cm.\ Deg.\ C.}$$

Probable error

The absolute determination of temperature does not need to be as accurate as the difference in temperature between the two sides of the material. Since the readings are taken over a temperature interval of around 8 °C the reading is only an average determination over that range. For graphing purposes the nearest degree to the middle of the range was chosen. As the rate of change of conductivity in most parts of the curve is less than $0.01 \times 10^{-4}/°C$. this introduces an error of less than 0.5%.

In the determination of the dimension factor it is difficult to tell to what extent the volume of the rubber changed in stretching. However, since in the two cases where two dimension factors were obtained for the same degree of

stretch the change was approximately 1/80, or 1.2%. This could be due partly to an increase in length after being stretched of 0.6% and also to slight differences in the degree of stretch.

Measurement of the degree of stretch was complicated by the fact that the strips were compressed on the sides. There was a very slight widening of the strip (less than 1%) caused by the clamping of the blocks. However, this was accounted for in the dimension factor, and because of the small changes caused by the amount of stretch would have little effect. As far as any one set of readings was concerned this would have no bearing on relative values.

The accuracy of determination of the temperatures difference is hard to estimate. The original calibration of thermocouples should be accurate at least to $\pm$ 2 microvolts, and since the readings were the result of averaging four thermocouples, and at no time was any significant difference of temperature throughout the copper blocks noted, the maximum e.m.f. error in each case should be less than 3 microvolts. This gives a maximum error in temperature difference of less than 2% of an 8 °C. interval.

The ammeter and voltmeter were tested and calibrated beforehand and during the tests proved to have a maximum error of less than 0.5%. Consequently, with correction for lead resistance (around 5%) the power factor should be reliable to within 1%.

Using the generally accepted approximations for specific heat of rubber and copper, it can be shown that a temperature drift of 1/30°C. per minute, (Corresponding to 1 microvolt/min.) corresponds to an absorption or emission of power amounting to less than 0.5% of the power input. Since all readings were taken for a drift less than 1 microvolt/min. this factor is not important. Experimentally it was found that very small changes in the power supplied would cause noticeable drift.

The total of these factors gives a maximum error of 5%, or a change in K of approximately 0.15×10^{-4}.

The rubber sample

The sample of rubber used was one of a group of samples obtained from the University of Notre Dame. It was prepared under carefully controlled conditions to make it possible for research to be done on rubber similar to commercial brands, and of exactly known composition.

The sample was prepared to the following specifications.

pure latex	100 parts		
carbon black	---		
zinc oxide	3		
stearic acid	4	Length of cure	120 min.
pine tar	2		
sulphur	2.7	Temperature of cure	274°F.
antioxidant	1.5		
captax	0.9		

This rubber was intended to be roughly comparable to standard tread stock with the exception that 50 parts of carbon black were omitted. Its measured properties

