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THERMAL CONDUCTIVITY OF SODIUM CHLORIDE WITHIN THE TEMPERATURE RANGE 375°K TO 637°K

BY

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THESIS

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1956

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Approved by William H. Bessey

Professor of Physics

ACKNOWLEDGMENT

The author wishes to express his thanks to Dr. William H. Bessey, Professor of Physics, at the Missouri School of Mines for his valuable suggestions given throughout this project and for his patience at the many inconveniences caused him.

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INTRODUCTION

The transport of heat in dielectric solids is attributed entirely to lattice waves whereas in metals there is in addition a transfer by the flow of valence electrons. The thermal conductivity of a non-electrical-conductor is limited by a number of scattering processes giving rise to thermal resistances. Scattering results from impurity atoms and from vacancies and dislocations within the crystal structure and from the interaction of the lattice vibrations amongst themselves. Scattering also occurs at the boundaries of the crystal. The thermal resistance of an ideal crystal at low temperatures is due almost entirely to boundary scattering and at high temperatures is due primarily to anharmonic coupling. With increasing temperature the former decreases and the latter increases and consequently the thermal conductivity passes through a maximum.

In 1914, Debye[1] showed from theoretical considerations that the conductivity is approximately proportional to 1/T for temperatures above the region of maximum conductivity. A more recent and rigorous treatment of the problem by Peierls[2], using quantum mechanics, resulted in the same temperature dependence. In 1941, Pomeranchuk[3], published

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(1) Debye, P., Vortrage uber die kinetische Theorie etc., by M. Planck et al., Teubner, Leipzig, p. 46, (1914).

(2) Peierls, R., Zur Kinetischem Theorie der Warmeleitung in Kristallen, Ann. Phys. (Leipzig) Vol. 3, pp. 1055-1101 (1929).

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(3) Pomeranchuk, On the Thermal Conductivity of Dielectrics at the Temperature Higher than the Debye Temperature, Journal of Physics, Moscow, Vol. 4, pp. 259-268, (1941).

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a paper showing the necessity of including an additional term in the interaction potential. His calculations showed a mixed type of conductivity proportional to $\frac{1}{T}$ and $\frac{1}{T^{3/2}}$.

Although a considerable amount of experimental work has been done in the past, most of it has dealt with temperatures below the boiling point of water. Consequently the measurements of thermal conductivities above this temperature have not been sufficiently extensive for a detailed comparison between theory and experiment to be made. The wide discrepancy in the results of early experimenters is believed to be due largely to the defects and impurities of the various samples used. Thus it seems that if a comparison between the experimental and theoretical values is to be made, the conductivities of a single crystal must be determined over a rather large temperature range. The ultimate goal of this project is to investigate the temperature dependence of the conductivity of various alkali halides up to their melting points.

Equipment was available at the beginning of this investigation that had been previously operated by Weisbrod[4]

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(4) Weisbrod, Harold, Determination of the Thermal Conductivity of Sodium Chloride at Elevated Temperatures, Missouri School of Mines, unpub. Masters Thesis (1954).

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and Brown[5]. The apparatus was designed to measure absolute

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(5) Brown, Howard, The Thermal Conductivity of Sodium Chloride at Elevated Temperatures, Missouri School of Mines, unpub. Masters Thesis (1955).

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conductivities rather than relative ones. Near perfect cylindrical crystals of sodium chloride whose length and diameter were approximately 1.2 and 1.5 centimeters respectively were available. The most apparent deficiency of the equipment was that of background (explained elsewhere). The error in the calculated conductivities resulting from this effect increased with increasing temperature and amounted to as much as 8% at 300°C as was shown by Brown. The purpose of this investigation was to improve the operating performance of the equipment and to reproduce and extend the work done by Weisbrod and Brown.

DESCRIPTION OF THE APPARATUS

The heat flow apparatus consists of a sink, source, source shield and radiation guard all of which can be maintained at a constant temperature. The sink is a comparatively large cylindrical copper block whose diameter is over three times that of the sodium chloride crystal that was used. The cylindrical crystal is centrally located and sandwiched between the source and the sink. Since the ambient temperature is considerably less than that of the apparatus it is necessary to prevent loss of heat from the source to the surroundings. This is accomplished by placing over the source a copper cap, the source shield, capable of being maintained at the same temperature as the source. A hollow cylindrical piece of ceramic material of low thermal conductivity whose length is the same as the crystal is placed between the sink and the shield and serves as a radiation guard.

Good thermal contact must be established between the copper and crystal faces. Tin foil (brought to its fusion point prior to the taking of data) between the surfaces tends to eliminate air spaces caused by surface roughness. The necessary pressure is maintained by a pressure foot extending downward through a hole in the center of the shield and held under spring tension. Thermal contacts at the faces of the radiation guard is accomplished in the same manner. A cross-sectional diagram of the assembly is shown in Figure 1.

The entire apparatus is enclosed in an evacuated chamber consisting of a bell jar and a sixteen inch diameter pump plate. A forepump maintains the necessary vacuum. Although a diffusion pump is also incorporated into the system it was found that the forepump alone was capable of maintaining pressures below one micron for operating temperatures below 370°C. This pressure assures a negligible amount of heat flow by convection currents.