TABLE I

NORMAL LENGTH

TC_1	TC_2	T_1	T_2	T_1-T_2	V	I	P	$Fx10^3$	Av.T	$Kx10^4$
mv.	mv.	°C.	°C.	°C.	volts	amps.	Cal/sec.	Cm^{-1}	°C.	
-1.084	- .875	27.34	22.17	5.17	2.30	.458	.240	7.84	+ 25	3.64
- .394	- .316	10.10	8.13	1.97	1.33	.264	.080	"	+ 9	3.19
.005	+ .272	- 0.13	- 7.15	7.02	2.63	.526	.316	"	- 4	3.53
-1.417	-1.161	+35.36	+ 29.20	6.16	2.53	.503	.290	"	+ 32	3.68
.516	.718	- 13.65	- 19.13	5.48	2.23	.446	.228	"	- 16	3.26
.965	1.248	- 25.90	-.33.86	7.96	2.70	.545	.336	"	- 30	3.22
1.490	1.643	- 40.81	- 45.27	4.46	1.89	.375	.161	"	- 43	2.84
1.904	2.041	- 52.99	- 57.16	4.17	1.57	.313	.112	"	- 55	2.10
2.314	2.465	- 65.59	- 70.35	4.76	1.91	.383	.167	"	- 68	2.74
2.554	2.867	- 73.20	- 83.43	10.23	2.93	.587	.393	"	- 78	3.01
2.661	2.825	- 76.65	- 82.06	5.41	2.07	.414	.195	"	- 79	2.83
3.540	3.740	-106.95	-104.42	7.47	2.27	.504	.260	"	-111	2.73
3.645	3.903	-110.86	-120.66	9.80	1.85	.373	.151	"	-116	1.21
3.543	3.768	-107.08	-115.47	8.39	2.49	.499	.283	"	-111	2.64
3.766	4.036	-115.39	-125.92	10.53	2.82	.572	.368	"	-120	2.74
2.965	3.139	- 87.74	- 92.69	5.95	2.03	.407	.187	"	- 90	2.49
3.218	3.613	- 95.44	-109.67	14.23	2.27	.453	.234	"	-102	1.29
3.726	3.842	-113.89	-118.31	4.42	1.64	.331	.124	"	-116	2.20
3.811	3.943	-117.12	-122.24	5.12	1.70	.343	.133	"	-120	2.04
3.836	4.076	-118.08	-127.52	9.44	2.64	.531	.320	"	-123	2.66
3.927	4.066	-121.61	-127.12	5.51	1.87	.378	.161	"	-124	2.30
3.966	4.225	-124.32	-133.63	9.31	2.53	.506	.292	"	-129	2.46
4.427	4.580	-142.22	-149.00	6.78	1.98	.399	.180	"	-146	2.08
4.058	4.341	-126.80	-138.51	11.71	1.88	.377	.161	"	-132	1.08
3.786	4.034	-116.15	-125.84	9.69	2.57	.514	.301	"	-121	2.44
3.559	3.783	-107.67	-116.04	8.37	2.43	.490	.272	"	-112	2.54
3.458	3.658	-103.96	-111.33	7.37	2.30	.462	.242	"	-107	2.58
3.101	3.320	- 91.38	- 99.00	7.62	2.43	.481	.266	"	- 95	2.74
2.839	3.041	- 82.50	- 89.32	6.82	2.27	.454	.234	"	- 86	2.70

TABLE I (cont'd)

TC_1	TC_2	T_1	T_2	T_1-T_2	V	I	P	$Fx10^3$	Av.T.	$Kx10^4$
mv.	mv.	°C.	°C.	°C.	volts	amps.	Cal/sec.	Cm^{-1}	°C.	
2.468	2.718	- 70.45	- 78.52	8.07	2.54	.508	.294	7.84	- 74	2.86
2.195	2.393	- 61.88	- 68.06	6.18	2.23	.446	.227	"	- 65	2.88
1.792	2.109	- 49.64	- 59.23	9.79	2.80	.575	.367	"	- 54	2.94
1.492	1.755	- 40.84	- 48.56	7.72	2.67	.533	.324	"	- 45	3.28
3.829	4.209	-117.81	-132.95	15.14	2.87	.578	.378	7.75	-125	1.94
4.186	4.515	-132.00	-146.09	14.09	2.67	.589	.358	"	-139	1.97
4.516	4.798	-145.87	-159.18	13.31	3.03	.613	.423	"	-152	2.46
4.800	5.017	-159.28	-170.05	10.77	2.50	.504	.287	"	-165	2.06
4.363	4.662	-139.44	-152.74	13.30	2.53	.509	.294	"	-146	1.71
3.898	4.248	-120.47	-134.59	14.12	2.63	.530	.318	"	-127	1.74
3.330	3.762	- 99.47	-115.34	15.87	2.87	.577	.378	"	-107	1.85
2.764	3.194	- 80.03	- 94.56	14.53	2.82	.567	.364	"	- 87	1.94
2.229	2.667	- 62.93	- 76.85	13.92	2.93	.587	.392	"	- 70	2.18
1.686	2.083	- 46.50	- 58.43	11.93	2.98	.598	.406	"	- 52	2.64
I.211	1.586	- 32.82	- 43.59	10.77	2.88	.577	.379	"	- 38	2.73
.752	1.138	- 20.03	- 30.73	10.70	2.93	.587	.392	"	- 25	2.84
.389	.745	- 10.25	- 19.84	9.59	2.83	.567	.366	"	- 15	2.96
.003	.344	- .08	- 9.04	8.96	2.97	.593	.401	"	- 5	3.47
.001	.182	- .03	- 4.76	4.73	1.97	.394	.177	"	- 2	2.90
.192	.523	- 5.02	- 13.81	8.79	2.87	.572	.375	"	- 0	3.31
.544	.861	- 14.38	- 23.02	8.64	2.82	.564	.362	"	- 19	3.26

TABLE II

50% STRETCH

TC_1 mv.	TC_2 mv.	T_1 °C.	T_2 °C.	T_1-T_2 °C.	V v.	I amp.	P Cal/sec.	$Fx10^3$ cm^{-1}	Av.T. °C.	$Kx10^4$
-1.284	-1.046	32.16	26.39	5.77	2.66	.528	.320	.759	+ 29	4.10
- .684	- .445	17.40	11.39	6.01	2.60	.520	.308	"	+ 14	3.82
.215	.537	- 5.67	- 14.22	8.59	2.98	.597	.394	"	- 10	3.44
.678	.935	- 18.09	- 25.18	7.09	2.50	.499	.284	"	- 22	3.04
1.148	1.380	- 30.90	-37.63	6.73	2.57	.511	.299	"	- 34	3.37
1.439	1.716	- 39.30	- 47.41	8.11	2.63	.527	.316	"	- 43	2.96
1.894	2.139	- 52.69	- 60.15	7.46	2.72	.546	.339	"	- 56	3.44
2.264	2.457	- 64.02	- 70.10	6.08	2.16	.434	.214	"	- 67	2.67
2.594	2.880	- 74.48	- 83.87	9.39	2.90	.582	.384	"	- 79	3.11
2.953	3.233	- 86.33	- 95.97	9.64	2.89	.570	.376	"	- 91	2.96
3.316	3.553	- 98.86	-107.45	8.59	2.69	.541	.332	"	-103	2.94
3.555	3.845	-108.18	-118.43	10.25	2.07	.598	.404	"	-113	2.99
3.838	4.098	-118.15	-128.41	10.26	2.89	.582	.384	"	-123	2.84
4.377	4.182	-131.14	-140.61	9.47	2.40	.481	.264	"	-136	2.12
4.312	4.614	-137.71	-150.55	12.84	2.33	.470	.250	"	-144	1.48
4.622	4.836	-150.88	-161.00	10.12	2.57	.572	.334	"	-156	2.50
4.591	4.907	-149.57	-164.49	14.92	2.47	.497	.280	"	-157	1.42
4.833	5.014	-160.86	-169.90	9.04	2.41	.489	.270	"	-165	2.27
4.680	4.916	-153.58	-164.95	11.37	2.81	.569	.364	"	-159	2.43
4.337	4.594	-137.02	-149.64	12.62	2.86	.577	.376	"	-143	2.26
4.034	4.291	-125.84	-136.38	10.54	2.89	.582	.383	"	-131	2.76
3.667	3.898	-111.66	-120.47	8.81	2.67	.535	.326	"	-116	2.80
3.862	4.233	-119.46	-133.96	14.50	2.83	.570	.368	"	-127	1.96
4.121	4.380	-129.35	-140.17	10.82	2.93	.590	.394	"	-135	2.76
4.276	4.532	-135.75	-146.85	11.10	2.88	.582	.382	"	-141	2.62
4.488	4.724	-144.89	-156.67	11.78	2.75	.559	.351	"	-151	2.26
4.639	4.910	-151.68	-164.65	12.97	2.43	.489	.271	"	-158	1.59
4.089	5.027	-159.71	-170.57	10.86	2.15	.436	.214	"	-165	1.49
4.475	4.714	-144.35	-155.30	10.85	2.77	.560	.354	"	-150	2.48
4.135	4.396	-129.92	-140.87	10.95	2.97	.599	.406	"	-135	2.82

TABLE II (cont'd)