All units are heated electrically and steady state conditions are established by the use of thyratron phase shifting circuits explained elsewhere. When thermal equilibrium has been established, the shield is at the same temperature as the source. Consequently the net heat exchange between source and shield by radiation should be zero. The temperature gradient along the inner surface of the radiation guard is nearly the same as that along the crystal surface and is assumed to be linear. That is, the same temperature exists at a point on the inner surface of the guard as exists at a point on the crystal at the same level and consequently the net radial flow of heat through the crystal is sensibly zero. As a result all the heat generated in the heating coils of the source passes through the crystal in a direction parallel to its axis, either by conduction or radiation. The existing temperature difference between the crystal faces is measured by chromel-alumel thermocouples and the power imput to the source is determined by the ammeter-potentiometer method. For these reasons, calculations can be made on the basis of the steady state, one dimensional heat flow equation.

THE CONTROL CIRCUITS

The sink and shield are heated almost entirely by A.C. currents ranging up to .6 amperes. Small pulsating D.C. currents through the thyratron serve as correcting currents necessary to maintain constant temperatures. The firing of a thyratron depends upon the magnitude and phase relationship of the anode and grid potential.[6] The voltage relationship can be changed by variations in either the capacitance or the resistance of the circuit. Power and controlling circuits for matching the source-shield temperature are shown in Figure 3.

A converging beam of light from a stationary light source reflects from the mirror of the galvanometer and forms a wedge shaped image on the grid of the photocell. The base current through the heating coil is set at a value slightly lower than that necessary to maintain the shield temperature as high as that of the source by adjusting R_1 at a time when the thyratron is not firing. With S_2 in the "on" position, the variable condenser is adjusted to such a value that the tube is on the verge of firing. R_2 limits the current through the tube to a value substantially less than its maximum allowable current.

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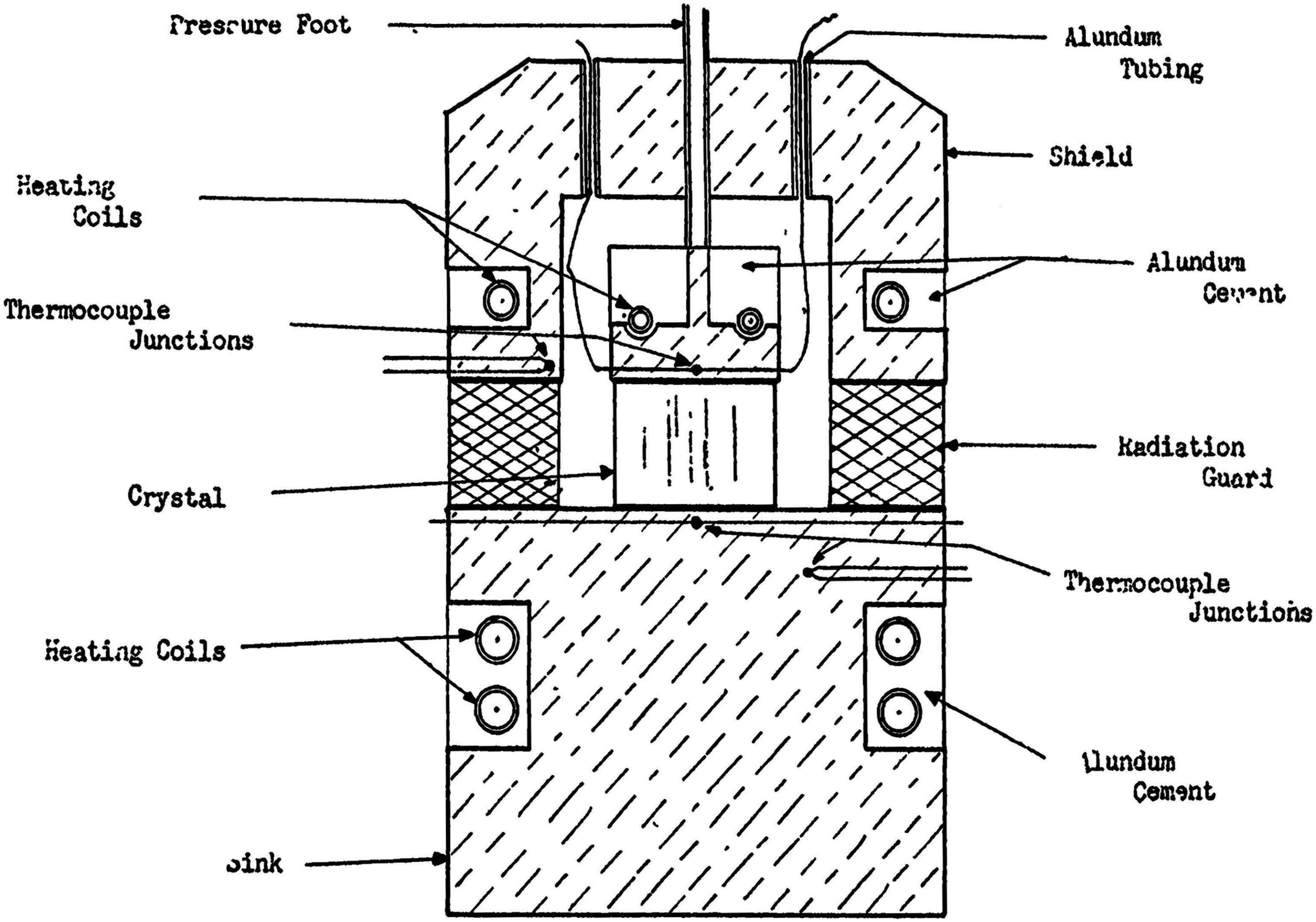
(6) Brown, op. cit., pp.22-24.