TC_1 mv.	TC_2 mv.	T_1 °C.	T_2 °C.	T_1-T_2 °C.	V v.	I amp.	P Cal/sec.	$Fx10^3$ Cm^{-1}	Av.T. °C.	$Kx10^4$
3.694	4.100	-112.68	-128.49	15.81	2.94	.595	.399	7.59	-120	1.91
3.625	3.864	-110.11	-119.15	9.04	2.78	.559	.354	"	-115	2.98
3.167	3.462	-193.65	-104.11	10.56	3.03	.608	.420	7.59	- 99	3.02
2.761	3.050	- 79.93	- 89.62	9.69	2.93	.592	.395	"	- 75	3.10
2.377	2.674	- 67.56	- 77.08	9.52	2.97	.598	.405	"	- 72	3.23
1.885	2.258	- 52.42	- 62.84	10.42	2.97	.598	.405	"	- 58	2.94
1.492	1.780	- 40.84	- 50.29	9.45	2.97	.598	.405	"	- 46	3.26
- .285	.061	+ 7.34	- 1.58	8.72	3.08	.615	.432	7.69	3	3.62
.370	.685	- 9.73	- 18.33	8.60	2.96	.593	.400	"	- 14	3.58
.670	.971	- 17.81	- 26.84	9.03	2.90	.581	.384	"	- 22	3.27
1.113	1.366	- 30.03	0 38.23	8.20	2.56	.509	.297	"	- 34	2.82
1.375	1.637	- 37.48	- 45.18	7.70	2.68	.535	.327	"	- 41	3.26
1.719	1.779	- 47.50	- 55.27	7.77	2.76	.551	.357	"	- 51	3.43
2.104	2.360	- 59.07	- 67.04	7.97	2.76	.553	.335	"	- 63	3.23
2.364	2.634	- 67.16	- 75.77	8.61	2.87	.574	.376	"	- 71	3.35
2.745	2.949	- 79.41	- 86.20	6.79	2.38	.476	.258	"	- 83	2.92
3.264	3.593	- 97.06	-108.93	11.87	2.99	.601	.410	"	-103	2.66
2.526	2.813	- 72.29	- 81.80	9.51	2.56	.509	.297	"	- 77	2.40
2.100	2.421	- 58.95	- 68.75	10.00	2.73	.548	.341	"	- 64	2.62
1.742	2.021	- 48.18	- 56.55	8.38	2.83	.569	.366	"	- 52	3.36
1.320	1.620	- 35.89	- 44.59	8.70	2.78	.558	.354	"	- 40	3.13
.793	1.145	- 21.15	- 30.03	9.78	3.04	.608	.421	"	- 26	3.31
.381	.731	- 10.03	- 19.46	9.43	3.00	.601	.411	"	- 15	3.36