A temperature difference between source and shield results in a current through the galvanometer causing the image to deflect across the grid of the photocell, decreasing its resistance. Consequently, the tube fires; the current increasing with increasing deflection due to the shape of the image. This correction current reduces the temperature difference in a near linear fashion and, of course, the tube quenches when the temperatures are matched.

The power and controlling circuits used in maintaining a constant sink temperature are identical to the ones explained with the exception of the opposing EMF's. In the case discussed, the opposing EMF's are those of the source and shield thermocouples. In the case of the sink temperature control circuits, one of the EMF's is generated in the junction of the sink thermocouple and the other is preset on a potentiometer as can be seen from Figure 2.



CROSS SECTION DIAGRAM OF THE HEAT FLOW APPARATUS

Figure 1

BACKGROUND

In an attempt to discover the reason for the inconsistent data originally obtained from the apparatus, steady state conditions were established at approximately 100°C with no power imput to the source. Since the temperature difference between the source and sink is determined by the power imput to the source and since the shield temperature when at thermal equilibrium matches the source temperature, it is obvious that with no power imput to the source, all three units should come to the same temperature. Such is not the case and the difference of temperature between source and sink has been termed "background".

The heat flow apparatus was placed inside an electrical furnace maintained at approximately the same temperature and it was found that the background was sensibly the same as when the units were heated by the usual means. In order to eliminate the possibility that the effect was due to the external circuit, background was again determined by another potentiometer placed near the furnace and using a different circuit entirely. The results were the same. These results strongly indicated that background might be due to the manner of making the thermocouple junctions or the manner of installing the thermocouples at their respective places.

Consequently the following experiment was performed. Nine thermocouples were made by welding the cleaned ends of the thermocouple wires with the aid of borax flux. The junctions were placed inside of a non-electrically-conducting container which was in turn placed inside of a hypsometer. Steam maintained the temperature of the junctions at a nearly constant temperature of approximately 100°C. One thermocouple was chosen as a standard and was alternately connected with the others in such a manner that any existing potential difference could be detected by a galvanometer. This experiment was repeated using thermocouples whose junctions were made by merely twisting the ends of the wires together and also by using thermocouples whose junctions were formed by welding with handi-flux. Although the thermocouples were arranged so that nearly the same thermal gradients would be present in all of them, no two were found in which a potential difference did not exist. Several extreme cases were found in which the indicated temperature difference was almost 2°C. From these results it appeared that at least part of the background was inherent in the thermocouples themselves and that it is impractical if not impossible to eliminate the effect.

OPERATING PROCEDURE

The operation of the apparatus will be explained with the use of Figures 2 and 3. First, the forepump is turned on, ice is placed in the dewar flasks, and the leads from the constant voltage transformers are plugged in. Since drifts in the terminal voltage of batteries decrease with time it is advisable to close switches S_4 and S_5 early in the experiment so that optimum conditions will exist when these circuits are used. R_4 is varied until a current through Am_1 of about 20 milliamperes is indicated. The battery charger is then plugged in and R_5 is adjusted until the currents through Am_1 and Am_2 are the same. Since copper oxidizes quite rapidly when heated in the presence of air, it is also advisable to reduce the pressure within the bell-jar to several tenths of a millimeter of mercury before heating the heat flow assembly. When this pressure has been reached, S_1 and S_2 are turned to the "on" position. The current necessary for maintaining the shield at the chosen operating temperature is estimated and R_1 is varied until this current is indicated by Am_3. Following this, the light source is plugged in and with no current through the galvanometer, the photocell is adjusted on its sliding mechanism until only a small portion of the wedge shaped image falls on its grid. The variable condenser, C_1, is adjusted until the thyraton "blinks". This zero position is noted and the position of the photocell is changed so that the maximum amount of light possible falls on it.