TABLE III

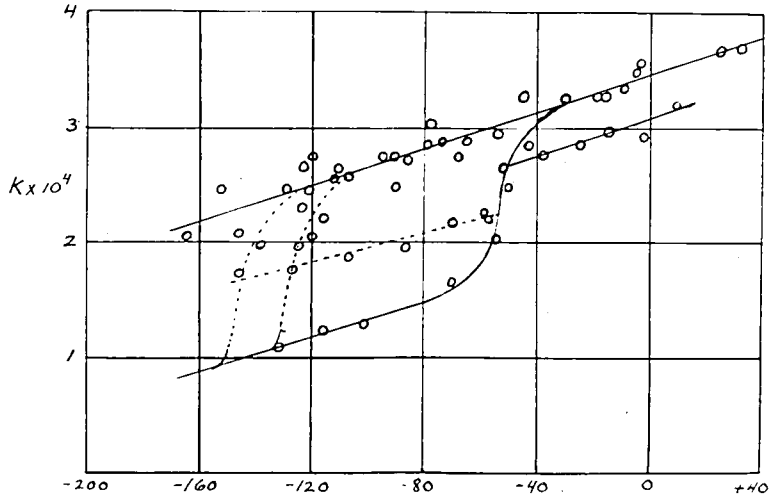
100% STRETCH

TC_1 mv.	TC_2 mv.	T_1 °C.	T_2 °C.	T_1-T_2 °C.	V volts	I amps.	P Cal/sec.	$Fx10^3$ $^{\circ}Cm^{-1}$	Av.T °C.	$Kx10^4$
-1.217	-1.029	30.55	25.98	4.57	2.20	.438	.225	7.34	28	3.61
- .750	- .407	19.05	10.43	8.62	3.03	.603	.417	"	15	3.55
- .252	.008	6.58	- .21	6.79	2.75	.551	.346	"	3	3.74
.311	.531	- 8.16	- 14.03	5.87	2.50	.498	.284	"	- 11	3.54
.736	.999	-19.59	- 26.86	7.27	2.60	.520	.308	"	- 23	3.12
.994	1.209	-26.72	- 32.74	6.02	2.45	.489	.274	"	- 30	3.33
1.476	1.675	- 40.38	- 46.18	5.80	2.35	.469	.252	"	- 43	3.18
1.083	1.302	-29.20	- 35.37	6.17	2.47	.491	.276	"	- 32	3.28
1.699	1.993	-46.89	- 55.70	8.81	2.81	.565	.362	"	- 51	3.01
2.000	2.216	-55.91	- 62.53	6.62	2.56	.509	.297	"	- 59	3.29
2.314	2.551	-65.59	- 73.10	7.51	2.68	.538	.329	"	- 69	3.21
2.689	2.870	-77.45	- 84.53	7.08	2.17	.433	.214	"	- 81	2.22
2.094	2.371	-58.77	- 67.37	8.60	2.91	.584	.388	"	- 63	3.31
2.381	2.658	-67.87	-76.55	8.68	2.73	.549	.342	"	- 72	2.89
2.681	2.960	-77.31	- 86.57	9.26	3.00	.603	.413	"	- 82	3.26
2.971	3.275	-86.95	- 97.44	10.49	2.59	.519	.306	"	- 92	2.14
3.279	3.482	-97.61	-104.84	7.23	2.37	.475	.257	"	-101	2.60
3.435	3.748	-103.15	-114.72	11.57	2.53	.507	.293	"	-108	2.86
3.775	4.006	-115.73	-124.72	8.99	2.59	.520	.307	"	-120	2.50
4.199	4.362	-132.54	-139.40	6.86	2.06	.415	.195	"	-136	2.08
4.469	4.708	-144.04	-154.90	10.85	2.11	.426	.205	"	-149	1.39
4.812	5.022	-159.86	-170.31	10.45	2.61	.530	.315	"	-165	2.22
- .694	- .433	17.65	11.09	6.56	2.73	.546	.340	"	14	3.80
.025	.371	- .65	- 10.76	10.11	3.10	.621	.439	"	- 6	3.18
.421	.751	- 11.10	- 20.00	8.90	3.02	.603	.415	"	- 16	3.42
.956	1.213	- 25.67	- 32.85	7.18	2.68	.535	.326	"	- 29	3.34
1.394	1.704	- 38.03	- 47.03	9.00	2.97	.596	.404	"	- 43	3.29
1.771	2.091	- 49.04	- 58.68	9.64	2.94	.589	.395	"	- 54	3.01

TABLE III (cont'd)

TC_1	TC_2	T_1	T_2	T_1-T_2	V	I	P	$Fx10^3$	Av.T	$Kx10^4$
mv.	mv.	°C.	°C.	°C.	volts	amps	Cal/sec.	Cm^{-1}	°C.	
2.406	2.696	- 68.47	- 77.80	9.33	3.04	.611	.424	7.34	- 73	3.34
2.844	3.125	-82.67	- 92.21	9.54	3.00	.604	.413	"	- 87	3.18
3.367	3.793	-100.68	-116.42	15.74	3.07	.614	.430	"	-109	2.00
3.228	3.574	- 95.79	-108.22	12.43	2.70	.543	.334	"	-102	1.97
2.965	3.254	- 86.74	- 96.70	9.96	2.40	.479	.262	"	- 92	1.93
2.852	3.090	- 82.93	- 91.00	8.07	2.59	.517	.320	"	- 87	2.91
3.271	3.569	- 97.30	-108.04	10.74	3.00	.603	.413	"	-102	2.82
3.608	3.866	-109.48	-119.22	9.74	2.76	.556	.350	"	-114	2.64
3.962	4.271	-122.98	-135.54	12.56	3.08	.621	.436	"	-129	2.54
4.359	4.618	-139.27	-150.73	11.46	2.86	.577	.376	"	-145	2.41
4.610	4.860	-150.37	-162.15	11.78	2.93	.587	.392	"	-156	2.44
4.816	5.041	-160.05	-171.33	11.28	2.47	.499	.281	"	-166	1.83
4.386	4.668	-139.66	-153.02	13.36	2.48	.499	.282	"	-146	1.55
4.061	4.312	-126.92	-137.38	10.46	2.82	.570	.366	"	-132	2.58
3.481	3.872	-105.02	-119.46	14.44	2.87	.577	.378	"	-112	1.92
3.185	3.420	- 94.29	-102.61	8.33	2.60	.520	.308	"	- 98	2.72
2.716	3.019	- 78.33	- 88.58	10.25	2.93	.587	.392	"	- 83	2.81
2.316	2.583	- 65.66	- 74.13	8.47	2.70	.541	.332	"	- 70	2.88
1.734	2.073	- 47.94	- 58.12	10.18	2.89	.579	.378	"	- 53	2.74
1.184	1.526	- 32.03	- 41.83	9. 80	2.94	.588	.394	"	- 37	2.95
.810	1.143	- 21.67	- 31.15	9.45	2.90	.582	.385	"	- 26	2.98