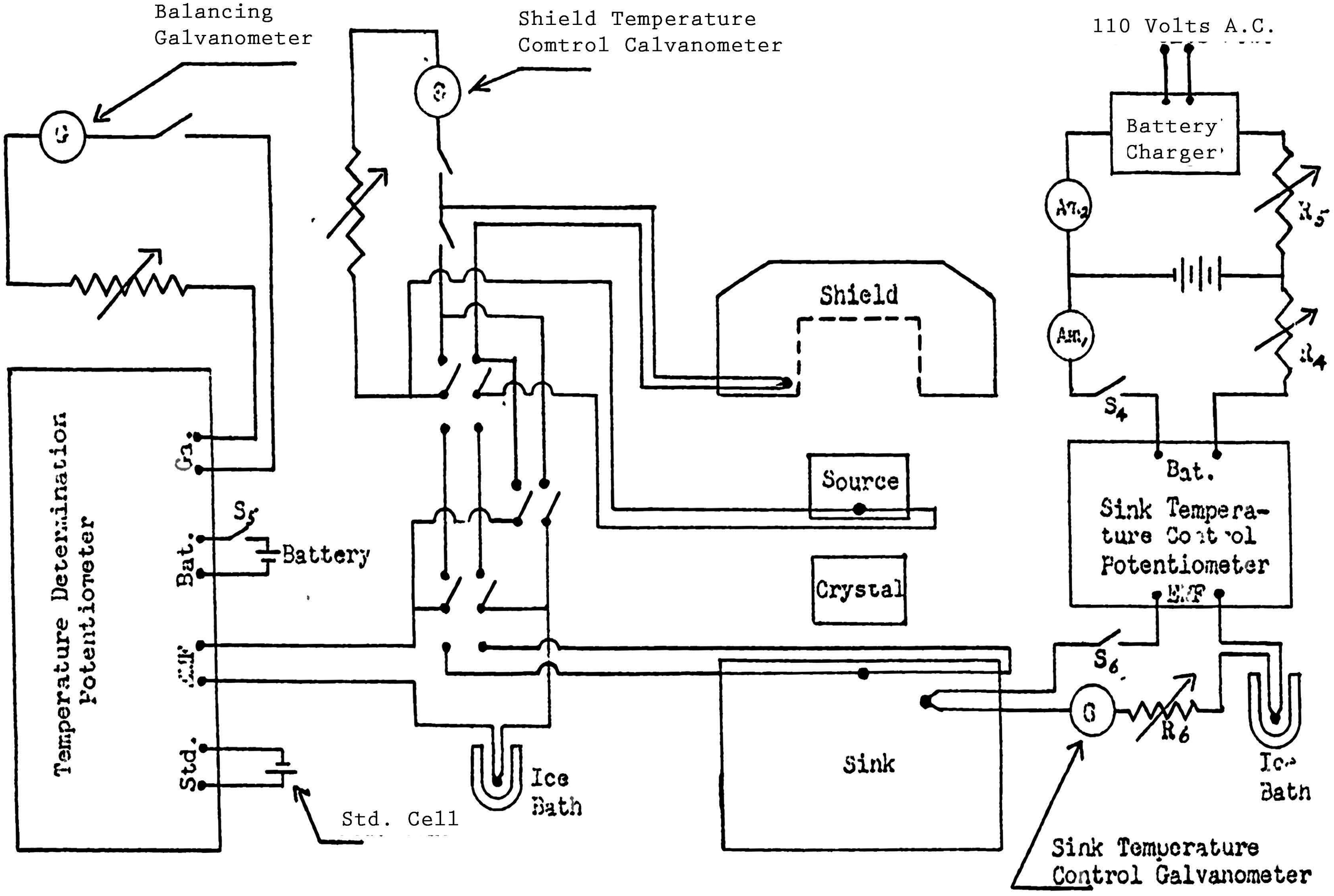
The increase of current (indicated on Am_3) should be about .03 amperes and is obtained by varying R_2. After this the photocell is returned to its zero position. It is then necessary to ascertain whether or not the phase shifting circuit is sensitive to changes in the light falling on the photocell. This can be determined by causing the image to oscillate slowly past the photocell. The thyratron should repeatedly fire and quench at about the same position of the image. If this is not the case, a more suitable combination of C_1 and R_2 must be found. Following this, S_2 is turned to the "off" position which puts R_1 and R_2 in parallel and results in an increased current through the heating coil. The K-2 potentiometer (temperature determination potentiometer) is then balanced and the shield temperature rise is noted. When the temperature reaches the desired value, S_2 is returned to the "on" position. Meanwhile, the sink temperature has been brought to the operating temperature in identically the same manner. If time permits it is advisable to make any necessary refining adjustments in the base currents before the phase shifting circuits are put in control. When it becomes apparent that the base currents are correct, R_6 is set at its maximum value, 10^4 ohms, and S_6 is closed. The EMF of the sink temperature control potentiometer is then adjusted visually by watching the wedge of light as it deflects across its photocell. The amount of light shining on the grid should be the same as that when the phase shifting circuit was preset. The resistance can be reduced to zero in less than thirty seconds by carefully adjusting the potentiometer. Following this, the base current through the sink heater windings is decreased .01 or .02 amperes. The phase shifting circuit for the matching of the source and shield temperatures is then put into control by the use of the switching arrangement shown in Figure 4. In this case, the resistance must be reduced quite slowly to retain control of the shield temperature and the base current is adjusted so that the thyratron fires approximately one-half the time.

The necessity of carefully adjusting the base currents must be emphasized. If they are too small, the thyratrons must carry excessive currents which results in excessive oscillations of the temperatures. On the other hand, if the currents are too large, fluctuations in the line frequency and voltage may increase the power to a value greater than that necessary and consequently the phase shifting circuits lose control.

The apparatus gradually falls into steady state conditions and the data is usually acceptable within two hours after control has been obtained. After the data has been obtained, power is supplied to the source and steady state conditions established again. If linearity (explained elsewhere) is to be established, data is taken for yet another power setting.

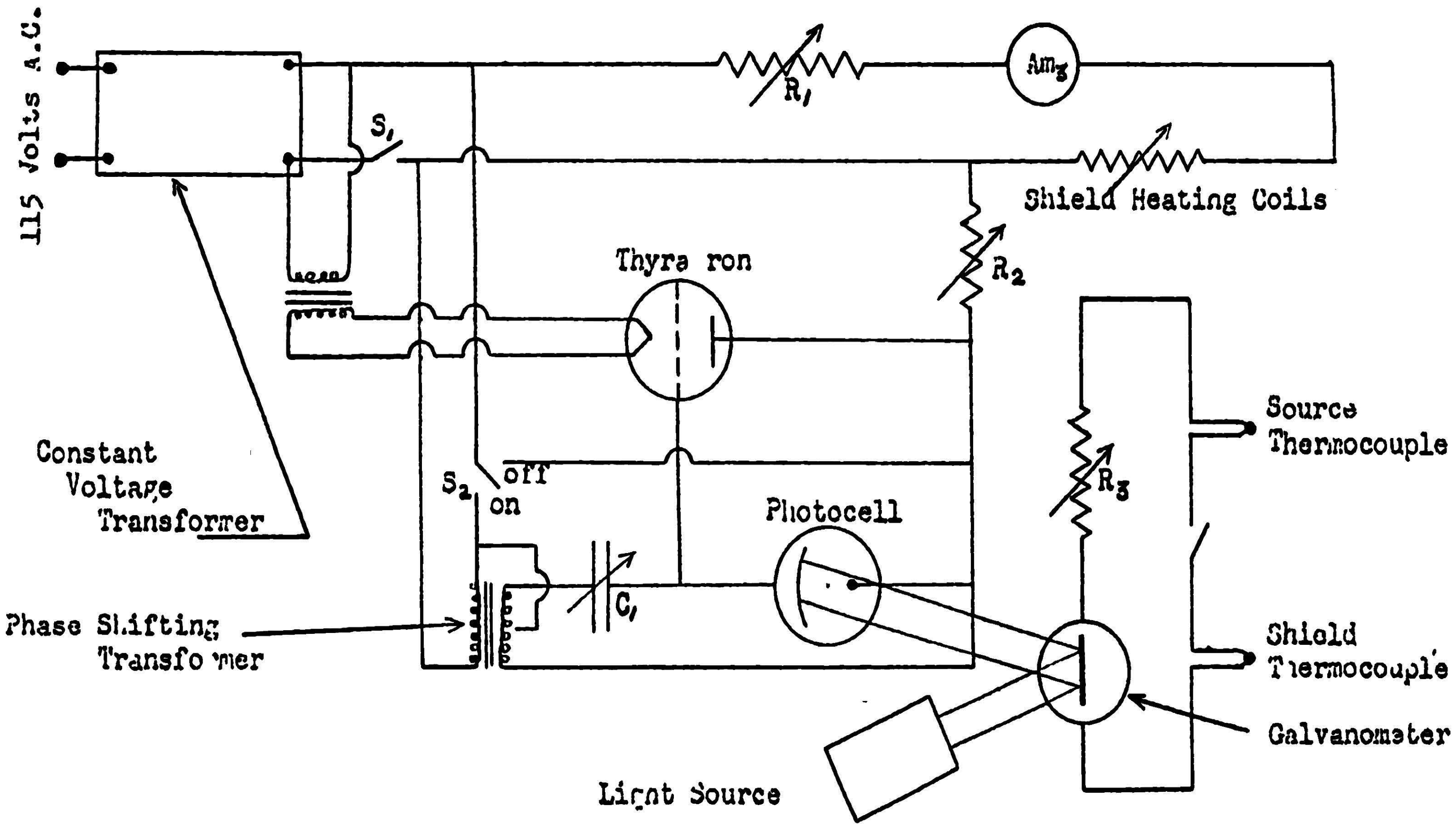
It might be thought that the procedure described is unnecessarily laborious since steady state conditions can be reached more quickly and easily by allowing the thyratons to carry a larger portion of the currents and by putting the phase shifting circuits into control sooner. This method, however, apparently leads to erratic firing of the thyratons for several hours after they carry large currents. More reliable data is therefore obtainable by adhering to the described procedure.

Thermal equilibrium can be affected by a number of influences over which the experimter has no control. Minute fluctuations in the line frequency and voltage result in variations of the base wattage and introduce an error in the settings of the phase-shifting circuits. The battery charger is subjected to these same fluctuations which lead to variations in the EMF of the sink temperature control potentiometer. As these effects are at a maximum during the daytime, the final data was obtained between the hours of 11:00 P.M. and 7:00 A.M. when more optimum voltage and frequency conditions existed. Also, the ambient temperature does not remain constant and the thyratons change their characteristics with time. Nevertheless, the temperatures could usually be held to a range of fluctuations of less than .03°C. for the 30 or 40 minutes during which the data was being recorded.



SCHEMATIC DIAGRAM OF THERMOCOUPLE AND POTENTIONMETER CIRCUTS

Figure 2



POWER AND CONTROLLING CIRCUITS FOR MATCHING OF TEMPERATURES

Figure 3

CALCULATIONS

As previously mentioned calculations are made on the basis of the one dimensional steady state heat flow equation; namely, $Q = KA(T_2 - T_1)t/L$. In the C.G.S. units the ratio $(T_2 - T_1)/L$, the thermal gradient, is expressed in °C/cm. A is the cross sectional area in centimeters squared, t is the time in seconds and Q is expressed in calories. The use of electrical heating means makes it more convenient to express the ration Q/t in terms of electrical units. Thermal conductivity can therefore be expressed as $LP/A(T_2 - T_1)$ where P is the constant power imput to the sourse in watts. Due to the presence of background, the quantity $(T_2 - T_1)$ cannot be accurately determined on the basis of only one power setting and consequently this equation must be modified slightly.

Since the thermal conductivity of sodium chloride is a non-linear function of temperature, the ration $P/(T_2 - T_1)$ is not constant. This ratio varies more rapidly with decreasing temperature but even at 100°C calculations show that this ratio changes by less than .35% for a one degree Centigrade change of operating temperature. This justifies the replacing of the ratio $P/(T_2 - T_1)$ by $\Delta P/\Delta T$ where ΔT is the change in the temperature difference resulting from a change in the power imput, ΔP. These facts suggested the plan of establishing thermal equilibrium twice; once with no power imput to determine background and again with a sufficiently low power imput to cause a change in the indicated temperature difference of less than one degree Centigrade. This latter change in the indicated temperature difference should be an accurate representation of ΔT in the above equation. Establishing thermal equilibrium a third time with yet another power imput to the source should yield information as to the effect of the exchange of radiant energy between the various surfaces of the heat flow apparatus and the reliability of the data. This plan was put into operation and proved to be satisfactory.