PLATE XIII



NORMAL LENGTH

include:

Specific gravity	.98
Tensile strength (lbs./sq. in.)	3365
% elongation possible	760
% set	14
Durometer hardness	40
300% stretch modulus (lbs./sq. in.)	198

For use in the apparatus two strips were used each approximately 15 cm. by 3 cm. by 0.2 cm. The same strips were used throughout.

Experimental Results

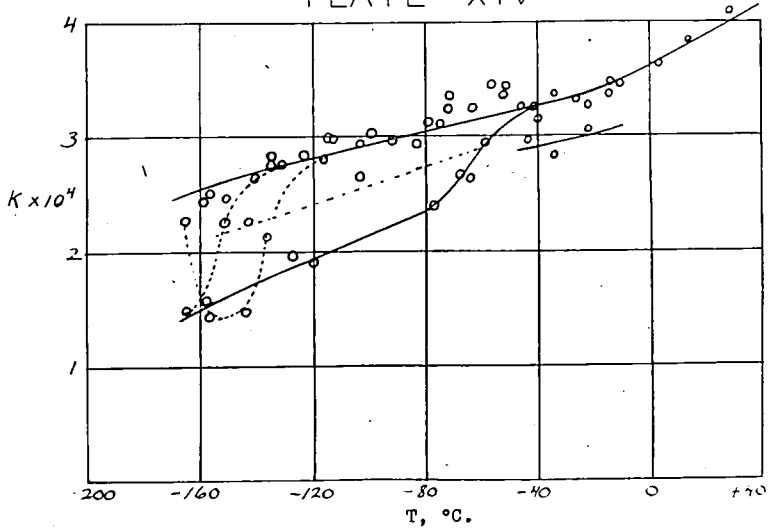
The readings and results obtained are tabulated in tables I, II and III. For convenient comparison the results obtained are shown graphically in Plates XIII, XIV and XV, as follows:

Normal Length	Table I	and Plate XIII
50% stretch	Table II	and Plate XIV
100% stretch	Table III	and Plate XV

Certain of the more evident lines have been drawn in. Those dotted are tentative lines. Some drops from the top curve to the bottom one have been shown to indicate the temperatures at which they occurred.

The average value of the thermal conductivity for this sample for all degrees of stretch appears to be between 3.5×10^{-4} and 3.8×10^{-4} Cal./cm.sec.deg.C. in the range around 0°C. This is in quite good agreement with the results obtained for a different type of rubber by Schallamach (8) who gets 3.1×10^{-4} and Frumkin and Dubinker (7) with 4.9×10^{-4}.

PLATE XIV



50% STRETCH

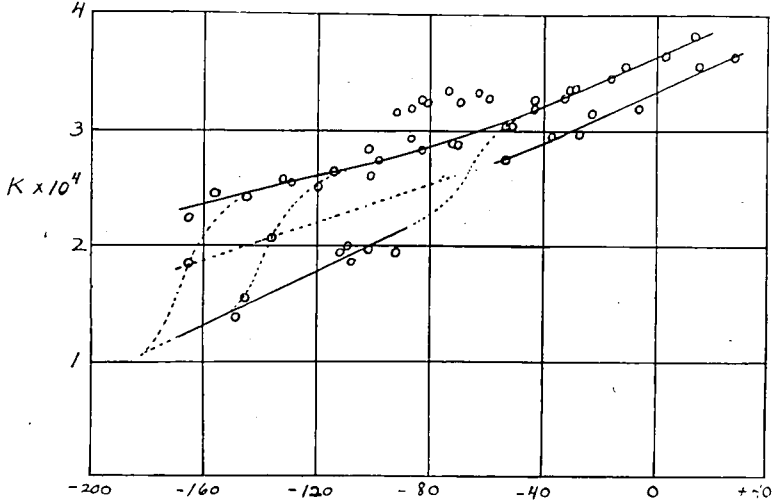
Actually it is difficult to compare these values as conductivity depends on composition and different rubbers vary greatly in this respect. An important point to note, also, is that high porosity tends to decrease conductivity by causing a smaller conducting area.