Strictly speaking, steady state conditions are never reached. That is, the temperature of the sink, source and shield drift somewhat but this drift can usually be held to less than .03°C for the time data is being recorded. The source and sink temperatures were noted at intervals of from eight to ten minutes and from four to six readings were taken depending on the temperature drift. Examination of the data reveals that the temperature difference remained sensibly constant over this time interval, especially at the lower temperatures. The average temperature difference was taken as the correct value for ΔT.

RESULTS

Data was taken for seven different temperatures ranging from 102°C to 364°C and is given in Table I. The values listed for ΔT are corrected for background. It is obvious that a plot of ΔP versus ΔT should be linear and the data necessary to establish linearity was taken for three temperatures: namely, 102, 256 and 364°C. The consistency and reliability of the data can be seen by inspection of Figure 4. For these temperatures the ratio $\Delta P/\Delta T$ was determined from the slope of the indicated curve. Maximum deviation from linearity occurred at the highest temperature and approached 3%. This comparatively large deviation was felt to be due mainly to the failure to establish steady-state conditions to the degree possible at lower temperatures.

A logarithmic plot of thermal conductivity versus temperature proved to be nearly linear with a negative slope of approximately 1.27. This plot is shown in Figure 5.

Table I
Thermal Conductivity of Sodium Chloride

Date	Power (watts)	Temperature Difference (°C)	$\frac{\text{Power}}{\text{Temp. Diff.}}$ (watts/°C)	Temp. (°K)	$K(\frac{\text{watts}}{\text{cm. °C}})$
Dec. 28	.02579	.4073	.06434	375	.0444
	.04432	.7050			
Dec. 26	.03109	.5000	.06218	380	.0425
Jan. 23	.02543	.4933	.05155	451	.0352
Dec. 30	.01676	4059	.04138	523	.0280
Jan. 1	.01676	.4098	.04129	529	.0276
	.03128	.7756			
Jan. 25	.01954	.5122	.03815	579	.0259
Jan. 8	.01426	.4333	.03225	637	.0220
	.02593	.8095			

GRAPH OF POWER INPUT VS.TEMPERATURE DIFFERENCE

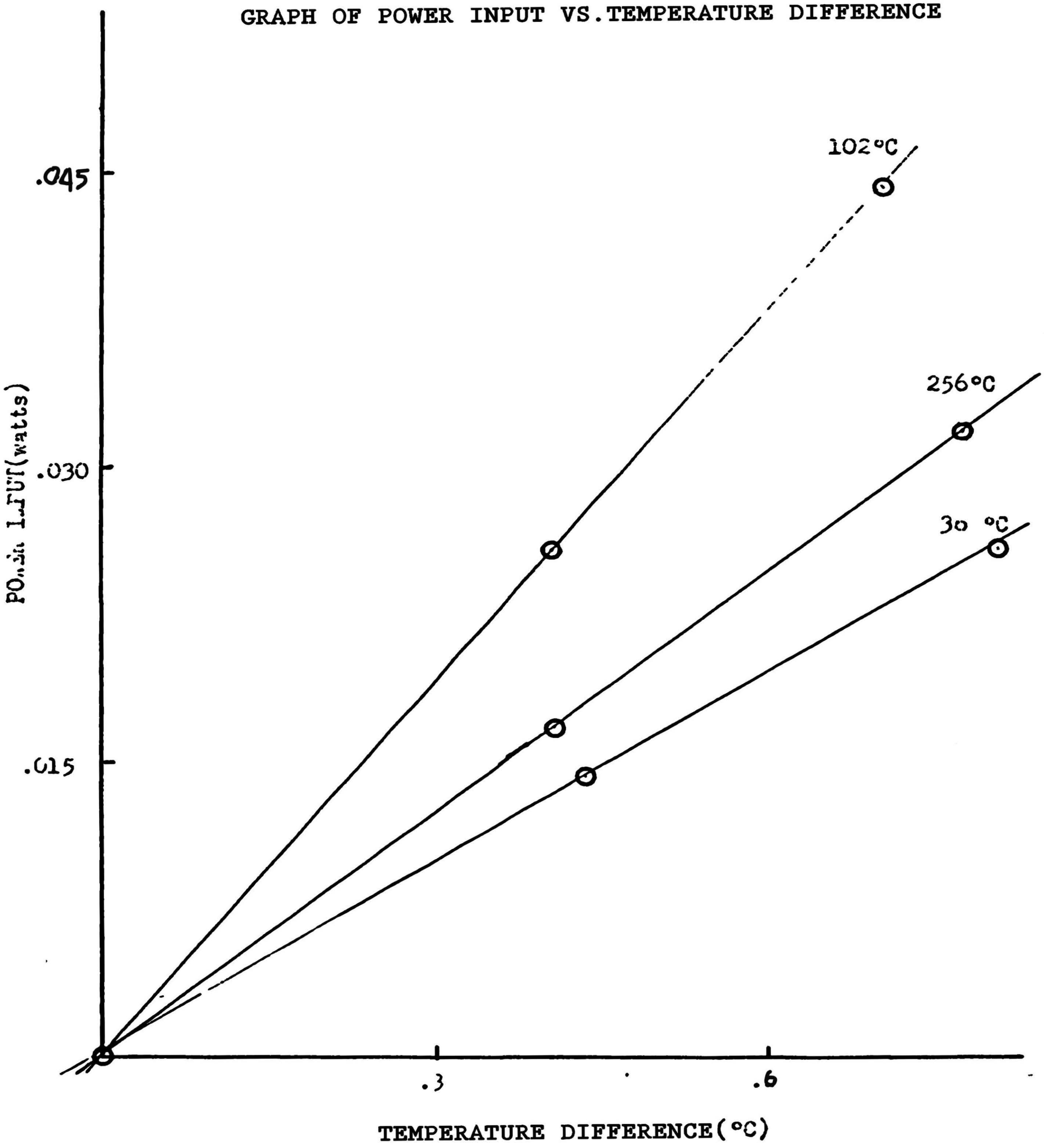


Figure 4

GRAPH OF EXPERIMENTAL VALUES OF
THERMAL CONDUCTIVITY vs TEMPERATURE

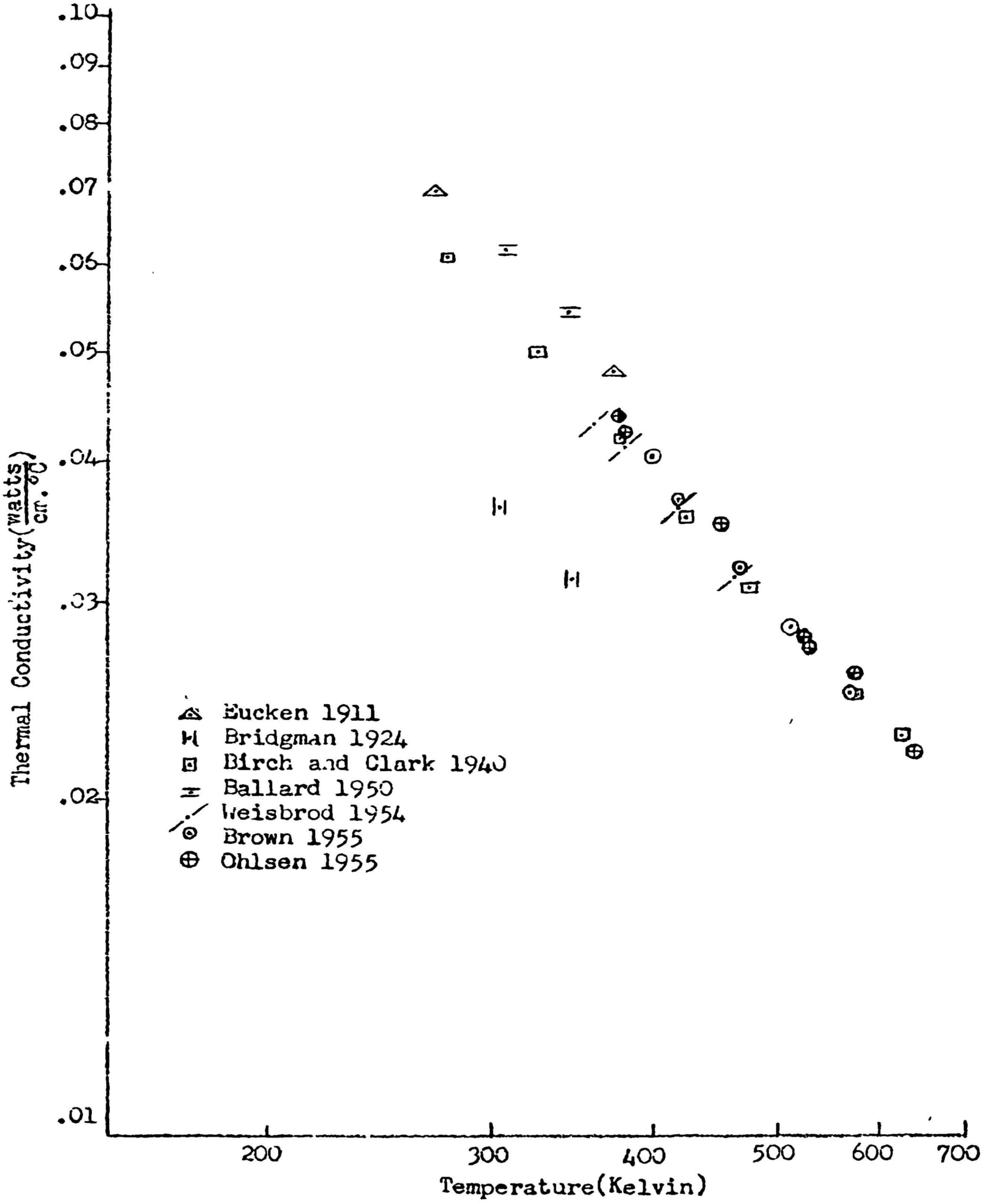


Figure 5

ERRORS

The taking of multiple data and thereby treating background as an additive constant provides a means of estimating some of the errors involved. Although the exchange of energy per second between the source and shield due to an existing temperature difference can be calculated by use of the equation $W = \sigma EA(T_2^4 - T_1^4)$, these calculations are questionable due to the difficulties in evaluating the paranthetical expression. However, for a given operating temperature, the magnitude of the mismatching remains constant for different power settings and any temperature difference across the face of the crystal resulting from the exchange of energy remains constant and consequently is interpreted as a portion of the background. The error introduced is therefore slight since background corrections were made on all of the data. Errors also arise due to slight drifts in the temperatures and inaccurate determination of ΔT. The sensitivity of the K-2 potentiometer and its balancing galvanometer is such that temperature changes of .005°C. are easily detected. The errors involved are therefore small and largely compensating since temperature differences are determined from numerous data. As all of the errors discussed above contribute toward deviation from linearity, the magnitude of the deviation is an indication of the errors. The combined errors have thus been estimated at a maximum of 3%.