There is definitely a decrease in conductivity with decrease of temperature. For all degrees of stretch there are no large changes in the slope of the top line of the graph. The decrease is not necessarily a linear change, as shown by Plates XIV and XV.

For normal length and 50% stretch there is no indication of two or more possible conductivities above 15°C. This is in agreement with temperature volume relationships (11) and specific heat curves (12) obtained by Bekkedahl and associates. However, for 100% stretch there is definitely an indication that two values of K can exist for temperatures as high as 30°C. Guth (14) reports that in some cases where two possible states occur at lower temperatures the effect comes up to room temperatures on stretching.

Below 10°C., in all cases, there are apparently two thermal conductivities possible. There seems to be no consistent pattern to decide which state the rubber will be in, since consecutive readings often gave points on different curves. In fact, on several occasions the change actually occurred while readings were being taken. This would indicate that there is not a very great energy difference between the two states. The difference of conductivity between the two

PLATE XV



100% STRETCH

states from 10°C. to -40°C. is around 0.5×10^{-4}. It is interesting to note that Schallamach (8) found no effect of this sort with North British Cycle Tubing which the company calls "pure electrodeposited latex." A possible explanation for this could be that electrodeposited rubber is purer and has more consistent particle size. However, Bekkedahl (11) found that his temperature volume relations definitely indicated two possible states below 11°C. for unstretched rubber, and Bekkedahl and Matheson (12) corroborated this when they found a definite peak in the specific heat curve at that point. (11°C.)

In the region below -70°C. there are also two possible curves; but the lower of the two is not identical with the corresponding one in the upper region. For zero stretch the separation appears to be around 1.3×10^{-4} and fairly constant. With increasing stretch the separation decreases at the upper end of the curves which are no longer parallel. Here again there is apparently no set pattern for change from one curve to the other as the points on the lower curve represent isolated readings in many cases. However, there does seem to be an increased tendency to drop off in the region between -120°C. and -160°C. The temperature at which the drop off occurrs being lower if the cooling is done quickly. The range in which this tendency seems greatest is indicated by dotted lines on the graphs. The fact that there are two states possible is amply corroborated by Schallamach (8)

and Bekkedahl (11) but the reversibility of the change from low to high conductivity observed by us is in marked contrast to Schallamach's work, as is the fact that points on the top curve occur as low as -165° C. Schallamach reported that in the neighbourhood of -120° C. the conductivity changed abruptly to the lower value, and thereafter all points were on the lower curve which rejoined the upper one in the region -80° C. to -60° C. with no discontinuity. It will be noticed that for the unstretched state this form occurred, but in isolated points both for increasing or decreasing temperatures, and in the region -70° C. to -35° C. Both Bekkedahl (11) and Guth (14) report that this change can be brought to higher temperatures by varying the composition. The same effect is indicated in readings for 50% stretch, but no points were obtained for that part of the curve for 100% stretch.

It will be seen that for all degrees of stretch points occurred about half way between the upper and lower curves. This is attributed to the fact that there were two pieces of rubber used simultaneously in each measurement, and one piece could be at the lower conductivity while the other was at the higher one, and vice-versa.

In view of the above results and from consideration of the graphs the following observations on the effect of increasing stretch may be made.

(a) The slope of the room temperature portion of the curve increases and conductivity tends to increase

slightly. At very low temperatures the slope decreases.

(b) The lower line appears to extend up to room temperatures, remaining about the same distance from the upper line.

(c) The slope of the lower curve at low temperatures increases, and the separation of the two curves becomes less.

(d) The top curve has a changing slope throughout its length.