The other errors are about the same as were found by Weisbrod and Brown. Failure to correct for the thermal expansion of the crystal would result in an error of about .5% per 100°C. temperature rise and these corrections were made. The use of a potentiometer to determine the voltage reduced the probable error in wattage to .75%. Heat losses through the lead wires to the source have been estimated to amount to less than 1% and non-linear heat flow resulting from imperfections in the crystal and poor thermal contacts have been estimated to contribute a maximum error of 5%.

CONCLUSIONS

The apparatus described is now capable of yielding reproducible and apparently reliable data. Improvements and modifications have resulted in extending the temperature range. Thermal conductivities obtainable from the apparatus are compared with the results of the other experimenters[7] in Figure 7. It appears that the experimentally determined

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(7) Ballard, S. S., and McCarthy, K.A., and Dav s, W. C. Review of Scientific Instruments. Vol. 21, No. 11, pp. 905-907 (1950)

Birch, Francis, and Clark, Harry. The Thermal Conductivity of Rocks and Its Dependence upon Temperature and Composition. American Journal of Science. Vol. 38, pp. 529-558 (1940)

Bridgman, P. W. American Journal of Science. Vol. 7, p. 81 (1924)

Eucken, A. Ann. Phys. (Leipzig) Vol. 32, p. 185 (1911)

Brown, op. cit., p. 28

Weisbrod, op. cit., p. 33

values of sodium chloride are in agreement with theory in that they are proportional to something between $\frac{1}{T}$ and $\frac{1}{T^{3/2}}$.

SUGGESTED IMPROVEMENTS

It was noted that temperature control became progressively more difficult as operating temperatures were increased. This effect is due primarily to the more rapid dissipation of energy from the external surfaces of the heat flow apparatus. It is doubtful whether satisfactory data can be obtained at temperatures above 400°C unless this difficulty is overcome. The obvious solution is to provide an enclosure about the assembly capable of being heated to a temperature somewhat less than the operating temperature.

As operating temperatures are forced upward, the need for more closely matched temperatures becomes more critical as can be seen from the Stefan-Boltzman equation for surfaces at nearly equal temperatures. The controlling circuits are now capable of satisfactorily accomplishing this. That is, the shield temperature was found to oscillate about the source temperature with an amplitude of several hundredths of a degree. It must be remembered, however, that these temperatures are only indicated temperatures and the actual existing temperature difference is probably greater than that determined. If the actual source-shield temperature difference could be obtained, it could be minimized by the introduction of the proper EMF's into the controlling circuits. Also, if the existing temperature difference across the length of the crystal were readily obtainable, it would be unnecessary to determine background which would result in a considerable saving of time. A possible way of accomplishing this is to measure all temperatures with the same thermocouple. There would undoubtedly be serious mechanical problems involved in this refinement in addition to difficulties in establishing good thermal contact between the thermocouple junction and various points of contact.

SUMMARY

An apparatus has been described for the determination of the thermal conductivities of dielectric solids employing the absolute steady-state method. Several refinements have been made on the heat flow assembly and the temperature control circuits since the beginning of this project. Investigations of background have led to the conclusion that this effect can be partially attributed to errors inherent in the thermocouples. A method of obtaining data and making calculations has been explained and although admittedly rather time-consuming has been shown to yield satisfactory results. Consistent and evidently reliable data has been recorded for numerous temperatures over the range 375 to 637°K. The calculated conductivities have been found to agree favorably with those of other experimenters. Results of this investigation indicate that the thermal conductivity is proportional to $\frac{1}{T^N}$ where N is approximately 1.27 in agreement with theory. Suggestions have been made that might possibly extend the temperature range several hundred degrees.

VITA

Paul E. Ohlsen, oldest son of Mr. and Mrs. Harry C. Ohlsen, was born near Schaller, Iowa, on October 19, 1927. He lived in that community until graduation from Schaller High School in 1945. Enlisting in the U.S. Navy immediately following graduation, he attended two service schools: Aviation Fundamentals School at Jacksonville, Florida, and Aviation Machinist's Mates School at Memphis, Tennessee. In October 1948, he was honorably discharged after serving thirty-eight months. He entered Buena Vista College in September of 1949. Illness in the family interrupted his education in his sophomore year. In August of 1952 he married Miss Marcine Christensen of Storm Lake, Iowa, and resumed his studies at Buena Vista College the following month. Majoring in Physics and Mathematics he received the degree of Bachelor of Science in May of 1954. He entered the Missouri School of Mines and Metallurgy at Rolla, Missouri, the following fall as a Graduate-Assistant in Physics. He has accepted a position with North American Aviation, Inc., located in Los Angeles, California, and plans to assume his duties there upon completion of the requirements (February 1956) for a Master's Degree in Physics.