As yet no mention has been made of the anomalous condition found in the -80°C. to -40°C. region and possibly below, as shown by points occurring above the top line of the graph in that region. To avoid confusion no lines have been drawn through these points, but it will be observed in the zero stretchgraph that a straight line could be drawn from -160°C. to -30°C. cutting at least five points well above the main curve. This, in itself, would hardly be conclusive, but at 50% stretch there is a definite high spot in the graph in the -80°C. to -40°C. region, and for 100% stretch there is a very definite series of points closely grouped and some distance from the main line. It should be pointed out that these points were not all obtained in one run, but occurred as more or less random readings in the same manner as the low conductivity points.

The obtaining of complete curves was complicated by several factors which cannot be shown graphically, but

which caused considerable inconvenience.

(a) Time lag. There was definite evidence that the value obtained for K in certain cases depended partly on the previous history of the run. It was noticed on several occasions that the drop from higher to lower curve that usually occurs around -140° C. did not occur until as low as -165° C. if the change from room temperature to that temperature had been rapid. Conclusive proof that time is a factor was obtained on one occasion when a steady state was obtained and in the space of approximately 10 minutes it was necessary to increase the current supplied gradually from .57 to .62 amperes in order to maintain the same temperature difference. This represents a power change of almost 20% or a change of conductivity of almost 0.5×10^{-4}. The time lag appeared to cause difficulty chiefly in the region from -170° C. to -110° C. and at temperatures above this region was less noticeable. This lag did not always occur; usually the apparatus could be held steady for some time. Guth (14) has reported that work on other phases of rubber research has been hampered considerably by this time lag effect, and has made it difficult to evaluate results. Bekkedahl (11) also reports a similar condition in the region -35° C. to -15° C. where a tendency to pass from one curve to another extended over a considerable period of time.

(b) The random nature of the occurrence of low conductivity readings. At no time was it possible to foretell

when low conductivity readings would occur. Consequently, many more readings than necessary were obtained for the upper curve in order to get enough points on the lower one. Because of this fact it was not possible to fill in the bottom curve completely in some regions.

(c) Both pieces of rubber not in the same state. As stated before there was some difficulty encountered when one piece of rubber was in a different state from the other. In many cases the values obtained gave a good idea of the separation of the two curves, but as far as exact determination of one of them were of little or no use. As the number of times the rubber had been stretched and cooled increased this tendency to change at different times became greater, indicating that the useful life of paired samples for conductivity work is limited.

(d) Varying conductivity within one piece. The commercial methods of making rubber do not, as a rule, produce a material that is completely homogeneous. Moreover, the measurements must be taken over a considerable area of any one piece. Consequently, it is possible that when a change occurred it did not always extend over the entire area covered by the central heating block. This would cause a poor reading. It will be noticed that certain readings do not fit in with the general pattern but might be explained in this manner. It would require an apparatus that employed only one piece of rubber but measured several adjacent parts simultaneously to

determine whether this actually occurred.

Interpretation

From these results it is possible to make some deductions, subject, of course, to verification by other lines of research, as to changes of state that may occur in rubber at the temperatures considered.

(a) The state existing ordinarily at room temperatures (amorphous) can exist as far down as -170° C.

(b) Below + 10° C. and above -60° C. a second state can exist. The upper limit of temperature for this state appears to rise with increased stretch, but this state does not appear to exist below -60 C.

(c) Below -60° C. there are still two states possible, but one is of much lower conductivity.

(d) In the region -80° C. to -40° C. a continuous, reversible transition is possible from the state of lower conductivity to that of higher conductivity.

(e) It is possible that a third state may exist in the -80° C. to -40° C. region with a higher conductivity. However, the higher points might be caused by a heat of fusion or crystallization in that region, although this seems unlikely, as no ordinary heat of fusion would be sufficient to maintain the reduced temperature interval for the period required for two complete sets of readings.

(f) Because of the frequency of transition, and its re-

versibility, it appears that the amount of energy involved in transitions between any two states must be fairly small.

IV. CONCLUSION

It is apparent from the above that a great deal remains to be done in the field of heat conductivity of elastomers. The work described herein is but the beginning of an extensive program which will be carried out with samples of different compositions which have been kindly provided by the Department of Physics of the University of Notre Dame.

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